SEVENTH EDITION

HEAT AND THERMODYNAMICS

MARK W. ZEMANSKY
RICHARD H. DITTMAN

Heat and Thermodynamics
An Intermediate Textbook

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SEVENTH EDITION

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To Adele C. Zemansky and Maria M. Dittman

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PREFACE

Mark Zemansky wrote the first five editions of *Heat and Thermodynamics* and we collaborated on the sixth edition. In this edition, Zemansky's pedagogical philosophy and style were my guide for making revisions. True to his tradition, the primary emphasis is placed on the thermodynamic (macroscopic) study of temperature, energy, and entropy, while recognizing that equations of state, temperature variations of specific heats, and valuable insight come from the statistical mechanical (microscopic) approach. Methods of measurement are explained throughout the book and actual data are given in graphs and tables. Mathematical theorems beyond elementary partial differentiation are derived and explained at the places where they are needed.

The sequence of topics in this edition is idential to the last edition and generally follows all previous editions, but changes were made to keep the book up to date or to assist the student. Listed below are the significant additions or changes:

- replacement of the symbol θ for ideal-gas temperatures by the symbol T for absolute temperatures in the first chapter, before the two quantities are proven equal using the second law;
- inclusion of the International Temperature Scale of 1990, which defined the practical temperature scale down to 0.65 K and eliminated the thermocouple as a primary standard thermometer;
- determination of the universal gas constant R from speed of sound measurements; this became the new standard in 1986 and eliminated the method based on the ideal-gas law;
- expression of the thermal efficiences of internal-combustion engines in terms of temperature rather than compression and expansion ratios, thus providing a better preparation for the Carnot engine;
- replacement of the axiomatic presentation of the second law of thermodynamics, according to Carathèodory, with the method of Carnot, Clausius, Kelvin, and Planck using cycles in a reversible heat engine;
- extension of the phase diagram for H_2O to include two very-high-pressure polymorphs of ice;
- use of Legendre transformations to organize the thermodynamic potentials for closed systems — internal energy, enthalpy, Helmholtz function, and Gibbs function;
- introduction of four thermodynamic potentials for open systems — grand function, Guggenheim function, Hill function, and Ray function — which greatly assist in the transition from thermodynamics to statistical mechanics.

Data and references were updated when appropriate.

No book can be written without the advice of others. It is a great pleasure to acknowledge the assistance of Henry J. Graben, David L. Hogenboom, Charles Kaufman, J. M. Marcano, Mark McKenna, Richmond B. McQuistan, Sue Nicholls (of Keyword Publishing Services), Dorn W. Peterson, George Rainey, John Ray, James E. Rutledge, Glenn Schmieg, Dale Snider, Leslie Spanel, and Anna Topal.

Richard H. Dittman

NOTATION

CAPITAL ITALIC		LOWER-CASE ITALIC	
A	Helmholtz function; first virial coefficient; area	a	Molar Helmholtz function; a dimension
B	Bulk modulus; second virial coefficient; chemical constituent	b	A dimension; a constant
C	Heat capacity; third virial coefficient; critical point	c	Molar or specific heat capacity; number of chemical constituents; thermocouple coefficients; speed of light
		c'	Components
D	A constant	d	Exact differential
E	Electrical field, ionization potential	e	Base of natural logarithms; equilibrium
F	Force; Faraday's constant	f	Final state; variance; function
G	Gibbs function	g	Molar Gibbs function; acceleration of gravity
		g	Degeneracy
H	Enthalpy; irradiance	h	Molar enthalpy; convection coefficient; Planck's constant
I	Irreversible engine; current	i	Initial state
J	Massieu function; grand function	j	Valence; summation index
K	Thermal conductivity; equilibrium constant	k	Hooke's constant; Boltzmann's constant
L	Length; logarithmic temperature scale; Hill function	l	Separation
M	Molar mass	m	Mass of a particle
N	Number of molecules	n	Number of moles; quantum number
P	Pressure	p	Partial pressure; linear momentum
Q	Heat	q	Molar heat

R	Molar gas constant; reversible Carnot engine; electric resistance; Ray function	r	Radius; ratio; number of individual reactions
S	Entropy	s	Molar entropy
T	Absolute temperature (Kelvin or Rankine)	t	Practical temperature (Celsiu or Fahrenheit); time
U	Internal energy	u	Molar internal energy
V	Volume	v	Molar volume
W	Work	w	Molar work; speed of wave c particle
X	Generalized displacement	x	Space coordinate; mole fraction
Y	Generalized force; Young's modulus; Planck function	y	Space coordinate; fraction liquefied
Z	Electric charge; Guggenheim function; partition function	z	Space coordinate; number of restricting equations

BOLDFACE CAPITAL ITALICS

$\boldsymbol{B}$	Magnetic induction
$\boldsymbol{D}$	Electric displacement
$\boldsymbol{E}$	Electric field intensity
$\boldsymbol{G}$	Gibbs function of a heterogeneous system
$\boldsymbol{M}$	Magnetization
$\boldsymbol{P}$	Dielectric polarization
$\boldsymbol{S}$	Entropy of a heterogeneous system
$\boldsymbol{V}$	Volume of a heterogeneous system

SCRIPT CAPITALS

SPECIAL SYMBOLS		$\mathcal{B}$	Magnetic induction
	đ		Inexact differential
$\mathcal{E}$	Electromotive force	C_C	Curie constant
$\mathcal{J}$	Tension	N_A	Avogadro's number
$\mathcal{H}$	Magnetic field	R'	Electric resistance
$\mathcal{M}$	Total magnetization	U'	Overall heat-transfer coefficient

$\mathscr{P}$	Total dielectric polarization
$\mathscr{R}$	Radiant exitance

ROMAN SYMBOLS FOR UNITS

atm	atmosphere (pressure)
dyn	dyne
kg	kilogram
m	meter
s	second

A	ampere
A/m	ampere · turn per meter
C	coulomb
Hz	hertz
J	joule
K	kelvin
N	newton
Pa	pascal
T	tesla
V	volt
W	watt

GREEK LETTERS

α	Linear expansivity; critical-point exponent
β	Volume expansivity; critical-point exponent; $1/kT$
Γ	Grüneisen coefficient
γ	Surface tension; ratio of heat capacities; electronic term in heat capacity; critical-point exponent
Δ	Finite difference
δ	Critical-point exponent
ϵ	Energy of a particle; permittivity; emissivity; degree of reaction or ionization; reduced temperature difference
ς	Riemann zeta function
η	Thermal efficiency; Joule coefficient
Θ	Debye temperature
θ	Empirical temperature; angle
κ	Compressibility
λ	Wavelength; Lagrangian multiplier
μ	Joule-Thomson coefficient; chemical potential
μ_0	Permeability of vacuum
ν	Frequency; molecular density; stoichiometric coefficient
Π	Osmotic pressure
ρ	Mass density
σ	Stefan-Boltzmann constant

τ	Period
ϕ	Function of temperature; angle
φ	Phase
ψ	Function of temperature
Ω	Solid angle; thermodynamic probability; ohm
ω	Angular speed; coefficient of performance

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PART I

Fundamental Concepts

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CHAPTER 1

Temperature and the Zeroth Law of Thermodynamics

1.1

MACROSCOPIC POINT OF VIEW

The study of any special branch of natural science starts with a separation of a restricted region of space or a finite portion of matter from its surroundings by means of a closed surface called the *boundary*. The region within the arbitrary boundary and on which the attention is focused is called the *system*, and everything outside the system that has a direct bearing on the system's behavior is known as the *surroundings*, which could be another system. If no matter crosses the boundary, then the system is *closed*; but if there is an exchange of matter between system and surroundings, then the system is *open*.

When a system has been chosen, the next step is to describe it in terms of quantities related to the behavior of the system or its interactions with the surroundings, or both. There are, in general, two points of view that may be adopted: the *macroscopic* point of view and the *microscopic* point of view. The macroscopic point of view considers variables or characteristics of a system at approximately the human scale, or larger; whereas the microscopic point of view considers variables or characteristics of a system at approximately the molecular scale, or smaller.

Let us take as a system the contents in a cylinder of an automobile engine. A chemical analysis would show a mixture of hydrocarbons and air before being ignited, and after the mixture has been ignited there would be combustion products describable in terms of new chemical compounds. A statement of the amounts of these chemicals describes both the *mass* and the *composition* of the system. At any moment, the system can be described further by specifying the *volume*, which varies as the piston moves in the cylinder. The volume can be easily measured and, in the laboratory, is recorded automatically by means of a device coupled to the piston. Another quantity that is indispensable in the description of our system is the *pressure* of the gases in the cylinder. After ignition of the mixture, the pressure is large; after the expulsion of the combustion products, the pressure is small. In the laboratory, a pressure gauge may be used to measure and record the changes of pressure as the engine operates. Finally, there is one more quantity without which we should have no adequate description of the operation of the engine. This quantity is the *temperature*, and, as we shall see, in many instances it can be measured just as simply as the other quantities.

We have described the contents in a cylinder of an automobile engine by specifying the quantities of mass, composition, volume, pressure, and temperature. These quantities refer to the large-scale characteristics, or aggregate properties, of the system and provide a *macroscopic description*. The quantities are, therefore, called *macroscopic coordinates*. For a system other than a gas, such as a paramagnetic salt, the different quantities must be specified to provide a macroscopic description of the system; but macroscopic coordinates, in general, have the following properties in common:

1. They involve no special assumptions concerning the structure of matter, fields, or radiation.
2. They are few in number needed to describe the system.
3. They are fundamental, as suggested more or less directly by our sensory perceptions.
4. They can, in general, be directly measured.

In short, a macroscopic description of a system involves the specification of a *few fundamental measurable properties* of a system. *Thermodynamics*, then, is the branch of natural science that deals with the macroscopic properties or characteristics of nature and always includes the macroscopic coordinate of temperature for every system. The presence of temperature distinguishes thermodynamics from other macroscopic branches of science, such as geometrical optics, mechanics, or electricity and magnetism.

1.2
MICROSCOPIC POINT OF VIEW

The microscopic point of view is the result of the tremendous progress of molecular, atomic, and nuclear science during the past hundred years. From this point of view, a system is considered to consist of an enormous number N of particles, each of which is capable of existing in a set of states whose energies are $\epsilon_1, \epsilon_2, \ldots$. The particles are assumed to interact with one another by means of collisions or by forces caused by fields. The system of particles may be imagined to be isolated or, in some cases, may be considered to be embedded in a set of similar systems, or *ensemble* of systems. The mathematics of probability is applied, and the equilibrium state of the system is assumed to be the state of highest probability. The fundamental problem is to find the number of particles in each of the microscopic energy states (known as the *populations* of the states) when equilibrium is reached. *Statistical mechanics*, then, is the branch of natural science that deals with the microscopic characteristics of nature.

Since statistical mechanics will be treated at some length in Chap. 12, it is not necessary to pursue the matter further at this point. It is evident, however, that a microscopic description of a system involves the following properties:

1. Assumptions are made concerning the structure of matter, fields, or radiation.
2. Many quantities must be specified to describe the system.
3. These quantities specified are not usually suggested by our sensory perceptions, but rather by our mathematical models.
4. They cannot be directly measured, but must be calculated.

In short, a microscopic description of a system involves various assumptions about the internal structure of the system and then calculations of system-wide characteristics.

1.3
MACROSCOPIC VS. MICROSCOPIC POINTS OF VIEW

Although it might seem that the two points of view are hopelessly different and incompatible, both points of view, applied to the same system, must lead to the same conclusion. The two points of view are reconciled because the few directly measurable properties whose specification constitutes the macroscopic description are really averages, over a period of time, of a large number of microscopic characteristics. For example, the macroscopic quantity, pressure, is the average rate of change of linear momentum due to the large number of molecular collisions made on a unit of area. Pressure, however, is a property that is perceived by our senses. We feel the effects of pressure. Pressure was experienced, measured, and used long before there was reason to believe in the existence of molecular impacts. If molecular theory is changed, for example, by incorporating the results of chaos, the concept of pressure will still remain and be understood by all normal human beings. The few measurable macroscopic properties are as sure as our senses. They will remain unchanged as long as our senses remain the same and are not deceived. Herein lies an important distinction between the macroscopic and microscopic points of view. The microscopic point of view, however, goes much further than our senses and many direct experiments. It assumes the structure of microscopic particles, their motion, their energy states, their interactions, etc., and then calculates measurable quantities. The microscopic point of view has changed several times, and we can never be sure that the assumptions are justified until we have compared some deduction made on the basis of these assumptions with a similar deduction based on the experimentally proven macroscopic point of view. In other words, when we seek to understand the physical reality of a result of a microscopic calculation, we look to the macroscopic point of view for guidance.

Throughout its history, the study of thermodynamics has always looked for general laws, relationships, and procedures for understanding macroscopic temperature-dependent phenomena. Because it makes no assumptions about the microscopic structure of matter, thermodynamics has not been disproved as the various specific microscopic classical and quantum models of matter have been incorporated into statistical mechanics.

1.4
SCOPE OF THERMODYNAMICS

It has been emphasized that a description of the large-scale characteristics of a system by means of a few of its measurable properties, suggested more or less directly by our sensory perceptions, constitutes a macroscopic description. Such descriptions are the historic starting point of all investigations in all branches of natural science. For example, in dealing with the mechanics of a rigid body, we adopt the macroscopic point of view in that only the external aspects of the rigid body are considered. The position of its center of mass is specified with reference to coordinate axes at a particular time. Position and time and a combination of both, such as velocity, constitute some of the macroscopic quantities used in classical mechanics and are called *mechanical coordinates*. The mechanical coordinates serve to determine the potential and the kinetic energy of the rigid body with reference to the coordinate axes, namely, the kinetic and the potential energy of the body as a whole. These two types of energy constitute the *external*, or *mechanical*, *energy* of the rigid body. It is the purpose of mechanics to find such relations between the position coordinates and the time as are consistent with Newton's laws of motion.

In thermodynamics, however, the attention is directed to the *interior* of a system. A macroscopic point of view is adopted, and emphasis is placed on those macroscopic quantities which have a bearing on the internal state of a system. It is the function of experiment to determine the quantities that are appropriate for a description of such an internal state. Macroscopic quantities, including temperature, having a bearing on the internal state of a system are called *thermodynamic coordinates*. Such coordinates serve to determine the *internal energy* of a system. It is the purpose of thermodynamics to find, among the thermodynamic coordinates, general relations that are consistent with the fundamental laws of thermodynamics.

A system that may be described in terms of thermodynamic coordinates is called a *thermodynamic system*. In engineering, the important thermodynamic systems are a gas, such as air; a vapor, such as steam; a mixture, such as gasoline vapor and air; and a vapor in contact with its liquid, such as liquid and vaporized freon. Chemical thermodynamics deals with these systems and, in addition, with reactions, surface films, and electric cells. Physical thermodynamics includes, in addition to the above, such systems as wire resistors, electric capacitors, and magnetic substances.

1.5

THERMAL EQUILIBRIUM AND THE ZEROTH LAW

We have seen that a macroscopic description of a gaseous mixture may be given by specifying such quantities as the composition, the mass, the pressure, and the volume. The last quantity specified in Sec. 1.1 was temperature, for which you have an intuitive understanding and some familiarity. This section begins the analytic development of the quantity, temperature. Experiment shows that, for a given composition and for a constant mass and temperature, many different values of pressure and volume are possible for a gas. If the pressure is kept constant, the volume may vary over a wide range of values, and vice versa. In other words, the pressure and the volume are independent coordinates but are related in a simple equation, namely, Boyle's law.

More recently, experiment has shown that, for a wire of constant mass, the tension and the length are independent coordinates, whereas, in the case of a surface film, the surface tension and the area may be varied independently. Some systems that, at first sight, seem quite complicated, such as an electric cell with two different electrodes and an electrolyte, may still be described with the aid of only two independent coordinates. On the other hand, some thermodynamic systems composed of a number of homogeneous parts require the specification of two independent coordinates for each homogeneous part. Details of various thermodynamic systems and their thermodynamic coordinates will be given in Chap. 2. For the present, to simplify our discussion, we shall deal only with systems of constant mass and composition, each requiring *only one pair* of independent coordinates for its description. This involves no essential loss of generality and results in a considerable saving of words. In referring to any unspecified system, we shall use the symbols X and Y for the pair of independent coordinates, where the symbol X refers to a generalized force (for instance, the pressure of a gas) and Y refers to a generalized displacement (for instance, the volume of a gas).

A state of a system in which the coordinates X and Y have definite values that remain constant so long as the external conditions are unchanged is called an *equilibrium* state. Experiment shows that the existence of an equilibrium state in one system depends on the proximity of other systems and on the nature of the boundary or *wall* separating the different systems. Walls are said to be either adiabatic or diathermic in ideal cases. If a wall is *adiabatic* [see Fig. 1-1(*a*)], an equilibrium state for system A may coexist with *any* equilibrium state of system B for all attainable values of the four quantities, X, Y and X', Y' — provided only that the wall is able to withstand the stress associated with the difference between the two sets of coordinates. Thick layers of wood, concrete, asbestos, felt, or polystyrene, as well as dewars, are, in this order, increasingly better experimental approximations to ideal adiabatic walls.

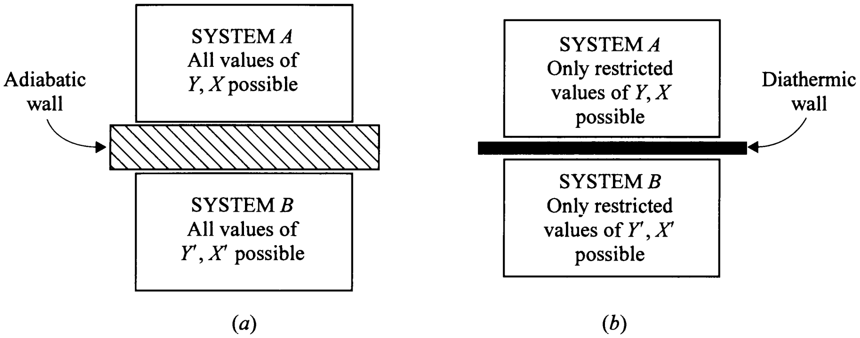
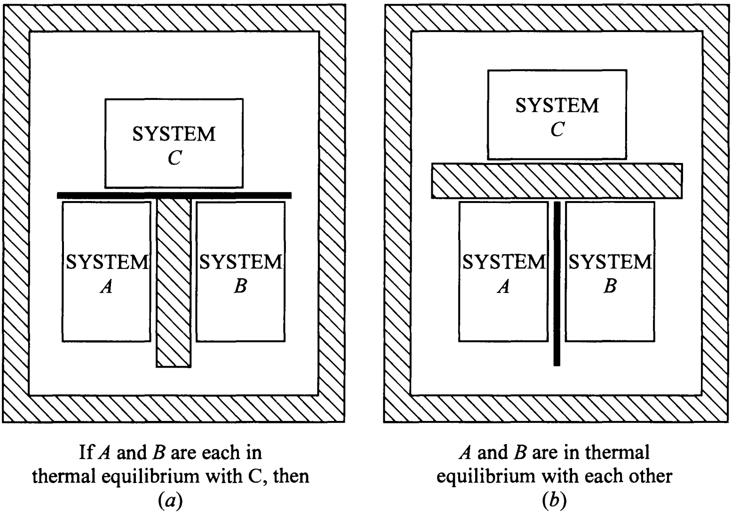


FIGURE 1-1
Properties of (*a*) adiabatic and (*b*) diathermic walls.

If the two systems are separated by a *diathermic* wall [see Fig. 1-1(*b*)], the values of X, Y and X', Y' will change spontaneously until an equilibrium state of the combined system is attained. The two systems are then said to be in *thermal equilibrium* with each other. The most common experimental diathermic wall is a thin metallic sheet. *Thermal equilibrium is the state achieved by two (or more) systems, characterized by restricted values of the coordinates of the systems, after they have been in communication with each other through a diathermic wall.* Unlike the diathermic wall, an *adiabatic* wall prevents two systems from communicating with each other and coming to thermal equilibrium with each other. Although we have not yet defined the concept of *heat*, it may be said that a diathermic wall is a boundary through which heat is communicated from one system to another system, yet remains closed to the transport of matter. An ideal adiabatic wall does not communicate heat.

Imagine two systems A and B, separated from each other by an adiabatic wall but each in contact *simultaneously* with a third system C through diathermic walls, the whole assembly being surrounded by an adiabatic wall as shown in Fig. 1-2(*a*). Experiment shows that the two systems will come to thermal equilibrium with the third system. No further change will occur if the adiabatic wall separating A and B is then replaced by a diathermic wall, as well as if the diathermic wall separating C from both A and B is also replaced by an adiabatic wall [Fig. 1-2(*b*)]. If, instead of allowing both systems A and B to come to equilibrium with C *at the same time*, we first establish equilibrium between A and C and later establish equilibrium between B and C (the state of system C being the same in both cases); then, when A and B are brought into communication through a diathermic wall, they will be found to be in thermal equilibrium with each other. We shall use the expression "two systems are in thermal equilibrium" to mean also that the two systems are in states such that, if the two *were* connected through a diathermic wall, the combined system *would be* in thermal equilibrium.



If *A* and *B* are each in thermal equilibrium with C, then
(*a*)

A and *B* are in thermal equilibrium with each other
(*b*)

FIGURE 1-2
The zeroth law of thermodynamics. (Adiabatic walls are designated by diagonal shading; diathermic walls, by heavy lines.)

These experimental facts may then be stated concisely in the following transitive relation: *Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.* As suggested by Ralph Fowler, this postulate of transitive thermal equilibrium has been numbered *the zeroth law of thermodynamics*, which establishes the basis for the concept of temperature and for the use of thermometers.

The postulate of thermal equilibrium is numbered the zeroth law, rather than the first law, because of the historical development in the understanding of the logical order of the laws of thermodynamics. The first law of thermodynamics, which establishes the conservation of energy, including heat, was clearly formulated in 1848 by Hermann Helmholtz and William Thomson (later Lord Kelvin) using experimental data gathered by James Prescott Joule (1843–1849) and insight provided by Julius Mayer (1842). The second law of thermodynamics was postulated earlier (1824) in Sadi Carnot's study of the working of steam engines. Logically, Carnot's principle must follow the first law if his principle is expressed as a restriction on the means by which energy can be communicated while still being conserved. As the postulates of thermodynamics were developed further, it was realized by Fowler (1931) that thermal equilibrium had to be defined before the first law could be stated. Unable to renumber the two previously established laws of thermodynamics, he was forced to adopt zero as the number of his law. It is unlikely that future developments will raise the possibility of the "minus first" law of thermodynamics.

1.6
CONCEPT OF TEMPERATURE

The concept of temperature is rich in interpretations and levels of abstraction. In its anthropomorphic understanding, temperature is a measure of the *hotness* of a given macroscopic object, as felt by the human body. Even though *coldness* is commonly used to express some temperatures, we prefer to avoid the word "coldness" for reasons provided by statistical mechanics. In the microscopic point of view, temperature is associated with the agitation, vibration, or motion of the object's constituent particles. Accordingly, coldness means "less hotness." To avoid ambiguity, it is suggested that the word "coldness" be avoided and let the concept of temperature be understood as the degree of hotness of an object above zero hotness.

A scientific understanding of the concept of temperature builds upon thermal equilibrium, established in the zeroth law of thermodynamics. Consider a system A in the state X_1, Y_1 in thermal equilibrium with another system B in the state X_1', Y_1'. If system A is removed and its state changed, there will be found a second state X_2, Y_2 that is in thermal equilibrium with the *original* state X_1', Y_1' of system B. Experiment shows that there exists a whole set of states — X_1, Y_1; X_2, Y_2; X_3, Y_3 — any one of which is in thermal equilibrium with this *same* state X_1', Y_1' of system B, and all of which, by the zeroth law, are in thermal equilibrium with one another. We shall suppose that *all* such states, when plotted on an X–Y diagram, lie on a curve such as I in Fig. 1-3, which we shall call an *isotherm. An isotherm is the locus of all points representing states in which a system is in thermal equilibrium with one state of another system.* We make no assumption as to the continuity of the isotherm, although experiments on simple systems indicate usually that at least a portion of an isotherm is a continuous curve.

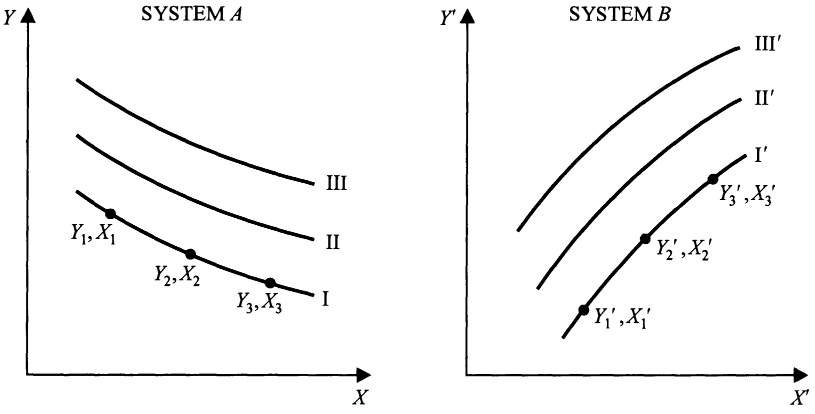


FIGURE 1-3
Isotherms of two different systems.

Similarly, with regard to system *B*, we find a set of states — X_1', Y_1'; X_2', Y_2'; X_3', Y_3' — all of which are in thermal equilibrium with *one* state (X_1, Y_1) of system *A*, and, therefore, in thermal equilibrium with one another. These states are plotted on the X'–Y' diagram of Fig. 1-3 and lie on the isotherm I′. From the zeroth law, it follows that all the states on isotherm I of system *A* are in thermal equilibrium with all the states on isotherm I′ of system *B*. We shall call curves I and I′ *corresponding isotherms* of the two systems.

If the experiments just outlined are repeated with different starting conditions, another set of states of system *A* lying on curve II may be found, every one of which is in thermal equilibrium with every state of system *B* lying on curve II′. In this way, a family of isotherms I, II, III, etc., of system *A* and a corresponding family I′, II′, III′, etc., of system *B* may be found. Furthermore, by repeated applications of the zeroth law, corresponding isotherms of still other systems *C*, *D*, etc., may be obtained.

All states of corresponding isotherms of all systems have something in common, namely, that they are in thermal equilibrium with one another. The systems themselves, in these states, may be said to possess a property that ensures their being in thermal equilibrium with one another. We call this property *temperature. The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems.*

The scalar character of temperature may be established on the basis of the zeroth law of thermodynamics. For systems *A* and *B* to be in thermal equilibrium, all the information that is needed is that both *A* and *B* are in thermal equilibrium with *C*. This is not true, for instance, for *mechanical* equilibrium of elastic crystalline solids; the *tensor* character of the stresses found in two crystalline bodies means that the two bodies need not necessarily be in mechanical equilibrium with each other just because each is in mechanical equilibrium with a third body.

Since temperature is a scalar quantity, the temperature of all systems in thermal equilibrium may be represented by a number. The establishment of a temperature scale is merely the adoption of a set of rules for assigning one number to a set of corresponding isotherms, and a different number to a different set of corresponding isotherms. Once this is done, the *necessary and sufficient* condition for thermal equilibrium between two systems is that they have the same temperature. Also, when the temperatures are different, we may be sure that the systems are not in thermal equilibrium.

To determine whether or not two beakers of water are in equilibrium, it is not necessary to bring them into contact by means of a diathermic wall and see if their properties change with time. Rather, an unmarked glass capillary tube filled with mercury (system *A*) is inserted into the first beaker (system *B*) and, shortly, some property of this device, such as the height of the mercury column, comes to rest. Then, by definition, the device has the same temperature as the water in the first beaker. The procedure is repeated with the other beaker of water (system *C*). If the heights of the mercury columns are the same, then the temperatures of *B* and *C* are equal. Furthermore, experiment shows that if the two beakers are now brought into contact, there are no changes in their properties. Notice that the mercury-filled glass capillary tube requires no scale; the requirement is only that the height of the mercury in the two tests must be the same. Such a device is a *thermoscope*, which indicates only equality of temperature for the corresponding isotherms of the systems. In order to assign a numerical value to the temperature, we perform experiments on a standard system.

1.7

THERMOMETERS AND MEASUREMENT OF TEMPERATURE

To establish an *empirical* temperature scale, we select some system with coordinates X and Y as a standard, which we call a *thermometer*, and adopt a set of rules for assigning a numerical value to the temperature associated with each of its isotherms. To every other system in thermal equilibrium with the thermometer, we assign the same number for the temperature. The simplest procedure is to choose any convenient path in the X–Y plane, such as that shown in Fig. 1-4 by the dashed line $Y = Y_1$, which intersects the isotherms at points each of which has the same Y-coordinate but a different X-coordinate. The temperature associated with each isotherm is then taken to be a convenient function of the X at this intersection point. The coordinate X is called the *thermometric property*, and the form of the *thermometric function* $\theta(X)$

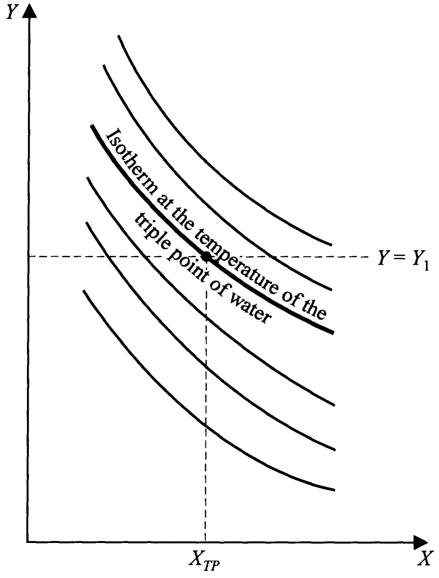


FIGURE 1-4
Setting up a temperature scale involves assignment of numerical values to the isotherms of an arbitrarily chosen standard system (the thermometer).

determines the empirical temperature scale. There are many different kinds of thermometer, each with its own thermometric property, and six modern thermometers are shown in Table 1.1

Let X stand for any one of the thermometric properties listed in Table 1.1, and let us decide *arbitrarily* to define the temperature scale so that the empirical temperature θ is directly proportional to X. The arbitrary choice of a linear function maintains the temperature scale first used in the historic mercury-in-glass thermometer. Thus, the temperature common to the thermometer *and to all systems in thermal equilibrium with it* can be given by the thermometric function,

$$\theta(X) = aX \qquad (\text{constant } Y), \tag{1.1}$$

where a is an arbitrary constant. Notice that as the coordinate X approaches zero, the temperature also approaches zero, because there is no arbitrary constant added to the function. In effect, the linear function in Eq. (1.1) also defines an absolute temperature scale, such as the Kelvin scale or the Rankine scale.

It should be noted further that *different* empirical temperature scales usually result when this arbitrary relation is applied to different kinds of thermometers and even when it is applied to different systems of the same kind, such as constant volume hydrogen or nitrogen thermometers. One must thus ultimately select, either arbitrarily or in some rational way, one kind of thermometer, such as a constant-volume gas thermometer, and one particular system, such as hydrogen gas, to serve as the standard thermometric instrument, which is how the first international temperature scale was established in 1887. But regardless of what standard is chosen, the value of the coefficient a in Eq. (1.1) must be established; only then does one have a numerical relation between the empirical temperature $\theta(X)$ and the thermometric property X.

Equation (1.1) applies, in general, to a thermometer placed in contact with a system whose temperature $\theta(X)$ is to be measured. Therefore, it applies when the thermometer is placed in contact with an arbitrarily chosen standard system in a *reproducible state*; such a state of an *arbitrarily chosen standard*

TABLE 1.1
Thermometers and thermometric properties

Thermometer	Thermometric property	Symbol
Gas (const. volume)	Pressure	P
Platinum resistance (const. tension)	Electric resistance	R'
Thermocouple (const. tension)	Thermal emf	$\mathcal{E}$
Helium vapor (saturated)	Pressure	P
Paramagnetic salt	Magnetic susceptibility	χ
Blackbody radiation	Radiant exitance	$\mathcal{R}_{bb}$

system is called *a fixed point*, that is, fixed temperature. The fixed point provides a reference temperature for the determination of temperature scales.

Before 1954, the international metric temperature scale was the Celsius scale, which was based on the *temperature interval* between two fixed points: (1) the temperature at which pure ice coexisted in equilibrium with air-saturated water at standard atmospheric pressure (the *ice point*); and (2) the temperature of equilibrium between pure water and pure steam at standard atmospheric pressure (the *steam point*). The temperature interval between these two fixed points was assigned 100 "degrees" (of hotness), abbreviated as 100°C. Hundreds of attempts were made all over the world to measure the temperature of the ice point with great accuracy — without much success. The main difficulty was achieving equilibrium between air-saturated water and pure ice. When ice melts, it surrounds itself with pure water that prevents intimate contact between ice and air-saturated water. Attempts to measure the steam point also present problems, because the temperature of the steam point is very sensitive to pressure.

In 1954, a *single* fixed point was chosen as the basis for a new international temperature scale, the Kelvin scale. The state in which ice, liquid water, and water vapor coexist in equilibrium, a state known as the *triple point of water*, provides the standard reference temperature. The temperature of the triple point of water, which can be very accurately and reproducibly measured, was assigned the value 273.16 kelvin, corresponding to 0.01°C, in order to maintain the magnitude of a unit of temperature. Notice that the word "degree" has been dropped from the Kelvin scale, so the triple-point temperature is abbreviated as 273.16 K.

We can now solve Eq. (1.1) for the coefficient a:

$$a = \frac{273.16\,\mathrm{K}}{X_{TP}}, \tag{1.2}$$

where the subscript TP identifies the property value X_{TP} explicitly with the triple-point temperature. In view of Eq. (1.2), the general Eq. (1.1) may be written

$$\theta(X) = 273.16\,\mathrm{K}\frac{X}{X_{TP}} \qquad (\text{constant } Y). \tag{1.3}$$

The temperature of the triple point of water is the *standard fixed point* of thermometry. To achieve the triple point, one distills water of the highest purity and of substantially the same isotopic composition of ocean water into a vessel depicted schematically in Fig. 1-5. When all air has been removed, the vessel is sealed off. With the aid of a freezing mixture in the inner well, a layer of ice is formed around the well. When the freezing mixture is replaced by a thermometer bulb, a thin layer of ice is melted nearby. So long as the solid, liquid, and vapor phases coexist in equilibrium, the system is at the triple point.

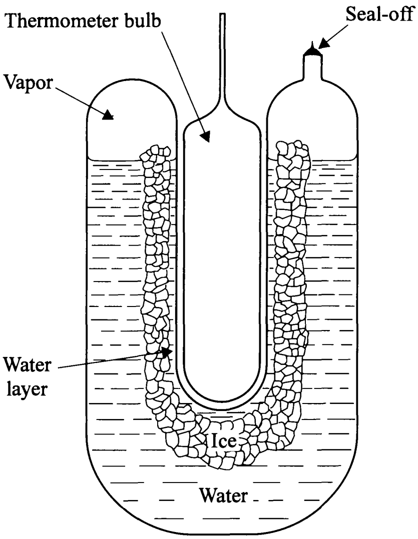


FIGURE 1-5
Triple-point cell.

1.8
COMPARISON OF THERMOMETERS

Applying the principles outlined in the preceding paragraphs to the first three thermometers listed in Table 1.1, we have three different ways of measuring temperature. Thus, for a gas at constant volume,

$$\theta(P) = 273.16\,\mathrm{K}\frac{P}{P_{TP}} \qquad \text{(constant } V\text{);} \tag{1.4}$$

for a platinum wire resistor,

$$\theta(R') = 273.16\,\mathrm{K}\frac{R'}{R'_{TP}};$$

and for a thermocouple,

$$\theta(\mathcal{E}) = 273.16\,\mathrm{K}\frac{\mathcal{E}}{\mathcal{E}_{TP}}.$$

Now, imagine a series of tests in which the temperature of a given system is measured simultaneously with each of the three thermometers. Such a comparison is shown in Table 1.2, where the constant-volume gas thermometer is used at high pressure and low pressure. The letters NBP stand for the *normal boiling point*, by which the word *normal* specifies that the temperature at which a liquid boils occurs at standard atmospheric pressure (101,325 Pa or 14.7 lb/in^2). Similarly, the letters NMP stand for the *normal melting point*,

TABLE 1.2
Comparison of thermometers

Fixed point	Copper-constantan thermometer		Platinum resistance thermometer		Constant-volume H_2 thermometer		Constant-volume H_2 thermometer	
	$\mathcal{E}$, mV	$\theta(\mathcal{E})$	R', Ω	$\theta(R')$	P, kPa	$\theta(P)$	P, kPa	$\theta(P)$
N_2 (NBP)	0.73	32.0	1.96	54.5	184	73	29	79
O_2 (NBP)	0.95	41.5	2.50	69.5	216	86	33	90
CO_2 (NSP)	3.52	154	6.65	185	486	193	73	196
H_2O (TP)	6.26	273	9.83	273	689	273	101	273
H_2O (NBP)	10.05	440	13.65	380	942	374	139	374
Sn (NMP)	17.50	762	18.56	516	1287	510	187	505

NSP for the *normal sublimation point*, and TP for the *triple point*, the temperature at which the solid, liquid, and vapor coexist in thermal equilibrium. The numerical values are not meant to be exact, and 273.16 has been written simply 273.

If one compares the θ columns in Table 1.2, it may be seen that at any fixed point, except the triple point of water, which is the *arbitrarily chosen* reference temperature for all thermometers, the thermometers disagree. Even the two hydrogen thermometers disagree slightly, but the variation among gas thermometers may be greatly reduced by using low pressures, so that a gas thermometer has been chosen as the standard thermometer to define the empirical temperature scale for temperatures not too far from ambient temperatures. At extremely low temperatures or extremely high temperatures, there are other standard thermometers. Within its operating range, the advantage of the gas thermometer is a well-understood equation of state, which permits the identification and elimination of sources of error.

1.9
GAS THERMOMETER

A simplified schematic diagram of a constant-volume gas thermometer is shown in Fig. 1-6. The materials, construction, and dimensions differ in the various laboratories throughout the world where these instruments are used and depend on the nature of the gas and the temperature range for which the thermometer is intended. The gas is contained in the glass bulb *B*, which communicates with the mercury column *M* through a capillary. The volume of the gas is kept constant by adjusting the height of the mercury column *M* until the mercury level just touches the tip of a small pointer (indicial point) in the space above *M*, known as the *dead space* or *nuisance volume*. The mercury column *M* is adjusted by raising or lowering the reservoir. The pressure in the system equals atmospheric pressure plus the difference in height *h* between the

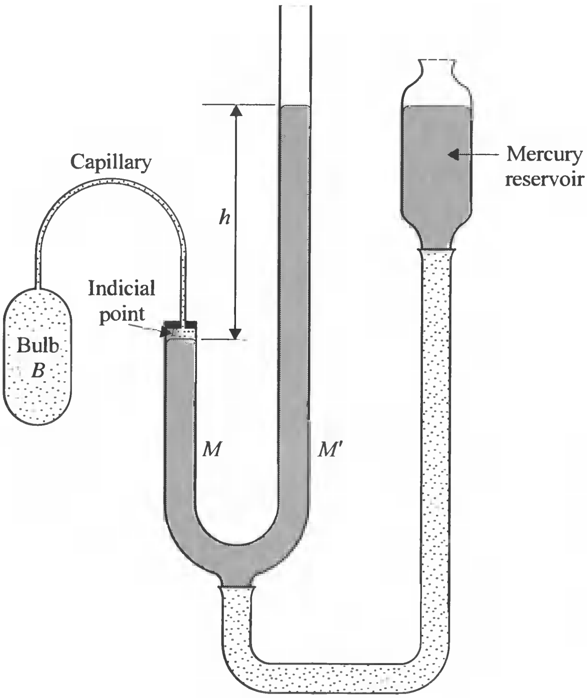


FIGURE 1-6
Simplified constant-volume gas thermometer. Mercury reservoir is raised or lowered so that the meniscus at the left always touches the indicial point. Bulb pressure equals *h* plus atmospheric pressure.

two mercury columns M and M' and is measured twice: when the bulb is surrounded by the system whose temperature is to be measured, and when it is surrounded by water at the triple point.

The various values of the pressure must be corrected to take account of many sources of error, such as:

1. The gas present in the dead space (and in any other nuisance volumes) is at a temperature different from that in the bulb.
2. The gas in the capillary connecting the bulb with the manometer has a temperature gradient; that is, it is not at a uniform temperature.
3. The bulb, capillary, and nuisance volumes undergo changes of volume when the temperature and pressure change.
4. A pressure gradient exists in the capillary when the diameter of the capillary is comparable to the mean free path of the gas particles.
5. Some gas is adsorbed on the walls of the bulb and capillary; the lower the temperature, the greater the adsorption.
6. There are effects due to temperature and compressibility of the mercury in the manometer.

Improvements and alternative ways of measuring pressure have been incorporated into the design of gas thermometers, so these errors can be estimated and eliminated from the data. As a result, the behavior of real gases approaches the behavior of the ideal gas in limiting conditions.

1.10
IDEAL-GAS TEMPERATURE

In the nineteenth century, no thermometer compared in effectiveness with the gas thermometer. It was officially adopted by the International Committee on Weights and Measures in 1887 as the standard thermometer to replace the mercury-in-glass thermometer. The theoretical basis for gas thermometry became the well-understood relationship between pressure, volume, and temperature embodied in the *ideal-gas law*, namely,

$$PV = nRT, \tag{1.5}$$

where P is the pressure of the system of gas, V is the volume of gas, n is the number of moles of gas, and R is the molar gas constant. The temperature T is the *theoretical* thermodynamic temperature. In this section, we show the experiment that yields reproducible and accurate *empirical* temperatures θ. Greek letter theta (θ) indicates the real-gas temperature and T the thermodynamic ideal-gas temperature. In Sec. 7.7, we will justify the identification of the ideal-gas temperature with the thermodynamic temperature. The ideal-gas temperature is found using a constant-volume gas thermometer. Applying Eq. (1.5) initially to the gas at the assigned temperature of 273.16 K and then to the gas at the unknown empirical temperature, one obtains the proportion

$$\frac{P}{P_{TP}} = \frac{\theta}{273.16\,\mathrm{K}},$$

or

$$\theta = 273.16\,\mathrm{K}\,\frac{P}{P_{TP}} \qquad (\text{constant } V). \tag{1.6}$$

It is no coincidence that Eq. (1.6) is the same as Eq. (1.4). The Kelvin temperature scale and gas thermometers evolved together.

Consider measuring the *ideal-gas temperature* at the normal boiling point (NBP) of water (the steam point). An amount of gas is introduced into the bulb of a constant-volume gas thermometer, and one measures P_{TP} when the bulb of the constant-volume thermometer is inserted in the triple-point cell shown in Fig. 1-5. Suppose that P_{TP} is equal to 120 kPa. Keeping the volume V constant, carry out the following procedures:

1. Surround the bulb with steam at standard atmospheric pressure, measure the gas pressure P_{NBP}, and calculate the empirical temperature θ using Eq. (1.6),

$$\theta(P_{NBP}) = 273.16\,\mathrm{K}\frac{P_{NBP}}{120}.$$

2. Remove some of the gas so that P_{TP} has a smaller measured value, say, 60 kPa. Measure the new value of P_{NBP} and calculate a new value,

$$\theta(P_{NBP}) = 273.16\,\mathrm{K}\frac{P_{NBP}}{60}.$$

3. Continue reducing the amount of gas in the bulb so that P_{TP} and P_{NBP} have smaller and smaller values, P_{TP} having values of, say, 40 kPa, 20 kPa, etc. At *each* value of P_{TP}, calculate the corresponding $\theta(P_{NBP})$.
4. Plot $\theta(P_{NBP})$ against P_{TP} and extrapolate the resulting curve to the axis where $P_{TP} = 0$. Read from the graph,

$$\lim_{P_{TP}\to 0} \theta(P_{NBP}).$$

The results of a series of tests of this sort are plotted in Fig. 1-7 for three different gases in order to measure $\theta(P)$ for the normal boiling point of water. The graph conveys the information that, although the readings of a constant-volume gas thermometer depend upon the nature of the gas at ordinary values of P_{NBP}, *all gases indicate the same temperature as* P_{TP} *is lowered and made to approach zero.*

Therefore, we define the *ideal-gas temperature* T by the equation

$$\boxed{T = 273.16\,\mathrm{K} \lim_{P_{TP}\to 0}\left(\frac{P}{P_{TP}}\right) \qquad (\text{constant } V).} \tag{1.7}$$

Although the ideal-gas temperature scale is independent of the properties of any one particular gas, it still depends on the properties of gases in general. Helium is the most useful gas for thermometric purposes for two reasons. At high temperatures helium does not diffuse through platinum, whereas hydrogen does. Furthermore, helium becomes a liquid at a temperature lower than any other gas, and, therefore, a helium thermometer may be used to measure temperatures lower than those which can be measured with any other gas thermometer.

The lowest ideal-gas temperature that can be measured with a constant-volume gas thermometer is about 2.6 K, provided that low-pressure ^{3}He is used. *The temperature* $T = 0$ *remains as yet undefined by means of thermometry.* In Chap. 7, the Kelvin temperature scale, which is independent of the properties of any particular substance, will be developed from the second law of thermodynamics. It will be shown that, *in the temperature region in which a gas thermometer may be used, the ideal-gas scale and the Kelvin thermodynamic scale are identical.* In anticipation of this result, we write K after an ideal-gas temperature. It will also be shown in Chap. 7 how the absolute zero of temperature is defined on the Kelvin scale. It should be remarked that the statement, found in some textbooks of elementary science, that at absolute zero all

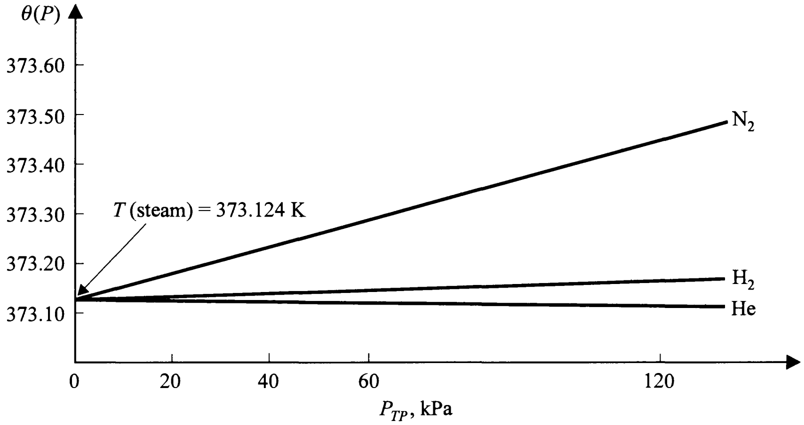


FIGURE 1-7
Readings of a constant-volume gas thermometer for the temperature of steam (NBP of water) when different gases are used at various arbitrary values of P_{TP}. (Limiting value obtained from R. L. Rusby, R. P. Hudson, M. Durieux, J. F. Schooley, P. P. M. Steur, and C. A. Swenson: *Metrologia*, vol. 28, pp. 9–18, 1991.)

atomic motion ceases is erroneous. First, such a statement involves an assumption connecting the purely macroscopic concept of temperature and the microscopic concept of atomic motion. If we want thermodynamics to be general, this is precisely the sort of assumption that must be avoided. Second, when it is necessary in statistical mechanics to correlate temperature to atomic or molecular motion, it is found that classical statistical mechanics must be modified with the aid of quantum mechanics and that, when this modification is carried out, the particles of a substance at absolute zero have a *finite* amount of residual vibrational energy, known as the *zero-point energy.*

1.11
CELSIUS TEMPERATURE SCALE

The Celsius temperature scale, named after the Swedish astronomer Anders Celsius, was the international temperature scale prior to the introduction of the Kelvin scale in 1954. The Kelvin temperature scale is based upon a degree of the same magnitude as that of the Celsius scale; the fixed point was shifted from the ice point of water (273.15 K) to the triple point of water, which was defined to be 0.01°C above the ice point of water, that is 273.16 K. In effect, the numerical values of the normal freezing point of water and the normal boiling point of water were left to be determined by experiment, rather than being defined fixed temperatures. So, if θ denotes the Celsius temperature, the relationship between the Celsius scale and the Kelvin scale is simply

$$\theta(^\circ\mathrm{C}) = T(\mathrm{K}) - 273.15. \tag{1.8}$$

For example, the Celsius temperature θ_{NBP} at which water boils at standard atmospheric pressure is

$$\theta_{NBP} = T_{NBP} - 273.15,$$

and reading T_{NBP} from Fig. 1-7,

$$\theta_{NBP} = 373.124 - 273.15 = 99.974^\circ\mathrm{C}.$$

It should not be surprising that the normal boiling point of water is no longer exactly 100°C. The only Celsius temperature that is fixed by *definition* after 1954 is that of the triple point of water. All other temperatures must be measured with respect to the triple point of water as the result of making the Kelvin scale the international standard for thermodynamic temperatures.

1.12
PLATINUM RESISTANCE THERMOMETRY

Although gas thermometers could provide thermodynamic temperatures, they are cumbersome and unsuited for many applications. A more practical thermometer is the platinum resistance thermometer, which is much more reproducible, simpler to use, and generally provides a greater range of operation than the gas thermometer. The platinum resistance thermometer is secondary to the gas thermometer, because any expression that describes the electrical resistance as a function of temperature contains unknown, temperature-dependent terms that we cannot calculate from first principles.

When the resistance thermometer is in the form of a long, fine wire, it is usually wound around a thin frame constructed so as to avoid excessive strains when the wire contracts upon cooling. In special circumstances, the wire may be wound on or embedded in the material whose temperature is to be measured. In the very low-temperature range, resistance thermometers often consist of small carbon-composition radio resistors or a germanium crystal, doped with arsenic and sealed in a helium-filled capsule. These may be bonded to the surface of the substance whose temperature is to be measured or placed in a hole drilled for that purpose.

Resistance measuring circuits may be divided into two groups: potentiometric types, in which at balance there is exactly zero direct current flowing in the voltage leads; and bridge circuits, in which at balance a negligible alternating current flows. Until the late 1960s, bridge circuits had no application in setting temperature standards. Since then, two factors have altered this situation. First, there is the development of the inductive voltage-divider, or ratio transformer, in bridge circuits. Second, there is the improvement in electronics, which has produced lock-in amplifiers of high sensitivity and excellent signal-to-noise characteristics. Elaborate self-balancing systems have also become available.

The *platinum* resistance thermometer may be used for very accurate work within the range 13.8033 to 1234.93 K (−259.3467 to 961.78°C). The calibration of the instrument involves the measurement of $R'(T)$ at various known defining temperatures and the representation of the results by an empirical formula. In a restricted range, the following quadratic equation is often used:

$$R'(T) = R'_{TP}(1 + aT + bT^2), \tag{1.9}$$

where $R'(T)$ is the resistance of the platinum wire at the temperature T, R'_{TP} is the resistance of the platinum wire when it is surrounded by water at the triple point, and a and b are constants. In order to avoid the need for precise absolute measurements of resistance, the calibration of thermometers is always in terms of the ratio $R'(T)/R'_{TP}$, known as $W(T)$. Thus, in effect, resistivities are measured rather than resistances. Another advantage is that $W(T)$ is relatively insensitive to the effects of strain or contamination of the wire.

1.13
RADIATION THERMOMETRY

Optical pyrometry, radiation pyrometry, infrared pyrometry, and spectral or total-radiation pyrometry are some of the methods of thermometry based on the measurement of thermal radiation, or so-called *blackbody* radiation.

In radiation thermometry, in contrast to resistance thermometry, we make use of a well-established equation, the Planck radiation law, which relates thermodynamic temperature to the measured spectral radiance. The thermal radiation existing inside a closed cavity (blackbody radiation) depends only on the temperature of the walls and not at all upon their shape or composition, provided that the cavity dimensions are much larger than the wavelengths of the thermal radiation. The radiation escaping from a small hole in the cavity is perturbed by the presence of the hole. By careful design, this perturbation can be made negligibly small, so that equilibrium blackbody radiation is available for measurement. Thus, in principle, thermodynamic temperature may be measured very precisely by means of radiation thermometry.

Radiation thermometers called *pyrometers* were developed for measuring high temperatures (greater than approximately 1100°C), and they have the advantage that they are noncontact thermometers. Optical pyrometers measure temperatures of objects by comparing the visible radiation from the hot objects over a narrow wavelength band with the radiation from a standard, preferably using a photoelectric detector for measurements rather than the human eye. Corrections for the emissivity of the source must be made to determine the temperature. Total-radiation pyrometers measure the whole spectrum of electromagnetic waves, including infrared radiated by the object, in order to determine the temperature. Total-radiation pyrometers are less accurate than optical pyrometers but can measure much lower temperatures, including the triple point of water!

1.14
VAPOR PRESSURE THERMOMETRY

Saturation vapor pressure thermometry is commonly used for the measurement of temperature in the range between 0.3 and 5.2 K, because of the sensitivity and convenience of this type of measurement. The thermometric substance is the vapor in equilibrium with the liquid of either of the two isotopes of helium: ^{3}He or ^{4}He. Helium vapor pressure is the thermometric parameter, because it depends only on a physical property of a pure element and can be reproduced at any time, it requires no interpolation device, and it is relatively easy to measure with sufficient precision over much of the temperature range.

The range of practical usefulness of the ^{4}He vapor pressure scale is from approximately 1.0 K (because of the small variation of pressure with temperature and complications due to superfluid behavior) to 5.2 K (because the liquid does not exist above this temperature: the *critical point*). The range for the ^{3}He scale is from approximately 0.30 K (because the pressure is inconveniently small to measure) to 3.32 K (the critical point).

1.15
THERMOCOUPLE

A schematic diagram of a thermocouple is shown in Fig. 1-8, where the temperature to be measured is located at the test junction. The thermal electromotive force (emf) is generated at the point where wire *A* and wire *B* are joined. The two thermocouple wires are connected to copper wires located at the reference junction, which is maintained at the temperature of melting ice.

A thermocouple is calibrated by measuring the thermal emf at the test junction at various known temperatures, the reference junction being kept at 0°C. The results of such measurements on most thermocouples can usually be represented by a cubic equation, as follows:

$$\mathcal{E} = c_0 + c_1\theta + c_2\theta^2 + c_3\theta^3,$$

where $\mathcal{E}$ is the thermal emf, and the constants c_0, c_1, c_2, and c_3 are different for each thermocouple. Within a restricted range of temperature, a quadratic equation is often sufficient. The temperature range of a thermocouple depends upon the materials of which it is composed. The type K thermocouple, made of a chromel wire (90% Ni and 10% Cr) and an alumel wire (95% Ni, 2% Al, 2% Mn, and 1% Si) has a temperature range of -270 to 1372°C.

The advantage of a thermocouple is that it quite rapidly comes to thermal equilibrium with the system whose temperature is to be measured, because its

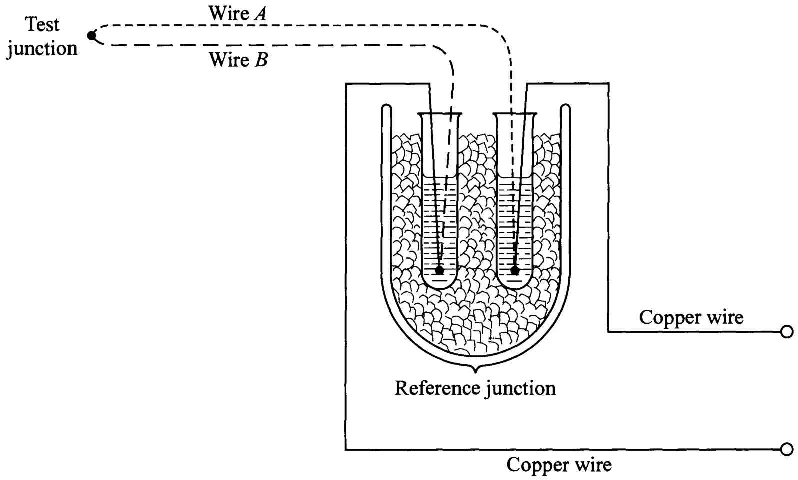


FIGURE 1-8
Thermocouple of wires *A* and *B* with a reference junction, consisting of two junctions with copper wires, ready to be connected to a measuring or monitoring circuit.

mass is small. Furthermore, the emf of the thermocouple is adaptable to electrical circuits, which monitor and control temperatures in many industrial, commercial, and residential furnaces, ovens, and cooling units. The disadvantage, as far as scientific temperature measurement is concerned, is that the imprecision is about 0.2 K, which is five to ten times larger than the imprecision of the platinum resistance thermometer at higher temperatures. Therefore, the thermocouple is no longer a standard thermometer used in the International Temperature Scale of 1990.

1.16
INTERNATIONAL TEMPERATURE SCALE OF 1990 (ITS-90)

The International Committee of Weights and Measures is concerned with two temperature scales: the first is the *theoretical* thermodynamic scale; the second is, at any given time, the current *practical* temperature scale. The use of a constant-volume gas thermometer for routine calibrations or for the usual measurement of thermodynamic temperature is impractical. In 1927, the first international practical temperature scale was adopted to provide the means for easy and rapid calibration of scientific and industrial instruments. The practical temperature scale was revised or amended in 1948, 1960, 1968, 1976, and 1990.

The International Temperature Scale of 1990 (ITS-90) consists of a set of defining fixed points measured with the primary gas thermometer, and a set of procedures for interpolation between the fixed points using secondary thermometers. Although ITS-90 is not intended to supplant the Kelvin thermodynamic scale, it is constructed so as to provide a very close approximation to it; the differences between the practical temperature scale T_{90} and the Kelvin thermodynamic temperature scale T are within the limits of accuracy of measurement attained in 1990.

The accurate measurement of temperature with a gas thermometer requires years of painstaking laboratory work and mathematical computation and, when completed, becomes an international event. Such work is published in the journal *Metrologia* and eventually is listed in tables of physical constants. The temperatures of the equilibrium states of a number of materials have been measured, and the results are tabulated in Table 1.3.

The lower temperature limit of ITS-90 is 0.65 K. Below this temperature, the scale is undefined in terms of a standardized thermometer, but research continues in order to select a reference thermometer from competing instruments. Various intervals of temperature on ITS-90 and secondary thermometers are established, as follows:

1. *From 0.65 to 5.0 K.* Between 0.65 and 3.2 K, the ITS-90 is defined by the vapor pressure–temperature relations of ^{3}He, and between 1.25 and

TABLE 1.3
Defining fixed points of ITS-90[†]

Material[‡]	Equilibrium state[§]	Temperature	
		T_{90} (K)	t_{90} (°C)
^{3}He and ^{4}He	VP	3 to 5	−270.15 to −268.15
e-H_2	TP	13.8033	−259.3467
e-H_2 (or He)	VP (or CVGT)	≈ 17	≈ 256.15
e-H_2 (or He)	VP (or CVGT)	≈ 20.3	≈ 252.85
Ne	TP	24.5561	−248.5939
O_2	TP	54.3584	−218.7916
Ar	TP	83.8058	−189.3442
Hg	TP	234.3156	−38.8344
H_2O	TP	273.16	0.01
Ga	NMP	302.9146	29.7646
In	NFP	429.7485	156.5985
Sn	NFP	505.078	231.928
Zn	NFP	692.677	419.527
Al	NFP	933.473	660.323
Ag	NFP	1234.93	961.78
Au	NFP	1337.33	1064.18
Cu	NFP	1357.77	1084.62

[†] H. Preston-Thomas: *Metrologia*, vol. 27, pp. 3–10, 1990.

[‡] e-H_2 indicates equilibrium hydrogen, that is, hydrogen with the equilibrium distribution of its ortho and para states. Normal hydrogen at room temperature contains 25 percent para-hydrogen and 75 percent ortho-hydrogen.

[§] VP indicates vapor pressure point; CVGT indicates constant-volume gas thermometer point; TP indicates triple point (equilibrium temperature at which the solid, liquid, and vapor phases coexist); NFP indicates normal freezing point, and NMP indicates normal melting point (the NFP and NMP are equilibrium temperatures at which the solid and liquid phases coexist under a pressure of 101,325 Pa, 1 standard atmosphere). The isotopic composition is that naturally occurring.

2.1768 K (the λ-point) and between 2.1768 and 5.0 K by the vapor pressure–temperature relations of ^{4}He.

2. *From 3.0 to 24.5561 K.* Between 3.0 and 24.5561 K, the ITS-90 is defined by the ^{3}He or ^{4}He constant-volume gas thermometer.
3. *From 13.8033 to 1234.93 K.* Between 13.8033 and 1234.93 K (−259.3467 to 961.78°C), the ITS-90 is defined by resistance ratios $W(T)$ of platinum resistance thermometers using the specified fixed points given in Table 1.3 and by reference functions and deviation functions of resistance ratios between the fixed points. Eleven subranges have been established to accommodate a variety of necessary measurements.
4. *Above 1234.93 K.* At temperatures above 1234.93 K (961.78°C), ITS-90 is defined by an optical pyrometer using the ratio of spectral concentrations of the radiance of a blackbody as calculated using Planck's radiation law. Only one reference temperature is required for the pyrometer: the freezing point of gold, the freezing point of silver, or the freezing point of copper.

Before ITS-90 was adopted, the thermocouple was the standardized thermometer for the upper temperatures. It was removed due to insufficient accuracy. The range of the platinum resistance thermometer has been extended upward to its present limit, and the optical pyrometer is the new standardized thermometer for the highest temperatures.

1.17
RANKINE AND FAHRENHEIT TEMPERATURE SCALES

Two temperature scales commonly used by engineers in the United States are based on a unit interval of temperature equal to five-ninths the size of a unit interval of temperature on the Kelvin and Celsius scales. By definition, the Rankine scale, named after the English engineer, is an absolute scale and is based solely on the temperature of the triple point of water. The Rankine scale, which does not use the word "degree," is related to the Kelvin temperature scale by the equation

$$T(\mathrm{R}) = \tfrac{9}{5}\, T(\mathrm{K}). \tag{1.10}$$

The Fahrenheit scale, named after the German instrument maker, is defined in relation to the Rankine scale by the equation

$$\theta(^\circ\mathrm{F}) = T(\mathrm{R}) - 459.67. \tag{1.11}$$

Thus, at the ice point, where the Kelvin temperature is 273.15, the Rankine temperature is (9/5)(273.15) = 491.67 R. Hence, the Fahrenheit temperature is

$$\theta(^\circ\mathrm{F}) = 491.67 - 459.67 = 32.00^\circ\mathrm{F}.$$

The Fahrenheit temperature is related to the Celsius temperature by the equation

$$\theta(^\circ\mathrm{F}) = \tfrac{9}{5}\theta(^\circ\mathrm{C}) + 32. \tag{1.12}$$

PROBLEMS

1.1. In the table below, a number in the top row represents the pressure of a gas in the bulb of a constant-volume gas thermometer (corrected for dead space, thermal expansion of bulb, etc.) when the bulb is immersed in a water triple-point cell. The bottom row represents the corresponding readings of pressure when the bulb is surrounded by a material at a constant unknown temperature. Calculate the ideal-gas temperature T of this material. (Use five significant figures.)

P_{TP}, kPa	133.32	99.992	66.661	33.331
P, kPa	204.69	153.54	102.37	51.190

1.2. The limiting value of the ratio of pressures of a gas at the steam point and at the triple point of water when the gas is kept at constant volume is found to be 1.365954. What is the ideal-gas temperature of the steam point to six significant figures?

1.3. The resistance R' of a particular carbon resistor obeys the equation

$$\sqrt{\frac{\log R'}{T}} = a + b\log R',$$

where $a = -1.16$ and $b = 0.675$.

(*a*) In a liquid helium cryostat, the resistance is found to be exactly 1000 Ω (ohms). What is the temperature?

(*b*) Make a log–log graph of R' against T in the resistance range from 1000 to 30,000 Ω.

1.4. The resistance of a doped germanium crystal obeys the equation

$$\log R' = 4.697 - 3.917\log T.$$

(*a*) In a liquid helium cryostat, the resistance is measured to be 218 Ω. What is the temperature?

(*b*) Make a log–log graph of R' against T from 200 to 30,000 Ω.

1.5. The resistance of a platinum wire is found to be 11.000 Ω at the ice point, 15.247 Ω at the steam point, and 28.887 Ω at the sulfur point. Find the constants a and b in the equation

$$R' = R'_0(1 + a\theta + b\theta^2),$$

and plot R' against Celsius temperature θ in the range from 0 to 660°C.

1.6. When the ice point i and the steam point s were chosen as fixed points with 100 degrees between them in the original Celsius scale, the ideal-gas temperature of the ice point was written

$$\theta_i = \frac{100}{r_s - 1},$$

where $r_s = \lim (P_s/P_i)$ at constant V.

(*a*) Show that the fractional error in T_i produced by an error in r_s is very nearly 3.73 times the fractional error in r_s, or

$$\frac{dT_i}{T_i} = 3.73\frac{dr_s}{r_s}.$$

(*b*) Any ideal-gas temperature may be written

$$T = T_i r,$$

where $r = \lim (P/P_i)$ at constant V. Show that the fractional error in T is

$$\frac{dT}{T} = \frac{dr}{r} + 3.73\frac{dr_s}{r_s}$$

(*c*) Now that the single fixed point of the ideal-gas temperature is a universal constant, show that the fractional error in T is

$$\frac{dT}{T} = \frac{dr}{r},$$

where $r = \lim (P/P_{TP})$ at constant V.

1.7. The length of the mercury column in the old-fashioned mercury-in-glass thermometer is 15.00 cm when the thermometer is in contact with water at its triple point. Consider the length of the mercury column as the thermometric property X and let θ be the empirical temperature determined by this thermometer.

(*a*) Calculate the empirical temperature when the length of the mercury column is 19.00 cm.

(*b*) If X can be measured with a precision of 0.01 cm, can this thermometer distinguish between the normal freezing point of water and the triple point of water?

1.8. The Rankine temperature scale assigns a numerical value of exactly 491.67 R to the triple point of water. The ratio of two temperatures is defined as the limiting ratio, as $P_{TP} \to 0$, of the corresponding pressures of a gas kept at constant volume.

(*a*) Find the best experimental value of the normal boiling point of water on this scale.

(*b*) Find the temperature interval between the freezing point and the boiling point.

1.9. What is the temperature on the Fahrenheit scale of the normal boiling point of H_2O, if this temperature is 99.974°C? (Use five significant figures.)

CHAPTER 2

Simple Thermodynamic Systems

2.1
THERMODYNAMIC EQUILIBRIUM

Suppose that experiments have been performed on a thermodynamic system and that the coordinates necessary and sufficient for a macroscopic description have been determined. When these coordinates change in any way whatsoever, either spontaneously or by virtue of outside influence, the system is said to undergo a *change of state.*† When a system is not influenced in any way by its surroundings, it is said to be *isolated.* In practical applications of thermodynamics, isolated systems are of little importance. We usually have to deal with a system that is influenced in some way by its surroundings. In general, the surroundings may exert forces on the system or provide contact between the system and a body at some definite temperature. When the state of a system changes, interactions usually take place between the system and its surroundings.

When there is no unbalanced force or torque in the interior of a system and also none between a system and its surroundings, the system is said to be in a state of *mechanical equilibrium.* When these conditions are not satisfied, either the system alone or both the system and its surroundings will undergo a change of state, which will cease only when mechanical equilibrium is restored.

When a system in mechanical equilibrium does *not* tend to undergo a spontaneous change of internal structure, such as a chemical reaction, or a transfer of matter from one part of the system to another, such as diffusion or solution, however slow, then it is said to be in a state of *chemical equilibrium.*

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† Notice that in general physics the expression "change of state" is often used to signify a transition from solid to liquid or liquid to gas, etc. Such a change in the language of thermodynamics is called a *change of phase.*

A system not in chemical equilibrium undergoes a change of state that, in some cases, is exceedingly slow. The change ceases when chemical equilibrium is reached.

Thermal equilibrium exists when there is no spontaneous change in the coordinates of a system in mechanical and chemical equilibrium when it is separated from its surroundings by diathermic walls. In other words, there is no exchange of heat between the system and its surroundings. In thermal equilibrium, all parts of a system are at the same temperature, and this temperature is the same as that of the surroundings. When these conditions are not satisfied, a change of state will take place until thermal equilibrium is reached.

When the conditions for all three types of equilibrium are satisfied, the system is said to be in a state of *thermodynamic equilibrium*; in this condition, it is apparent that there will be no tendency whatever for any change of state, either of the system or of the surroundings, to occur. *States of thermodynamic equilibrium can be described in terms of macroscopic coordinates that do not involve the time, that is, in terms of thermodynamic coordinates.* Thermodynamics does not attempt to deal with any problem involving the rate at which a process takes place. The investigation of problems involving the time dependence of changes of state is carried out in other branches of science, as in the kinetic theory of gases, hydrodynamics, and chemical kinetics.

When the conditions for any one of the three types of equilibrium that constitute thermodynamic equilibrium are not satisfied, the system is said to be in a *nonequilibrium state.* Thus, when there is an unbalanced force or torque in the interior of a system, or between a system and its surroundings, the following phenomena may take place: acceleration, turbulence, eddies, waves, etc. While such phenomena are in progress, a system passes through nonequilibrium states. If an attempt is made to give a macroscopic description of any one of these nonequilibrium states, it is found that the pressure varies from one part of a system to another. There is no single pressure that refers to the system as a whole. Similarly, in the case of a system at a different temperature from its surroundings, a nonuniform temperature distribution is set up and there is no single temperature that refers to the system as a whole. Therefore, we conclude that *when the conditions for mechanical and thermal equilibrium are not satisfied, the states traversed by a system cannot be described in terms of thermodynamic coordinates referring to the system as a whole.*

It must not be concluded, however, that we are entirely helpless in dealing with such nonequilibrium states. If we divide the system into a large number of small mass elements, then thermodynamic coordinates may be found in terms of which a macroscopic description of each mass element may be approximated. There are also special methods for dealing with systems in mechanical and thermal equilibrium but not in chemical equilibrium. All these special methods will be considered later. At present, we shall deal exclusively with systems in thermodynamic equilibrium.

2.2
EQUATION OF STATE

Imagine, for the sake of simplicity, a constant mass of gas, that is, a *closed* system, in a vessel so equipped that the pressure, volume, and temperature may be easily measured. If we fix the volume at some arbitrary value and cause the temperature to assume an arbitrarily chosen value, then we shall not be able to vary the pressure at all. Once V and T are chosen by us, the value of P at equilibrium is determined by nature. Similarly, if P and T are chosen arbitrarily, then the value of V at equilibrium is fixed. That is, of the three thermodynamic coordinates P, V, and T, only two are independent variables. This implies that there exists an equation of equilibrium which connects the thermodynamic coordinates and which robs one of them of its independence. Such an equation, called an *equation of state*, is a mathematical function relating the appropriate thermodynamic coordinates of a system in equilibrium. Every thermodynamic system has its own equation of state, although in some cases the relation may be so complicated that it cannot be expressed in terms of simple mathematical functions. For a closed system, the equation of state relates the temperature to two other thermodynamic variables.

An equation of state expresses the individual peculiarities of one system as compared with another system and must, therefore, be determined either by experiment or by molecular theory. A general theory like thermodynamics, based on general laws of nature, is incapable of generating an equation of state of any system. An equation of state, therefore, is not a theoretical deduction from thermodynamics, but is usually an experimental addition to thermodynamics. It expresses the results of experiments in which the thermodynamic coordinates of a system were measured as accurately as possible, within a limited range of values. An equation of state is, therefore, only as accurate as the experiments that led to its formulation, and holds only within the range of values measured. As soon as this range is exceeded, a different form of equation of state may be valid.

For example, a system consisting of a gas at very low pressure has the simple equation of state of an ideal gas,

$$PV = nRT, \tag{2.1}$$

where n is the number of moles and R is the molar gas constant. Equation (2.1) is often rewritten as

$$Pv = RT,$$

where lower-case v indicates the molar volume, that is, volume V per mole n. At higher pressures, the equation of state is more complicated, being fairly well represented by the van der Waals equation, which takes into account particle interactions and the finite size of the particles. Thus,

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT, \tag{2.2}$$

where a and b are constants appropriate to the specific gas. As far as thermodynamics is concerned, the important idea is that an equation of state exists, not whether we can write it down in simple mathematical form.

It is obvious that no equation of state exists for the states traversed by a system that is not in mechanical and thermal equilibrium, since such states cannot be described in terms of thermodynamic coordinates referring to the system as a whole. For example, if a gas in a cylinder were to expand and to impart to a piston an accelerated motion, the gas might have, at any moment, a definite volume and temperature, but the corresponding pressure, calculated from an equation of state, would not apply to the system as a whole. The pressure would not be a thermodynamic coordinate, because it would depend not only on the velocity and the acceleration of the piston but would also vary from point to point.

The example of a gas at equilibrium is a special case of a general class of systems that can be described in terms of the three thermodynamic coordinates P, V, and T. The next section is devoted to a consideration of such systems. There are many other types of systems that may be described at least to a first approximation by means of three thermodynamic coordinates, which may be given the generalized designations X, Y, and Z. Such "*XYZ systems*" will be called simple systems. The hydrostatic or PVT system represents an important type of simple system. The PVT system is most often encountered, because of the simple ideal-gas equation of state, so that the PVT system is often thought of as *the only* type of system to which thermodynamics applies. However, the one-dimensional stretched wire, the two-dimensional surface, and other systems will be considered later in this chapter and in subsequent chapters.

2.3

HYDROSTATIC SYSTEMS

Any isotropic system of constant mass and constant composition that exerts on the surroundings a uniform hydrostatic pressure, in the absence of gravitational, electric, and magnetic effects, we shall call a *hydrostatic system*. These systems are divided into the following categories:

1. A *pure substance*, which is a single chemical compound in the form of a solid, a liquid, a gas, a mixture of any two, or a mixture of all three.
2. A *homogeneous mixture of different compounds*, such as a mixture of inert gases, a mixture of chemically active gases, a mixture of liquids, or a solution.
3. A *heterogeneous mixture*, such as a mixture of different gases in contact with a mixture of different liquids.

Experiments show that the states of equilibrium† of a hydrostatic system of a single phase can be described in an equation of state by three coordinates,

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† In the remainder of this book, the word "equilibrium," unmodified by an adjective, will refer to thermodynamic equilibrium.

namely, the pressure P exerted by the system on the surroundings, the volume V, and the temperature T. The pressure is measured in the SI unit of pascal (newton per square meter), the volume in cubic meter, and the temperature in kelvin. Other units of pressure, such as pound per square inch, atmosphere, and millimeter of mercury are used in various applications of thermodynamics and will be found occasionally in this book. In the absence of any special remarks about units, however, it will be understood that SI units are to be employed.

Every hydrostatic system, that is, PVT system, has an equation of state expressing a relation among these three coordinates that is valid for equilibrium states. If the system undergoes a small change of state whereby it passes from an initial state of equilibrium to another state of equilibrium very near the initial one, then all three coordinates, in general, undergo slight changes. If the change of, say, V is very small in comparison with V and very large in comparison with the space occupied by a few molecules, then this change of V may be written as a differential dV. If V were a geometrical quantity referring to the volume of *space*, then dV could be used to denote a portion of that space arbitrarily small. Since, however, V is a macroscopic coordinate denoting the volume of *matter*, then, for dV to have a meaning, it must be large enough to include enough particles to warrant the use of the macroscopic point of view.

Similarly, if the change of P is very small in comparison with P and very large in comparison with local fluctuations of pressure caused by momentary variations in microscopic concentration, then it also may be represented by the differential dP. *Every infinitesimal in thermodynamics must satisfy the requirement that it represents a change in a quantity which is small with respect to the quantity itself and large in comparison with the effect produced by the behavior of a few molecules.* The reason for this is that thermodynamic coordinates such as volume, pressure, and temperature have no meaning when applied to a few particles. In other words, thermodynamic coordinates are macroscopic coordinates.

We may imagine the equation of state solved for any coordinate in terms of the other two. Thus,

$$V = \text{function of } (T, P), \qquad \text{or} \qquad V = V(T, P).$$

An infinitesimal change from one state of equilibrium to another state of equilibrium involves a dV, a dT, and a dP, all of which we shall assume satisfy the condition laid down in the previous paragraph. A fundamental theorem in partial differential calculus enables us to write the differential of the volume V,

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

where the partial derivative $(\partial V/\partial T)_P$ means the infinitesimal change in V for an infinitesimal change in *T with P held constant* during the operation of differentiation. Notice that each partial derivative can be a function of T

and P. Both partial derivatives have an important physical meaning. Recall from general physics a quantity called the average coefficient of volume expansion. This was defined as

$$\text{Average coefficient of vol. expansion} = \frac{\text{change of vol. per unit vol.}}{\text{change of temp.}},$$

where the changes occur at constant pressure. If the change of temperature is made smaller and smaller until it becomes infinitesimal, then the change in volume also becomes infinitesimal and we have what is known as the differential coefficient of volume expansion, or, simply, the *volume expansivity*, which is denoted by β. Thus,

$$\boxed{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P.} \tag{2.3}$$

Notice that β is almost always a positive number, except for a few notable exceptions. Liquid water between 0 and 4°C experiences a *decrease* in V when T increases, and so too for an ordinary rubber band at room temperature. Strictly speaking, volume expansivity β is a function of T and P, but experiments to be described later show that there are many substances for which β is quite insensitive to a change in P and varies only slightly with T. Consequently, within a small temperature range, β may, as a rule, be regarded as a constant. It is clear that β is expressed in the unit of reciprocal kelvin (K^{-1}).

In many textbooks of general physics, a quantity called the average bulk modulus is introduced in the discussion of a sound wave. It is defined thus:

$$\text{Average bulk modulus} = -\frac{\text{change of pressure}}{\text{change in volume per unit volume}}.$$

Since a positive change (increase) of pressure always produces a negative change (decrease) of volume, the minus sign is introduced to make the bulk modulus a positive number. If the change of pressure is made infinitesimal, then the volume change is also infinitesimal and we have the differential bulk modulus. If we further require that the temperature be kept constant, the resulting quantity is called the *isothermal bulk modulus* and is denoted by B. Thus,

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

For calculations in thermodynamics, the more useful quantity is the *reciprocal* of the isothermal bulk modulus, called the *isothermal compressibility* and denoted by the symbol κ (Greek letter kappa). Thus,

$$\boxed{\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.} \tag{2.4}$$

The unit of compressibility is reciprocal pressure (Pa^{-1}). The value of κ for solids and liquids varies only slightly with temperature and pressure, so that κ may often be regarded as constant.

The definitions of volume expansivity β and isothermal compressibility κ in Eqs. (2.3) and (2.4) are very important, serving as a connection between experimental values on the left side and partial derivatives of thermodynamic coordinates on the right side. If either equation is analytically or numerically integrated, as shown in the next section, then the change of a thermodynamic coordinate can be found from a calculation, whereas it might be difficult or impossible to determine the change of that coordinate from an experiment.

If the equation of state is solved for P, then

$$P = \text{function of } (T, V), \qquad \text{or} \qquad P = P(T, V),$$

and

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV.$$

Finally, if T is imagined as a function of P and V, then

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV.$$

In all the above equations, the closed system was assumed to undergo an infinitesimal process from an initial state of equilibrium to another. This enabled us to use an equation of equilibrium (equation of state) and to solve it for any coordinate in terms of the other two. The differentials dP, dV, and dT, therefore, are differentials of actual functions and are called *exact differentials*. If dz is an exact differential of a function of, say, x and y, then dz may be written

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy.$$

An infinitesimal that is not the differential of an actual function is called an *inexact differential* and cannot be expressed by an equation of the above type. There are other distinctions between exact and inexact differentials that will be made clear later in Sec. 10.4.

2.4
MATHEMATICAL THEOREMS

There are two simple theorems in partial differential calculus that are used very often in this subject. The proofs are as follows. Suppose that there exists a functional relationship among the three coordinates x, y, and z; thus,

$$f(x, y, z) = 0.$$

Then, x can be imagined as a function of y and z, and

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz.$$

Also, y can be imagined as a function of x and z, and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz.$$

Substituting the second equation into the first, we have

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz,$$

or

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz.$$

Of the three coordinates, only two are independent. Choosing x and z as the independent coordinates, the above equation must be true for all sets of values of dx and dz. Thus, if $dz = 0$ and $dx \neq 0$, it follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1,$$

or

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z}.} \tag{2.5}$$

If $dx = 0$ and $dz \neq 0$, it follows that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0,$$

and

$$\boxed{\begin{gathered}\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.\end{gathered}} \tag{2.6}$$

In the case of a PVT system, the second theorem yields the result

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

The volume expansivity β and the isothermal compressibility κ were defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

and
$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

Therefore,
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}.$$

An infinitesimal change in pressure may now be expressed in terms of these physical quantities. Thus,

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV,$$

or
$$dP = \frac{\beta}{\kappa}\,dT - \frac{1}{\kappa V}\,dV. \tag{2.7}$$

At constant volume,

$$dP = \frac{\beta}{\kappa}\,dT.$$

If we cause the temperature to change a finite amount from T_i to T_f at constant volume, the pressure will change from P_i to P_f, where the subscripts i and f denote the initial and final states, respectively. Upon integrating between these two states, we get

$$P_f - P_i = \int_{T_i}^{T_f} \frac{\beta}{\kappa}\,dT.$$

The right-hand member can be integrated if we know the way in which β and κ vary with T at constant volume. If the temperature range T_f to T_i is small, very little error is introduced by assuming that both are constant. With these assumptions, we obtain

$$P_f - P_i = \frac{\beta}{\kappa}(T_f - T_i),$$

from which the final pressure may be calculated. For example, consider the following problem. A mass of mercury at standard atmospheric pressure and a temperature of 15°C is kept at constant volume. If the temperature is raised to 25°C, what will be the final pressure? From tables of physical constants, β and κ of mercury remain practically constant within the temperature range of 15 to 25°C and have the values

$$\beta = 1.81 \times 10^{-4}\,\mathrm{K}^{-1},$$

and
$$\kappa = 4.01 \times 10^{-11}\,\mathrm{Pa}^{-1};$$

hence,
$$P_f - P_i = \frac{1.81 \times 10^{-4}\,\mathrm{K}^{-1} \times 10\,\mathrm{K}}{4.01 \times 10^{-11}\,\mathrm{Pa}^{-1}}$$

$$= 4.51 \times 10^{7}\,\mathrm{Pa},$$

and, since the initial atmospheric pressure is approximately $P_i = 1 \times 10^5\,\text{Pa}$, we have

$$\begin{aligned} P_f &= 4.51 \times 10^7\,\text{Pa} + 0.01 \times 10^7\,\text{Pa} \\ &= 4.52 \times 10^7\,\text{Pa} = 452\,\text{atm}. \end{aligned}$$

In other words, approximately 450 atm of pressure is needed to hold the volume of the mercury constant for a temperature increase of only 10°C.

Much of the development of thermodynamics has been based on the hydrostatic or *PVT* system, which is still important. But systems of other geometric dimensions and other physical variables have become important also.

2.5
STRETCHED WIRE

A wire can be thought of as a one-dimensional system, because its length is long compared with its area. Experiments on stretched wires are usually performed under conditions in which the pressure remains constant at standard atmospheric pressure and changes in volume are negligible. For most practical purposes, it is found unnecessary to include the pressure and the volume among the thermodynamic coordinates. A sufficiently complete thermodynamic description of a wire is given in terms of only three coordinates:

1. The tension *in* the wire $\mathcal{J}$, measured in newtons (N).
2. The length of the wire L, measured in meters (m).
3. The absolute temperature T, measured in kelvin (K).

The states of thermodynamic equilibrium are connected by an equation of state that, as a rule, cannot be expressed by a simple equation. For a wire at constant temperature within the limit of elasticity, however, Hooke's law holds; namely, for the tension $\mathcal{J}$ in a stretched wire,

$$\mathcal{J} = -k(L - L_0), \tag{2.8}$$

where k is Hooke's constant and L_0 is the length at zero tension. If the tension is not balanced by an external force, the wire will describe some sort of accelerated motion, such as vibration, and will pass through states that cannot be described in terms of thermodynamic coordinates referring to the wire as a whole.

If a wire undergoes an infinitesimal change from one state of equilibrium to another, then the infinitesimal change of length is an exact differential and can be written

$$dL = \left(\frac{\partial L}{\partial T}\right)_{\mathcal{J}} dT + \left(\frac{\partial T}{\partial \mathcal{J}}\right)_T d\mathcal{J},$$

where both partial derivatives are functions of T and $\mathcal{J}$. These derivatives are connected with important physical quantities. In general physics, the average linear coefficient of expansion was defined as

$$\text{Average linear coefficient of expansion} = \frac{\text{change of length per unit length}}{\text{change of temperature}},$$

the tension being considered constant. If the change of temperature becomes infinitesimal, then the change of length also becomes infinitesimal and we have the *linear expansivity* α, which is given by

$$\boxed{\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathcal{J}}.} \tag{2.9}$$

Since the length of a wire L increases when the temperature T increases for metals, the linear expansivity α is most often a positive number for metals. However, a rubber band, which may be considered a one-dimensional system, has a negative linear expansivity because it has a negative volume expansivity. The experimental measurement of α will be considered later. Data for α show that it depends only slightly on $\mathcal{J}$ and varies mostly with T. In a small temperature range, however, it may be regarded as practically constant. The linear expansivity α is measured in the unit of reciprocal kelvin (K^{-1}).

In general physics, the average Young's modulus was defined as

$$\text{Average Young's modulus} = \frac{\text{change of tension per unit area}}{\text{change of length per unit length}},$$

the temperature remaining constant. When the change of tension becomes infinitesimal, we have what is known as the *isothermal Young's modulus*, denoted by Y. Thus,

$$\boxed{Y = \frac{L}{A}\left(\frac{\partial \mathcal{J}}{\partial L}\right)_T,} \tag{2.10}$$

where A denotes the cross-sectional area of the wire. Notice that the partial derivative in Eq. (2.10) is always positive. The isothermal Young's modulus is found experimentally to depend slightly on $\mathcal{J}$ and mostly on T. For a small temperature range, it may be regarded as practically constant. The unit of Y is newton per square meter (N/m^2).

From the second theorem in Sec. 2.4,

$$\left(\frac{\partial \mathcal{J}}{\partial T}\right)_L = -\left(\frac{\partial \mathcal{J}}{\partial L}\right)_T\left(\frac{\partial L}{\partial T}\right)_{\mathcal{J}};$$

hence,
$$\left(\frac{\partial \mathcal{J}}{\partial T}\right)_L = -\alpha A Y,$$

which means that for an increase in temperature, the change of tension will be opposite to the sign of the linear expansivity.

2.6
SURFACES

The study of a surface, which can be considered to be a two-dimensional system, is an interesting branch of physical chemistry. The surfaces of liquids and solids have properties that are distinctly different from the bulk properties of the underlying material. There are some important examples of surfaces:

1. The interface of a liquid in equilibrium with a vapor.
2. A soap bubble stretched across a wire framework, consisting of two surfaces trapping a small amount of liquid.
3. A thin film of oil on the surface of water.
4. A monolayer of a gas on the surface of a solid catalyst.

A surface, such as a soap bubble on a wire framework, is somewhat like a stretched membrane. The surface on one side of any imaginary line pulls perpendicular to this line with a force equal and opposite to that exerted by the surface on the other side of the line. The force acting perpendicularly to a line of unit length is called the *surface tension* γ (Greek letter gamma). An adequate thermodynamic description of a surface is given by the specifying three coordinates:

1. The surface tension γ, measured in newtons per meter (N/m).
2. The area of the film A, measured in square meters (m^2).
3. The absolute temperature T, measured in kelvin (K).

In dealing with a surface, which is a thin layer on a substrate, the underlying substrate must always be considered as part of the system. This may be done, however, without introducing the pressure and volume of the composite system because, as a rule, the pressure remains constant and volume changes are negligible. The surface of a pure liquid in equilibrium with its vapor has a particularly simple equation of state. Experiment shows that the surface tension of such a surface does not depend on the area but is a function of the temperature only. For most pure liquids in equilibrium with their vapor phase, the surface tension has an equation of state of the form originated by van der Waals, but further developed by Guggenheim:

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^n, \tag{2.11}$$

where γ_0 is the surface tension at a standard temperature, usually 20°C, T_c is the critical temperature (the temperature above which no amount of pressure will condense vapor into liquid, discussed in Secs. 9.1 and 9.2), and n is a constant that lies between 1 and 2. It is clear from this equation that the surface tension decreases as T increases, becoming zero when $T = T_c$.

The equation of state of a thin film of insoluble oil on water is particularly interesting. If γ_w denotes the surface tension of a clean water surface and γ the surface tension of the water covered by the oil, then, within a restricted range of values of area A,

$$(\gamma - \gamma_w)A = aT, \tag{2.12}$$

where a is a constant. The difference $\gamma - \gamma_w$ is sometimes called the *surface pressure* or "two-dimensional" pressure. Equation (2.12) is the surface analog of the ideal-gas law. Oil films can be compressed and expanded and, when deposited on glass, produce the interesting optical effect of Newton's rings.

2.7
ELECTROCHEMICAL CELL

Consider a battery with electrodes that provide the voltage (potential difference) for a circuit to be analyzed. In thermodynamics, attention is directed inside the battery to the source of the voltage, which is an electrochemical cell, or series of cells.

An electrochemical cell consists of two electrodes of different materials, each immersed in a different electrolyte. Chemical reactions deposit ions on the electrodes, which take the polarity of the ions. Thus, a chemical force produces the electrostatic force that moves the charge in the external circuit. The integral around a closed path of the force per unit charge, known as the *electromotive force* and abbreviated simply emf, is generated between the two electrodes and depends on the nature of the solid electrodes, the concentrations of the liquid electrolytes, and the temperature. In Fig. 2-1, a schematic diagram of a rechargeable electrochemical cell, called the *Daniell cell,* is shown. A copper electrode, immersed in a saturated $CuSO_4$ solution, is separated by a porous wall from a zinc electrode, immersed in a saturated solution of $ZnSO_4$. Experiment shows that the copper electrode is positively charged and the zinc electrode is negatively charged, producing an emf of approximately 1.1 V.

Suppose that the cell is connected to an external resistor. In this case, the current flows externally from the copper electrode to the zinc electrode. Internally, zinc goes into solution, zinc sulfate is formed, copper is deposited, and copper sulfate is used up as the cell discharges. These changes are summarized by the chemical reaction

$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4.$$

When the cell is connected to an external battery with a potential difference greater than the Daniell cell, current flows externally from the zinc electrode to the copper electrode; and the reaction proceeds in the reverse direction as the cell is being charged; thus,

$$Cu + ZnSO_4 \rightarrow Zn + CuSO_4.$$

The important feature of an electrochemical cell is that the chemical changes accompanying the transfer of *charge* for a reaction take place to the same

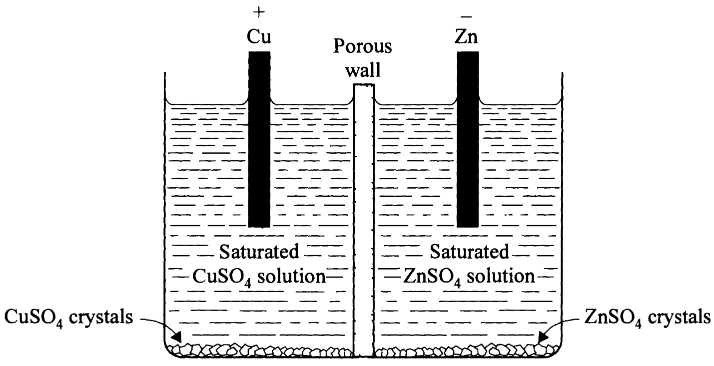

FIGURE 2-1
The Daniell cell.

extent for the reverse reaction when the same quantity of charge is transferred in the opposite direction.

The lead storage battery found in automobiles is probably the most familiar example of the use of electrochemical cells. The battery's negative electrode is lead, its positive electrode is lead oxide, and the common electrolyte is sulfuric acid. The automobile battery comprises six cells connected in series inside the casing and produces an emf of between 12 and 13 V. The potential difference on the battery's electrodes is less than the emf, due to the voltage drop from the battery's internal resistance.

The process of charge flow is one of electrolysis, which is described by one of Faraday's laws of electrolysis. It states that the simultaneous dissolving of 1 mol of zinc and the depositing of 1 mol of copper are accompanied by the transfer of exactly jF coulombs of charge, where j is the valence and F is Faraday's constant, or 96,485 C per mole of electrons. We may, therefore, define a quality Z, called the *charge of the cell*, as a number whose absolute magnitude is unimportant but whose change is numerically equal to the amount of charge that is transferred during the chemical reaction, the change being negative when the current flows externally from the positive to the negative electrode. Thus, if Δn moles of zinc disappear and Δn moles of copper are deposited, the charge of the cell changes from Z_i to Z_f, where

$$Z_f - Z_i = -\Delta njF. \tag{2.13}$$

It we limit ourselves to electrochemical cells that operate at constant atmospheric pressure, we may ignore the pressure and the volume and describe the cell with the aid of three thermodynamic coordinates only:

1. The emf $\mathcal{E}$, measured in volts (V).
2. The charge Z, measured in coulombs (C).
3. The absolute temperature T, measured in kelvin (K).

When the cell is on open circuit, there is a tendency for diffusion to take place slowly and the cell is not in equilibrium. If the cell is connected to a high-impedance voltmeter, however, there is no current and the emf of the cell is balanced and the cell is in mechanical and chemical equilibrium. When thermal equilibrium is also satisfied, the cell is then in thermodynamic equilibrium. The states of thermodynamic equilibrium of an electrochemical cell are connected by an equation of state among the coordinates $\mathcal{E}$, Z, and T. If the electrolytes are saturated solutions, a current driven by the chemical reaction at constant temperature and pressure will not alter the concentrations of the electrolytes. The emf will, therefore, remain constant. Experiment shows that the emf of a saturated rechargeable cell at constant pressure is a function of the temperature only. The equation of state for an electrochemical cell is usually written

$$\mathcal{E} = \mathcal{E}_{20} + \alpha(\theta - 20^\circ) + \beta(\theta - 20^\circ)^2 + \gamma(\theta - 20^\circ)^3, \tag{2.14}$$

where θ is the Celsius temperature, $\mathcal{E}_{20}$ is the emf at 20°C, and α, β, and γ are constants depending on the materials. We shall see later that, once the equation of state of an electrochemical cell is known, all the quantities of interest in the chemical reaction in the cell can be determined.

2.8
DIELECTRIC SLAB

Consider a capacitor consisting of two parallel conducting plates of area A with linear dimensions that are large in comparison with their separation l, filled with an isotropic solid or liquid dielectric material. If a constant voltage is established across the plates, then a uniform electric field $\boldsymbol{E}$ exists *in the dielectric* between the plates. If the center of charge of the individual positive and negative charges within each molecule originally coincided, that is, if the molecules of the dielectric are originally *nonpolar*, such as carbon tetrachloride, the effect of the electric field is to separate the electric charges of each molecule so as to make each molecule *polar* in the direction of the electric field. If the molecules are naturally polar, such as water, with the polar axes distributed at random, the effect of the electric field is to produce a partial orientation of the molecular polar axes in the direction of the electric field. The effect is the same in either case, and the degree to which either the natural or induced polar molecules are oriented in the direction of the field is provided by the electric charge induced on either face of the dielectric multiplied by the thickness of the dielectric, a quantity called either the *electric dipole moment per unit volume* or the *dielectric polarization* $\boldsymbol{P}$. Owing to the symmetry of the system under consideration, $\boldsymbol{P}$ is uniform and perpendicular to the plates in this case. From the study of electrodynamics, the *electric displacement* $\boldsymbol{D}$ of the dielectric is given by the vector equation

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P}, \tag{2.15}$$

where ϵ_0 is the permittivity of vacuum and a scalar in this case, and vector quantities are represented by bold letters. The dielectric material has been chosen to be isotropic, so $\boldsymbol{E}$, $\boldsymbol{P}$, and $\boldsymbol{D}$ have the same direction.

In the study of thermodynamics, however, it is *not* customary to refer to the unit volume of a material, as $\boldsymbol{P}$ does, because the thermodynamic coordinate volume would be implicit in the polarization. To show the explicit dependence on volume, we introduce in thermodynamics the *total polarization* $\wp$, where the electrodynamic polarization $\boldsymbol{P}$ equals $\wp/V$. So Eq. (2.15) becomes, for our purposes,

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \frac{\wp}{V}. \tag{2.16}$$

The total polarization $\wp$ produced by a field $\boldsymbol{E}$ depends on the nature of the dielectric, upon the temperature, and, of course, upon the volume. Typically, a dielectric substance experiences insignificantly small volume changes in an experiment performed at constant atmospheric pressure. Therefore, the pressure and volume can be ignored. Furthermore, it is not necessary to retain the vector notation for the total polarization, because in simple systems in thermodynamics the quantities are homogeneous and isotropic, and, therefore, are treated mathematically as scalar quantities. We may describe a dielectric with the aid of the three thermodynamic coordinates:

1. The electric field E, measured in volts per meter (V/m).
2. The total polarization $\wp$, measured in coulomb-meters (C · m).
3. The absolute temperature T, measured in kelvin (K).

There are many dielectrics whose equation of state at temperatures above about 10 K is given by

$$\frac{\wp}{V} = \left(a + \frac{b}{T}\right) E, \tag{2.17}$$

where a and b are constants.

2.9
PARAMAGNETIC ROD

A paramagnet, unlike a ferromagnet such as iron, has no permanent magnetism and no hysteresis. Upon being introduced into an external magnetic field, a paramagnet becomes slightly magnetized in the direction of the field. Within the paramagnetic material, microscopic currents are induced by the magnetic field. The macroscopic effect of the induced currents is called the *magnetic dipole moment per unit volume* or the *magnetization* $\boldsymbol{M}$. The magnetization $\boldsymbol{M}$ is analogous to the polarization $\boldsymbol{P}$, even to the extent of defining a quantity that is analogous to the electric displacement $\boldsymbol{D}$, namely, the magnetic field (strength) $\mathcal{H}$:

$$\mathcal{H} = \frac{\mathcal{B}}{\mu_0} - \boldsymbol{M}, \tag{2.18}$$

where μ_0 is the permeability of vacuum and a scalar quantity for isotropic paramagnets and $\mathcal{B}$ is the magnetic induction. Furthermore, the vectors $\mathcal{B}$, $\boldsymbol{M}$, and $\mathcal{H}$ have the same direction.

As in the case of the electrodynamic $\boldsymbol{P}$, which had to be replaced by the thermodynamic $\mathcal{P}$ in order to make explicit the thermodynamic coordinate volume, so, too, we introduce the *total magnetization* $\mathcal{M}$, where the electrodynamic magnetization $\boldsymbol{M}$ equals $\mathcal{M}/V$ multiplied by the system's volume. Then, Eq. (2.18) becomes

$$\mathcal{H} = \frac{\mathcal{B}}{\mu_0} - \frac{\mathcal{M}}{V}. \tag{2.19}$$

Experiments on paramagnetic materials are not usually performed on arbitrarily shaped samples, but must be performed on samples in the form of a long cylinder, ellipsoid, or sphere. The restricted geometry is necessary in order to solve Ampère's law in closed form. We shall limit ourselves to a long, thin cylinder (a rod) inside a current-carrying solenoid. Most experiments on magnetic rods are performed at constant atmospheric pressure and involve only negligible volume changes. Consequently, we may ignore the pressure and the volume and describe a paramagnetic solid with the aid of only three thermodynamic coordinates, which are scalar quantities in simple thermodynamic systems:

1. The magnetic field $\mathcal{H}$, measured in amperes per meter (A/m).
2. The total magnetization $\mathcal{M}$, measured in ampere-meter squared ($\mathrm{A \cdot m^2}$).
3. The temperature T, measured in kelvin (K).

The states of thermodynamic equilibrium of a paramagnetic solid can be represented by an equation of state among these coordinates. Experiment shows that the magnetization of many paramagnetic solids is a function of the ratio of the magnetic intensity to the temperature. For small values of this ratio, the function reduces to a very simple form, namely,

$$\mathcal{M} = \frac{C_C \mathcal{H}}{T}, \tag{2.20}$$

which is known as *Curie's law* — C_C being called the *Curie constant*. The SI unit for the Curie constant in Eq. (2.20) is expressed as

$$\text{Unit of } C_C = \frac{\mathrm{A \cdot m^2}}{\mathrm{A/m}} \mathrm{K} = \mathrm{m^3 \cdot K}.$$

Since the Curie constant depends upon the amount of material, its unit may be taken to be any one of the four listed in Table 2.1.

TABLE 2.1
Units of the Curie constant

Total	Per mole	Per kilogram	Per cubic meter
$m^3 \cdot K$	$\dfrac{m^3 \cdot K}{mol}$	$\dfrac{m^3 \cdot K}{kg}$	K

Materials exhibiting either electronic paramagnetism or nuclear paramagnetism are particularly important in thermodynamics. It will be seen later how they are used to obtain extremely low temperatures.

2.10
INTENSIVE AND EXTENSIVE COORDINATES

Imagine a system in equilibrium to be divided into two equal parts, each with equal mass. Those properties of each half of the system that remain the same are said to be *intensive*; those that are halved are called *extensive*. The intensive coordinates of a system, such as temperature and pressure, are independent of the mass; the extensive properties are proportional to the mass. The thermodynamic coordinates that have been introduced in this chapter are listed in Table 2.2.

TABLE 2.2
Intensive and extensive coordinates

Simple systems	Intensive coordinate	Extensive coordinate
Hydrostatic system	Pressure P	Volume V
Stretched wire	Tension $\mathcal{J}$	Length L
Surface	Surface tension γ	Area A
Electrochemical cell	Electromotive force (emf) $\mathcal{E}$	Charge Z
Dielectric slab	Electric field E	Total polarization $\wp$
Paramagnetic rod	Magnetic field $\mathcal{H}$	Total magnetization $\mathcal{M}$

PROBLEMS

2.1. The equation of state of an ideal gas is $PV = nRT$, where n and R are constants.
(*a*) Show that the volume expansivity β is equal to $1/T$.
(*b*) Show that the isothermal compressibility κ is equal to $1/P$.

2.2. The equation of state of a van der Waals gas is given as

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

where a, b, and R are constants. Calculate the following quantities:
(*a*) $(\partial P/\partial v)_T$;
(*b*) $(\partial P/\partial T)_v$.
From parts (*a*) and (*b*) calculate $(\partial v/\partial T)_P$.

2.3. The equilibrium states of superheated steam are represented by Callendar's equation, thus:

$$v - b = \frac{rT}{P} - \frac{a}{T^m},$$

where b, r, a, and m are constants. Calculate the volume expansivity β as a function of T and P.

2.4. (*a*) A block of copper at a pressure of 1 atm (approximately 100 kPa) and a temperature of 5°C is kept at constant volume. If the temperature is raised to 10°C, what will be the final pressure?
(*b*) If the vessel holding the block of copper has a negligibly small thermal expansivity and can withstand a maximum pressure of 1000 atm, what is the highest temperature to which the system may be raised?
(*Note*: The volume expansivity β and isothermal compressibility κ are not always listed in handbooks of data. However, β is three times the linear expansion coefficient α, and κ is the reciprocal of the bulk modulus B. For this problem, assume that the volume expansivity and isothermal compressibility remain practically constant within the temperature range of 0 to 20°C at the values of $4.95 \times 10^{-5}\,\mathrm{K}^{-1}$ and $6.17 \times 10^{-12}\,\mathrm{Pa}^{-1}$, respectively.)

2.5. A block of copper at a pressure of 1 atm, a volume of $100\,\mathrm{cm}^3$, and a temperature of 10°C experiences a rise in temperature of 5°C and an increase in volume of $0.005\,\mathrm{cm}^3$. Assuming the volume expansivity and isothermal compressibility given in Prob. 2.4, calculate the final pressure.

2.6. Consider a wire that undergoes an infinitesimal change from an initial equilibrium state to a final equilibrium state.
(*a*) Show that the change of tension is equal to

$$d\mathcal{J} = -\alpha A Y dT + \frac{AY}{L} dL.$$

(*b*) A nickel wire of cross-sectional area $0.0085\,\mathrm{cm}^2$ under a tension of 20 N and a temperature of 20°C is stretched between two rigid supports 1 m apart. If the temperature is reduced to 8°C, what is the final tension? (*Note*: Assume that α and Y remain constant at the values of $1.33 \times 10^{-5}\,\mathrm{K}^{-1}$ and $2.1 \times 10^{6}\,\mathrm{Pa}$, respectively.)

2.7. The equation of state of an ideal elastic substance is

$$\mathcal{J} = KT\left(\frac{L}{L_0} - \frac{L_0^2}{L^2}\right),$$

where K is a constant and L_0 (the value of L at zero tension) is a function of temperature only.
(*a*) Show that the isothermal Young's modulus is given by

$$Y = \frac{\mathcal{J}}{A} + \frac{3KT L_0^2}{AL^2}.$$

(*b*) Show that the isothermal Young's modulus at zero tension is given by

$$Y_0 = \frac{3KT}{A}.$$

(*c*) Show that the linear expansivity is given by

$$\alpha = \alpha_0 - \frac{\mathcal{J}}{AYT} = \alpha_0 - \frac{1}{T}\frac{L^3/L_0^3 - 1}{L^3/L_0^3 - 2},$$

where α_0 is the value of the linear expansivity at zero tension, or

$$\alpha_0 = \frac{1}{L_0}\frac{dL_0}{dT}.$$

(*d*) Assume the following values for a sample of rubber: $T = 300\,\mathrm{K}$, $K = 1.333 \times 10^{-2}\,\mathrm{N/K}$, $A = 1 \times 10^{-6}\,\mathrm{m}^2$, $\alpha_0 = 5 \times 10^{-4}\,\mathrm{K}^{-1}$. When this sample is stretched to length $L = 2L_0$, calculate $\mathcal{J}$, Y, and α.

2.8. The surface tension of water γ in dynes per centimeter is given by the empirical equation (W. D. Harkins: *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952, p. 76.),

$$\gamma = 75.796 - 0.145\theta - 0.00024\theta^2,$$

where θ is the Celsius temperature. Calculate the change of surface tension with respect to temperature θ, $d\gamma/d\theta$, at 10°C and 60°C.

2.9. From the critical point, 5.2 K, down to the λ-point, 2.2 K, of liquid ^{4}He, the surface tension is given approximately by

$$\gamma = 0.05\frac{\mathrm{N}}{\mathrm{m}}\left(1 - \frac{T}{5.2\,\mathrm{K}}\right).$$

Plot γ against T in this temperature range.

2.10. The emf of a Weston rechargeable electrochemical cell varies with temperature according to Eq. (2.14), where

$$\mathcal{E}_{20} = 1.01827\,\mathrm{V},$$
$$\alpha = -4.06 \times 10^{-6}\,\mathrm{V/deg},$$
$$\beta = -9.5 \times 10^{-7}\,\mathrm{V/deg}^2,$$
$$\gamma = +1.0 \times 10^{-8}\,\mathrm{V/deg}^3.$$

Calculate $\mathcal{E}$ and $d\mathcal{E}/dT$ at 25°C.

2.11. Calculate $(\partial E/\partial T)_{\mathcal{P}}$ and $(\partial \mathcal{P}/\partial T)_E$ for a dielectric material obeying Eq. (2.17),

$$\frac{\mathcal{P}}{V} = \left(a + \frac{b}{T}\right)E.$$

2.12. Calculate $(\partial \mathcal{H}/\partial T)_{\mathcal{M}}$ and $(\partial \mathcal{M}/\partial T)_{\mathcal{H}}$ for a paramagnetic material that obeys Eq. (2.20),

$$\mathcal{M} = \frac{C_C \mathcal{H}}{T},$$

where C_C is the Curie constant.

CHAPTER 3

Work

3.1 WORK

If a system undergoes a displacement under the action of a force, *work* is said to be done, the amount of work being equal to the product of the force and the component of the displacement parallel to the force. If a system as a *whole* exerts a force on its surroundings and a displacement takes place, the work that is done either by the system or on the system is called *external work.* Thus, a gas, confined in a cylinder and at uniform pressure, while expanding and imparting motion to a piston does external work on its surroundings. The work done, however, by one part of a system on another part is called *internal work.* The interactions of molecules, atoms, or electrons on one another constitute internal work.

Internal work cannot be discussed in macroscopic thermodynamics. Only the work that involves an interaction between a system and its surroundings is analyzed. When a system does external work, the changes that take place can be described by means of macroscopic quantities referring to the system as a whole, in which case the changes may be imagined to accompany the raising or lowering of a suspended weight, the winding or unwinding of a spring, or, in general, the alteration of the position or *configuration* of some external mechanical device. This may be regarded as the ultimate criterion as to whether external work is done or not. It will often be found convenient throughout the remainder of this book to describe the performance of external work in terms of, or in conjunction with, the operation of a mechanical device, such as a suspended weight or deformed spring. *Unless otherwise indicated, the word work, unmodified by any adjective, will mean external work.*

A few additional examples may be helpful. If an electrochemical cell is disconnected from a circuit, changes that take place in the cell (such as diffusion) are not accompanied by the performance of work. If, however, the cell is connected to an external circuit through which charge flows, the current may be imagined to produce rotation of the armature of a motor, thereby lifting a weight or winding a spring. Therefore, *for an electrochemical cell to do work, it must be connected to an external circuit.* As another example, consider a magnet far removed from any external electric conductor. A change of magnetization within the magnet is not accompanied by the performance of work. If, however, the magnet undergoes a change of magnetization while it is surrounded by an electric conductor, then eddy currents are set up in the conductor, constituting an external transfer of charge. Hence, *for a magnetic system to do work, it must interact with an external electric conductor or with other magnets.*

In mechanics, we are concerned with the behavior of systems acted on by external forces. When the resultant force exerted *on* a mechanical system is in the same direction as the displacement of the system, the work of the force is positive, work is said to be done *on* the system, and the energy of the system increases. For thermodynamics to be consistent with mechanics, we adopt the same sign convention for work. Thus, when work is done *on* the system, the work is regarded as *positive.* Conversely, when work is done *by* the system, the work is regarded as *negative.* This sign convention disagrees with engineering practice, in which positive work is done by the system on an external object.

3.2
QUASI-STATIC PROCESS

A system in thermodynamic equilibrium satisfies the following stringent requirements:

1. *Mechanical equilibrium.* There are no unbalanced forces or torques acting on any part of the system or on the system as a whole.
2. *Thermal equilibrium.* There are no temperature differences between parts of the system or between the system and its surroundings.
3. *Chemical equilibrium.* There are no chemical reactions within the system and no motion of any chemical constituent from one part of a system to another part.

Once a system is in thermodynamic equilibrium and the surroundings are kept unchanged, no motion will take place and no work will be done. If, however, the sum of the external forces is changed so that there is a finite unbalanced force acting on the system, then the condition for mechanical equilibrium is no longer satisfied and the following situations may arise:

1. Unbalanced forces or torques may be created within the system; as a result, turbulence, waves, etc., may be set up. Also, the system as a whole may execute some sort of accelerated motion.

2. As a result of this turbulence, acceleration, etc., a nonuniform temperature distribution may be brought about, as well as a finite difference of temperature between the system and its surroundings.
3. The sudden change in the forces and in the temperature may produce a chemical reaction or the motion of a chemical constituent.

It follows that a finite unbalanced force may cause the system to pass through nonequilibrium states. If it is desired, during a process, to describe every state of a system by means of system-wide thermodynamic coordinates, then the process must *not* be performed using a finite unbalanced force or torque. We are led, therefore, to imagine an *ideal* situation in which the external forces acting on a system are varied only slightly so that the unbalanced force is infinitesimal, and the process proceeds infinitesimally slowly. A process performed in this ideal way is said to be *quasi-static. During a quasi-static process, the system is at all times infinitesimally near a state of thermodynamic equilibrium*, and all the states through which the system passes can be described by means of thermodynamic coordinates referring to the system as a whole. An equation of state is valid, therefore, for all these states. A quasi-static process is an *idealization* that is applicable to all thermodynamic systems, including electric and magnetic systems. The conditions for such a process can never be rigorously satisfied in the laboratory, but they can be approached with almost any degree of accuracy.

The purpose of introducing quasi-static processes is to allow us to make calculations without addressing the complications of friction within the system, for example. This approach is no different from that of mechanics with its massless springs and ideal pulleys, or that of circuit theory with wires with no resistance or batteries with constant voltage. At this point, a quasi-static process is synonymous with a reversible process, because dissipative processes are ignored. In Chap. 6, it will be shown that quasi-static hydrostatic processes are irreversible when friction is taken into account.

In the next few sections, it will be seen that all the systems introduced in the last chapter experience idealized quasi-static processes in exchanging work with the surroundings. The procedure will be to calculate an infinitesimal amount of work for each system by forming the dot-product of the force and the differential displacement. The force and displacement are parallel and yield positive work when work is done on the system. During the quasi-static process, the external force differs only by an infinitesimal amount from the internal force. In other words, the variables in an equation of state are essentially the same in both the system and the surroundings during a quasi-static process *with the proper boundary*. For example, the temperature is the same on both sides of a diathermic wall, but not for an adiabatic wall; the pressure is the same on both sides of a movable piston, but not for a rigid wall. Let us begin with the most common system, the hydrostatic system.

3.3
WORK IN CHANGING THE VOLUME OF A HYDROSTATIC SYSTEM

Imagine any hydrostatic system contained in a closed cylinder equipped with a frictionless movable piston on which the system and the surroundings may act. Suppose that the cylinder has a cross-sectional area A, and that the pressure exerted *by the system* at the piston face is P. The force on the internal face of the piston is, therefore, PA. The surroundings also exert an opposing force on the piston. The origin of the external force is irrelevant; it might be due to the force from a spring or a weight, or external friction, or a combination of these. The system within the cylinder does not have to know how the external force originated. The important condition that must be satisfied is that the force F from the surroundings must differ only slightly from the force PA of the system. If, under these conditions, the piston moves in an infinitesimal distance dx during compression, as shown in Fig. 3-1, then the surroundings perform an infinitesimal amount of positive work $đW$ (the differential symbol with the line drawn through it, and read *dee-bar W*, will be explained in Sec. 3.5) on the system, equal to

$$đW = F\,dx = PA\,dx.$$

But, during compression, the volume of the system is decreasing, so

$$A\,dx = -dV,$$

and, hence

$$\boxed{đW = -P\,dV.} \tag{3.1}$$

The presence of the minus sign before $P\,dV$ ensures that a negative dV (a compression) gives rise to positive work done *on* the system and, conversely, a positive dV (an expansion) yields negative work done *by* the system, which is based on the convention that work done on a system increases the energy of

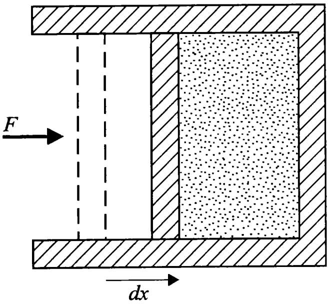

FIGURE 3-1
Quasi-static compression of a hydrostatic system enclosed by an adiabatic cylinder and piston.

the system. The SI unit of pressure P is the pascal, abbreviated Pa, and that of volume V is the cubic meter. The unit of work is, therefore, the joule, abbreviated J. It is often convenient to take standard atmospheric pressure (101,325 Pa) as a unit of P and the liter as a unit of V. The unit of work is then a liter-atm, which is equal to approximately 100 J. In some books, the expression for work given in Eq. (3.1) omits the negative sign in accordance with the convention from engineering that the expansion of a chamber in an engine performs positive work.

During an expansion or contraction of a hydrostatic system, there might be a chemical reaction or a transport of a chemical from one point to another, taking place slowly enough to keep the system near mechanical equilibrium; or we might have some dissipative process, such as friction, taking place, or even all these processes. The lack of chemical equilibrium (and, therefore, of complete thermodynamic equilibrium) or the presence of dissipation *does not preclude* writing $đW = -P\,dV$, where P is the system pressure. A lack of mechanical equilibrium, however, such as exists when there are waves or turbulence within the system, definitely prevents expressing $đW = -P\,dV$, because the pressure of the system is no longer defined. It should be noted that the validity of Eq. (3.1) does not depend upon the piston-and-cylinder device used in its derivation; it can be applied to any expanding or contracting hydrostatic system of arbitrary shape.

In a *finite* quasi-static process in which the volume changes from V_i to V_f, the amount of work W done by the system is

$$W = -\int_{V_i}^{V_f} P\,dV. \tag{3.2}$$

If the change in volume is performed quasi-statically, the system pressure P is at all times not only equal to the external pressure, but the pressure is also a thermodynamic coordinate. Thus, the pressure can be expressed as a function of temperature T and volume V by means of an equation of state. The evaluation of the integral can be accomplished once the behavior of T is specified, because then P can be expressed as a function of V only. If P is expressed as a function of V, the *path* of integration through successive equilibrium states is defined. Along a particular quasi-static path, the work done by a system in going from an initial volume V_i to a larger volume V_f is expressed as

$$W_{if} = -\int_{V_i}^{V_f} P\,dV;$$

however, in contracting from state f to state i, *along the same path of integration* but in the opposite direction (order of equilibrium states), the work done on the system is

$$W_{fi} = \int_{V_f}^{V_i} P\,dV.$$

When the integration occurs for a quasi-static process, the result is

$$W_{if} = -W_{fi}.$$

Sufficient approximation to a quasi-static process may be achieved, in practice, by having the external pressure differ from the pressure of the system by only a small finite amount, so that the system passes through equilibrium states.

3.4
PV DIAGRAM

As the volume of a hydrostatic system (shown in Fig. 3-1) changes because of the motion of a piston in a cylinder, the position of the piston at any moment is proportional to the volume. A chart recorder with a pen that follows exactly the motion of the piston will trace out a line along the x-axis that is proportional to the volume. Simultaneously, the pen moves along the y-axis according to the measured pressure. The resulting diagram, in which pressure is plotted along the x-axis and volume along the y-axis, is called a *PV diagram* (an *indicator diagram* in engineering).

In Fig. 3-2(*a*), the pressure and volume changes of a gas during expansion are indicated by curve I. The integral $-\int_{V_i}^{V_f} P\,dV$ for this process is evidently the shaded area under curve I. Similarly, for compression of the gas, the work is represented by the shaded area under curve II in Fig. 3-2(*b*). Notice that the directions of curves I and II are opposite. For curve I, an expansion, the volume increases, dV is positive, and the integral $-\int_{V_i}^{V_f} P\,dV$ is negative. For curve II, where the gas is being compressed, the volume decreases, so the integral $-\int_{V_i}^{V_f} P\,dV$ is positive. According to the sign convention for work,

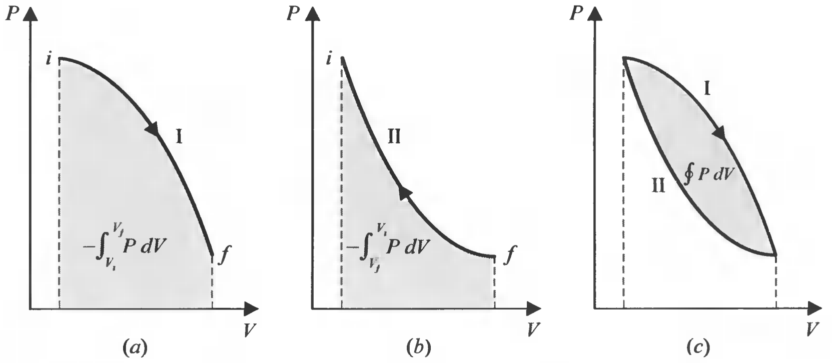

FIGURE 3-2
PV diagram of a gas with shaded area to show work done by the system or work done on the system. (*a*) Curve I, expansion; (*b*) curve II, compression; (*c*) curves I and II together constitute a cycle.

work is done *by* the system in the process represented by curve I, and work is done *on* the system in the process represented by curve II. In Fig. 3-2(*c*), curves I and II are drawn together so that they constitute two processes that bring the gas back to its initial state. Such a series of two or more processes, represented by a closed figure, is called a *cycle*. The area within the closed figure in Fig. 3-2(*c*) is obviously the difference between the areas under curves I and II and, therefore, represents the *net* work done in the cycle. Notice that the cycle is traversed in a direction such that the net work is negative, and net work is done *by* the system. If the direction of the cycle were reversed, then the net work would be positive as net work is done *on* the system.

3.5
HYDROSTATIC WORK DEPENDS ON THE PATH

On the *PV* diagram depicted in Fig. 3-3, an initial equilibrium state (characterized by the coordinates P_i, V_i, and T_i) and a final equilibrium state (coordinates P_f, V_f, and T_f) of a hydrostatic system are represented by the two points *i* and *f*, respectively. There are many ways in which the system may expand from *i* to *f*. For example, the pressure may be kept constant from *i* to *a* (*isobaric process*) and then the volume kept constant from *a* to *f* (*isochoric process*), in which case the work done is equal to the area under the line *ia*, which is equal to $-2P_0V_0$ and negative, because work is done *by* the system. Another possibility is the path *ibf*, in which case the work is the area under the line *bf*, or $-P_0V_0$. The straight line from *i* to *f* represents another path, where the work is $-\frac{3}{2}P_0V_0$. We can see, therefore, that the *work*

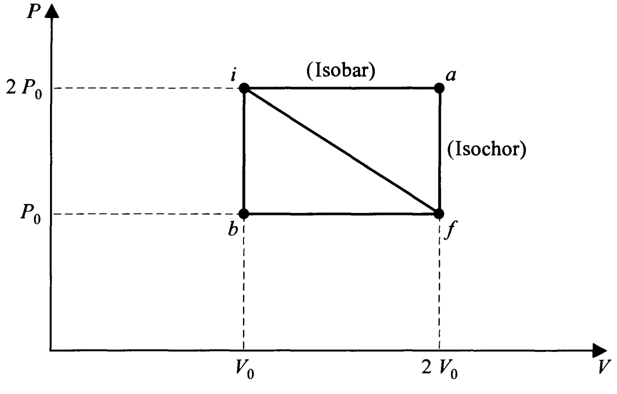

FIGURE 3-3
Work depends on the path of integration from the initial state equilibrium *i* to the final equilibrium state *f*. The most work is done by the system traversing path *iaf*, which does more work than traversing path *if*, which does more work than traversing path *ibf*.

done by a system depends not only on the initial and final states but also on the intermediate states, namely, on the path of integration. This is merely another way of saying that, for a quasi-static process, the expression

$$W = -\int_{V_i}^{V_f} P\,dV$$

cannot be integrated until P is specified as a function of V using an appropriate equation of state.

The expression $-P\,dV$ is an infinitesimal amount of work and has been represented by the symbol $đW$). There is, however, an important distinction between an infinitesimal amount of work and the other infinitesimals, such as dP or dV. An infinitesimal amount of hydrostatic work is an *inexact differential*; that is, $đW$ is *not* the differential of an actual function of the thermodynamic coordinates. To indicate that an infinitesimal amount of work is *not* a mathematical differential of a function W and to emphasize at all times that it is an inexact differential, a line is drawn through the differential sign, thus: $đW$. Another explanation of the symbolism is that dV is a very small *change* in the value of the volume, whereas $đW$ is a very small value of work.

There are various interpretations of the fact that thermodynamic work is an inexact differential. Already it has been shown that work is a path-dependent integral; in other words, work is *not* a state function. There is no function of the thermodynamic coordinates representing the work *in* a body. The physical interpretation of thermodynamic work is that the performance of work is an external *activity* or *process* that leads to a change in the state of the body, namely, to increase or decrease the energy. The phrase "work in a body" has no meaning. Notice that work is not a quantity that itself moves, but is a process that moves another quantity, namely, energy of some type.

Inexact differentials do not occur when work is first discussed in a course on general physics. In a calculation of work in which the displacement occurs in one dimension, the integration is always path-independent and only the limits of integration are necessary. In a course on mechanics the displacement occurs in two or more dimensions, such as moving a mass under the influence of only gravity. The calculation of work is still path-independent, because the gravitational force is conservative and the curl of the force vanishes.†

The difference between the exact differential of work in mechanics and the inexact differential in thermodynamics is that, in mechanics, the forces usually depend only on the coordinates of position, whereas in thermodynamics, the pressure depends not only on the coordinate of volume, but the coordinate of temperature as well. Consequently, the calculation of work in thermodynamics is path-dependent and indeterminate unless other conditions are imposed, such as an *isothermal* (constant temperature) process (discussed in the next section) or an adiabatic process (discussed in Sec. 5.5). Of course, the

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† V. Barger and M. Olsson: *Classical Mechanics*, McGraw-Hill, Inc., New York, 1995, pp. 61–62.

calculation of thermodynamic work is trivial for an isobaric process or an isochoric process.

3.6
CALCULATION OF $\int P\,dV$ FOR QUASI-STATIC PROCESSES

The preceding ideas are clarified by the following examples in which the integration can be carried out, because the path of integration is provided by an equation of state or a state function:

Quasi-static isothermal expansion or compression of an ideal gas. The work is given by

$$W = -\int_{V_i}^{V_f} P\,dV,$$

but the equation of state for an ideal gas is

$$PV = nRT,$$

where n and R are constants. Substituting for P, we get

$$W = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV,$$

and, since T is also constant,

$$W = -nRT\int_{V_i}^{V_f} \frac{dV}{V},$$

and the integration can be performed to yield

$$W = -nRT \ln\frac{V_f}{V_i}.$$

Let us calculate the work in compressing 2 mol of an ideal gas kept at a constant temperature of 20°C from a volume of 4 liters to 1 liter. Then, we have $n = 2\,\text{mol}$, $R = 8.315\ \text{J/mol}\cdot\text{K}$, $T = 293\,\text{K}$, $V_i = 4 \times 10^{-6}\,\text{m}^3$, and $V_f = 1 \times 10^{-6}\,\text{m}^3$. Thus,

$$\begin{aligned} W &= -(2\,\text{mol})(8.315\,\text{J/mol}\cdot\text{K})(293\,\text{K})(\ln\tfrac{1}{4}) \\ &= 6753\,\text{J}. \end{aligned}$$

The positive value of W indicates that work was done *on* the gas.

Quasi-static isothermal increase of pressure on a solid. In this case, the path of integration is determined by the isothermal compressibility, which is a continuous function between the limits of integration. Suppose that the pressure on 10 g of solid copper is increased quasi-statically and isothermally at 20°C from 0 to 1000 atm. The work is calculated as follows:

$$W = -\int P\,dV,$$

but dV can be expressed as

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

Since the isothermal compressibility is

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,$$

the change of volume dV at constant temperature is

$$dV = -\kappa V\,dP.$$

Substituting this result for dV in the expression for work, we obtain

$$W = \int_{P_i}^{P_f} \kappa V P\,dP.$$

At constant temperature, κ and V are practically constant, so they may be taken out of the integrand. Hence,

$$W \approx \frac{\kappa V}{2}(P_f^2 - P_i^2).$$

Since the volume is equal to the mass m divided by the density ρ,

$$W \approx \frac{m\kappa}{2\rho}(P_f^2 - P_i^2).$$

For copper at 20°C, $\rho = 8.96 \times 10^3\,\mathrm{kg/m^3}$, $\kappa = 7.16 \times 10^{-12}\,\mathrm{Pa^{-1}}$, $m = 10^{-2}\,\mathrm{kg}$, $P_i = 0$, and $P_f = 1000\,\mathrm{atm} = 1.01 \times 10^8\,\mathrm{Pa}$. Hence,

$$\begin{aligned} W &= \frac{(10^{-2}\,\mathrm{kg})(7.16 \times 10^{-12}\,\mathrm{Pa^{-1}})(1.01 \times 10^8\,\mathrm{Pa})^2}{2(8.96 \times 10^3\,\mathrm{kg/m^3})} \\ &= 0.408 \times 10^1\,\mathrm{Pa \cdot m^3} \\ &= 4.08\,\mathrm{J}. \end{aligned}$$

The positive value of W indicates that work was done *on* the copper. Notice how little work was done in raising the pressure on the copper compared with the work in compressing the gas in the first example. The reason is that the volume of the copper changed very little. So, when a gas is compressed, we can usually neglect the work done on the material of the container.

3.7
WORK IN CHANGING THE LENGTH OF A WIRE

If the length of a wire, in which there is a tension $\mathcal{J}$, is changed an infinitesimal length dL by an external force equal and opposite to the tension, then the infinitesimal amount of work that is done on the wire is equal to

$$\boxed{đW = \mathcal{J}\, dL,} \tag{3.3}$$

where $\mathcal{J}$ is a function of length L and temperature T. A positive value of dL means stretching the wire, for which positive work must be done *on* the wire. When tension $\mathcal{J}$ is measured in newtons and the length L in meters, the work W will be expressed in joules.

For a finite change of length from L_i to L_f,

$$W = \int_{L_i}^{L_f} \mathcal{J}\, dL,$$

where $\mathcal{J}$ indicates the value of the tension at any moment during the process. If the wire is undergoing a motion involving large unbalanced forces, then the integral cannot be evaluated in terms of thermodynamic coordinates referring to the wire as a whole. If, however, the external force is maintained at all times only slightly different from the tension, then the process is sufficiently quasi-static to warrant using an equation of state, in which case the integration can be carried out once $\mathcal{J}$ is known as a function of L.

3.8
WORK IN CHANGING THE AREA OF A SURFACE FILM

Consider a soap film, which consists of two surfaces enclosing water, stretched across a wire framework. The right side of the wire framework is movable, as shown in Fig. 3-4. If the movable wire has a length L and the surface tension in one surface is γ, then the external force F exerted on both surfaces is equal in magnitude to $2\gamma L$. For an infinitesimal displacement dx, the work is

$$đW = 2\gamma L\, dx;$$

but, for two films,

$$2L\, dx = dA,$$

where A is the total surface area. Hence,

$$\boxed{đW = \gamma\, dA.} \tag{3.4}$$

When surface tension γ is expressed in newtons per meter and area A in square meters, the work W is expressed in joules. Although Eq. (3.4) was derived for

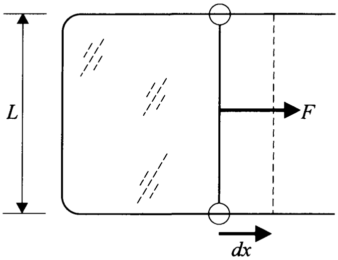


FIGURE 3-4
A soap film stretched across a rigid wire framework, known as the Maxwell frame, which has a movable wire on the right. An external force F displaces the movable wire an infinitesimal distance dx.

a film with two surfaces, it is also valid for a single surface, such as the boundary between the bulk of a liquid and the gaseous environment.

For a finite change from an initial area A_i to a final area A_f, the expression for work is

$$W = \int_{A_i}^{A_f} \gamma \, dA.$$

A quasi-static process may be approximated by maintaining the external force at all times only slightly different from the force exerted by the film.

3.9
WORK IN MOVING CHARGE WITH AN ELECTROCHEMICAL CELL

The conventional description of an electric current is that it is the motion of positive charge from a region of higher electric potential to a region of lower electric potential. Although this is opposite to the direction of electron drift, the convention is used in electrical circuit analysis, so it is appropriate to use the same convention in thermodynamics. Imagine an electrochemical cell of emf $\mathcal{E}$ to be connected to a variable resistor so that a wide range of potential difference may be obtained. The circuit is shown in Fig. 3-5. The external potential difference may be made equal to, slightly less, or slightly more than the emf $\mathcal{E}$ of the electrochemical cell by means of the variable resistor.

If the external potential difference is made infinitesimally smaller than the emf $\mathcal{E}$ of the electrochemical cell, then some charge dZ flows through the external circuit in a direction from the positive to the negative electrode of the cell. In this case, work is done by the cell on the resistor. If the external potential difference is made slightly larger than $\mathcal{E}$, charge is driven in the opposite direction and work is done on the rechargeable cell. In either case, the amount of work is

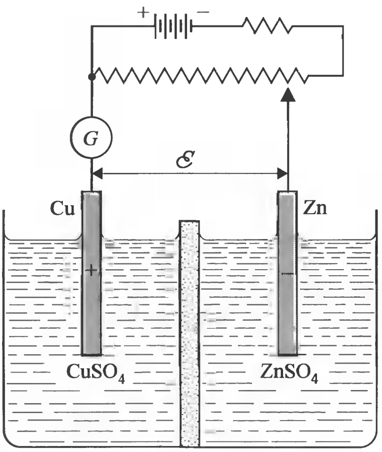


FIGURE 3-5
A circuit for the movement of charge through an electrochemical cell having an emf $\mathscr{E}$. The external battery controls the direction of the current.

$$\boxed{đW = \mathscr{E}\, dZ.} \tag{3.5}$$

The quantity Z is connected with the *state of charge* of the cell, while dZ is the actual quantity of charge moved around the circuit. Charging the cell involves a positive dZ, as work is done on the cell to increase the concentration of reactants in the cell. Discharging the cell, indicated by a negative dZ, reverses the direction of the motion of the charge in the external circuit, as work is done on the surroundings by the reacting chemicals. With the emf $\mathscr{E}$ expressed in volts and the charge Z in coulombs, the work will be expressed in joules.

If Z changes by a finite amount, then

$$W = \int_{Z_i}^{Z_f} \mathscr{E}\, dZ.$$

As a practical matter, the charge is usually not measured. Instead, the current I is measured, where during the time dt the quantity $dZ = I\, dt$. So,

$$W = \int_i^f \mathscr{E} I\, dt.$$

In this book, we will use Eq. (3.5) for expressing the infinitesimal amount of work, in order to avoid using time t as a variable.

3.10
WORK IN CHANGING THE TOTAL POLARIZATION OF A DIELECTRIC SOLID

Consider a slab of isotropic dielectric material placed between the conducting plates of a parallel-plate capacitor, as shown in Fig. 3-6. The surface area A of the capacitor plates has linear dimensions large compared with the separation l. A constant potential difference equal to the emf $\mathcal{E}$ may be maintained on the plates by a battery, if no current is drawn.

The effect of a potential difference on the plates is to set up an electric field E between the plates. The electric field will be nearly uniform between the plates and given by

$$E = \frac{\mathcal{E}}{l}.$$

Moreover, one plate is given a charge $+Z$ and the other a charge $-Z$. When the charge of the capacitor is changed an infinitesimal amount dZ, the work done is found using Eq. (3.5),

$$\begin{aligned} \text{đ}W &= \mathcal{E}\, dZ \\ &= El\, dZ. \end{aligned}$$

The charge Z on the plates is equal to

$$Z = DA,$$

where D is the *electric displacement*. Therefore,

$$\begin{aligned} \text{đ}W &= AlE\, dD \\ &= VE\, dD, \end{aligned} \tag{3.6}$$

where V is the volume of the dielectric material.

If $\wp$ is the *total polarization* of the material (assumed to be isotropic), then we have the relation

$$D = \epsilon_0 E + \frac{\wp}{V}, \tag{3.7}$$

where ϵ_0 is the permittivity of vacuum. Therefore,

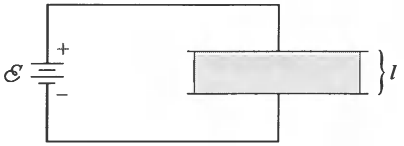


FIGURE 3-6
Changing the polarization $\wp$ of a dielectric solid that fills a parallel-plate capacitor, with plate separation l and maintained at a potential difference $\mathcal{E}$.

$$\text{đ}W = V\epsilon_0 E\,dE + E\,d\mathcal{P}.$$

The first term is the work required to increase the electric field by dE and would be present even if a vacuum existed between the plates of the capacitor. The second term is the work required to increase the total polarization of the dielectric by $d\mathcal{P}$; it is zero when no material is present between the capacitor plates. We shall be concerned with changes of the material only, brought about by work done on or by the dielectric material (which is the system) and not in work done in changing the electric field. Consequently, the net work done on the dielectric is

$$\boxed{\text{đ}W = E\,d\mathcal{P}.} \tag{3.8}$$

Although the derivation has been specific for the case of a dielectric in a parallel-plate capacitor, the result is general for any dielectric in a uniform electric field. When the electric field E is measured in volts per meter and total polarization $\mathcal{P}$ in coulomb-meters, then the work is expressed in joules.

If the total polarization is changed a finite amount from $\mathcal{P}_i$ to $\mathcal{P}_f$, then the work will be

$$W = \int_{\mathcal{P}_i}^{\mathcal{P}_f} E\,d\mathcal{P}.$$

Experiments on dielectric materials are performed on samples of such shapes that the electric field E is uniform. For solid dielectrics, the capacitor plates are plane and parallel, either circular or square. For liquid or gaseous dielectrics, the capacitor plates are coaxial right cylinders. Regardless of the electrode configuration, there must be guard electrodes extending beyond the measuring electrodes. The guard electrodes minimize the "fringing" of the electric field at the edge of the measuring electrode.

3.11

WORK IN CHANGING THE TOTAL MAGNETIZATION OF A PARAMAGNETIC SOLID

Consider a sample of paramagnetic material in the form of a ring of cross-sectional area A and of mean circumference L. Suppose that an insulated wire is wound around the sample, forming a toroidal winding of N closely spaced turns, as shown in Fig. 3-7. A constant current may be maintained in the winding by a battery and changed by means of the variable resistor.

The direct current in the winding sets up a magnetic induction $\mathcal{B}$. If the dimensions are as shown in Fig. 3-7, then $\mathcal{B}$ will be nearly uniform over the cross-section of the toroid. Suppose that the current is changed and that in time dt the magnetic induction changes by an amount $d\mathcal{B}$. Then, by Faraday's principle of electromagnetic induction, there is induced in the winding a back emf $\mathcal{E}$, where

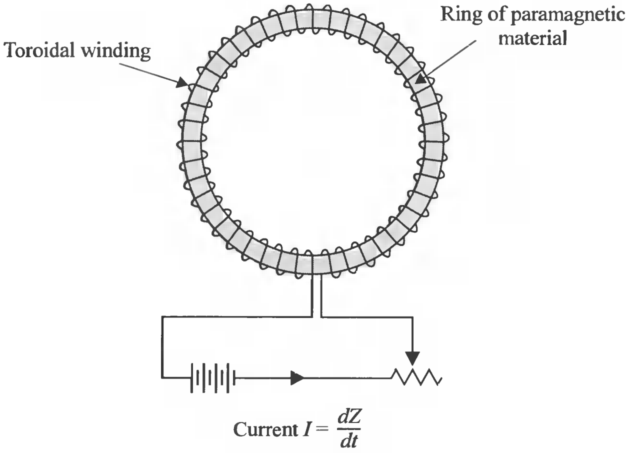


FIGURE 3-7
Changing the magnetization $\mathcal{M}$ of a paramagnetic solid in the form of a toroid. The windings surrounding the paramagnet carry a current I.

$$\mathcal{E} = -NA\,\frac{d\mathcal{B}}{dt}.$$

During the time interval dt, a quantity of charge dZ moves in the circuit, and the work done *by* the battery to maintain the current is calculated from Eq. (3.5),

$$\begin{aligned} đW &= -\,\mathcal{E}\,dZ \\ &= NA\,\frac{d\mathcal{B}}{dt}\,dZ \\ &= NA\,\frac{dZ}{dt}\,d\mathcal{B} \\ &= NAI\,d\mathcal{B}, \end{aligned}$$

where the current I equals dZ/dt.

The magnetic field $\mathcal{H}$ due to a current I inside a toroidal winding is given by

$$\mathcal{H} = \frac{NI}{L} = \frac{NAI}{AL} = \frac{NAI}{V},$$

where V is the volume of paramagnetic material. Therefore,

$$NAI = V\mathcal{H},$$

and

$$đW = V\mathcal{H}\,d\mathcal{B}. \tag{3.9}$$

If $\mathcal{M}$ is the *total magnetization* of the paramagnet (assumed to be isotropic), then we have the relation

$$\mathcal{B} = \mu_0\mathcal{H} + \mu_0 \frac{\mathcal{M}}{V}. \tag{3.10}$$

Therefore, $$đW = V\mathcal{H}\, d(\mu_0\mathcal{H}) + \mu_0\mathcal{H}\, d\mathcal{M}.$$

If no material were present within the solenoidal winding, then $\mathcal{M}$ would be zero, $\mathcal{B}$ would equal $\mu_0\mathcal{H}$, and

$$đW = V\mathcal{H}\, d(\mu_0\mathcal{H}) \qquad \text{(vacuum only)}.$$

This is the work necessary to increase the magnetic field in a volume V *of empty space* by an amount $d(\mu_0\mathcal{H})$. The second term, $\mu_0\mathcal{H}\, đ\mathcal{M}$, is the work done in increasing the total magnetization of the material by an amount $đ\mathcal{M}$. We shall be concerned in this book with changes of temperature, energy, etc., of the paramagnet only, brought about by work done on or by the material. Consequently, for the purpose of this book,

$$\boxed{đW = \mu_0\mathcal{H}\, đ\mathcal{M}.} \tag{3.11}$$

If $\mu_0\mathcal{H}$ is measured in newtons per ampere-meter and the total magnetization $\mathcal{M}$ in ampere-square meters, then the work W will be expressed in joules.

If the total magnetization is caused to change a finite amount from $\mathcal{M}_i$ to $\mathcal{M}_f$, the work will be

$$W = \mu_0 \int_{\mathcal{M}_i}^{\mathcal{M}_f} \mathcal{H}\, đ\mathcal{M}.$$

Experiments on paramagnetic materials are usually performed on samples in the form of cylinders or ellipsoids, not toroids. In these cases, the value of the magnetic field inside the material is somewhat smaller than the value of magnetic field generated by the current in the surrounding winding because of the demagnetizing effect of induced currents that form on the surfaces of samples. In longitudinal magnetic fields, the demagnetizing effect may be rendered negligible by using cylinders whose length is much larger than the diameter, or it may be corrected for. In transverse magnetic fields, a correction factor must be applied. We shall limit ourselves to toroids or to long, thin cylinders of paramagnets in uniform fields where the values of the magnetic field are the same inside and outside the sample.

In any actual case, a change of total magnetization is accomplished very nearly quasi-statically, and, therefore, an equation of state may be used in the integration of the expression denoting the work.

TABLE 3.1
Work of simple systems

Simple system	Intensive coordinate (generalized force)	Extensive coordinate (generalized displacement)	Work, J
Hydrostatic system	P, in Pa	V, in m^3	$-P\,dV$
Wire	$\mathcal{J}$, in N	L, in m	$\mathcal{J}\,dL$
Surface film	γ, in N/m	A, in m^2	$\gamma\,dA$
Electrochemical cell	$\mathcal{E}$, in V	Z, in C	$\mathcal{E}\,dZ$
Dielectric solid	E, in V/m	$\mathcal{P}$, in C · m	$E\,d\mathcal{P}$
Paramagnetic solid	$\mu_0\mathcal{H}$, in N/A · m	$\mathcal{M}$, in A · m^2	$\mu_0\mathcal{H}\,d\mathcal{M}$

3.12
GENERALIZED WORK

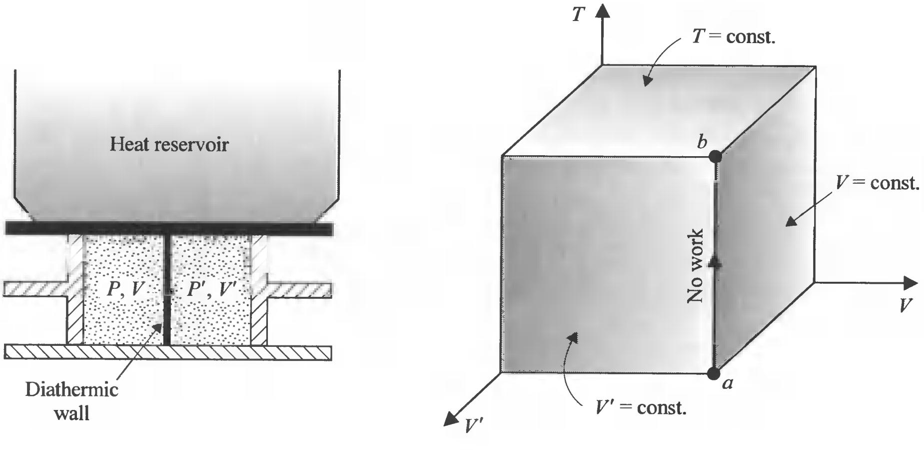
The expressions for work in the simple systems are summarized in Table 3.1. It should be noted that each expression for work is the product of an intensive and an extensive coordinate; consequently, *work is an extensive coordinate.*

We have seen that a work diagram is obtained if any one of the intensive coordinates is plotted against its corresponding extensive coordinate. There are, therefore, as many work diagrams as there are systems. It is desirable at times, for the sake of argument, to formulate a work diagram which does not refer to one system in particular but which represents the behavior of any system. If we designate the intensive quantities P, $\mathcal{J}$, γ, $\mathcal{E}$, E, and $\mu_0\mathcal{H}$ as *generalized forces* and their corresponding extensive quantities V, L, A, Z, $\mathcal{P}$, and $\mathcal{M}$ as *generalized displacements*, we may represent the work done by any simple system on a *generalized work diagram* by plotting the generalized force Y against the generalized displacement X. Conclusions based on such a diagram will hold for any simple system. Because of the units used in the SI system, the magnetic field $\mathcal{H}$ must be multiplied by μ_0 in order to produce a "force-like" quantity.

3.13
COMPOSITE SYSTEMS

Up to this point, we have dealt exclusively with simple systems, whose equilibrium states are described with the aid of three thermodynamic coordinates, one of which is always the temperature. A single equation of state was found to exist in each case, so that only two of the coordinates are independent. The laws of thermodynamics, however, which are to be developed in the next few chapters, must apply to any system, no matter how complicated, that is, to systems having more than three coordinates and more than one equation of state.

Consider the composite system depicted schematically in Fig. 3-8(a) with two different simple hydrostatic systems separated by a diathermic wall, which



(a) (b)

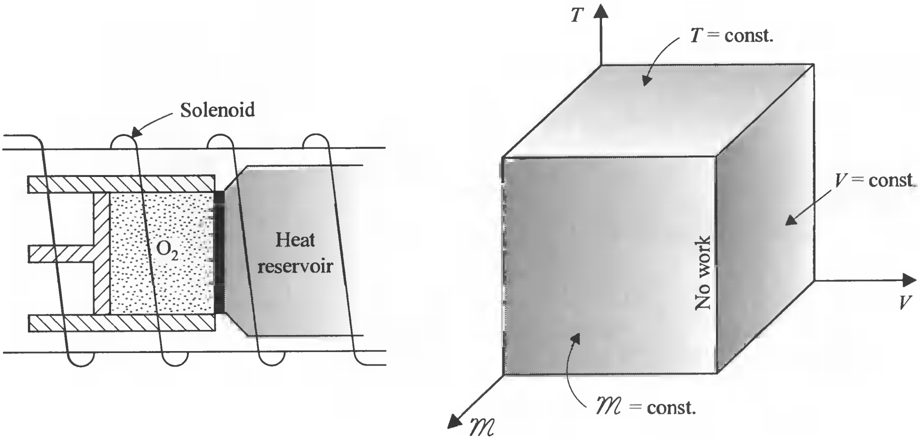
FIGURE 3-8
(*a*) A composite system composed of two cylinders separated from each other by a rigid diathermic wall. The two gas-filled chambers may be connected to a series of different heat reservoirs that hold the composite system at the same temperature as the reservoir. The thermodynamic coordinates are P, V, P', V', and T. (*b*) A graph of the independent coordinates V, V', and T.

ensures that both parts have the same temperature. There are five thermodynamic coordinates (P, V, P', V', and T) and two equations of state, one for each of the simple systems. Consequently, only three of the five coordinates are independent. In any small displacement of each piston, the work is

$$đW = -P\,dV - P'\,dV'.$$

The most convenient diagram to use in demonstrating the features of this system is a three-dimensional diagram with T, V, and V' plotted along rectangular axes, as shown in Fig. 3-8(*b*). A typical isothermal process would be a curve on a plane such as the one marked for constant temperature ($T =$ const.). A curve on a plane for constant volume, such as that marked $V =$ const., would represent a process in which no work is done by the left-hand part. The points *a* and *b* lie on a vertical line, every point of which refers to a constant V and V'. Therefore, the straight line *ab* represents a process in which no work is done by the composite system.

Two simple systems do not have to be separated spatially by a diathermic wall in order to have two equations of state and a common temperature. Consider an ideal paramagnetic gas, such as oxygen at low pressures, as depicted schematically in Fig. 3-9(*a*). The oxygen may have its pressure P and volume V varied with the aid of a piston–cylinder combination, and it is immersed in a magnetic field, which may be changed by varying the current in the surrounding solenoid. The gas is kept at a uniform temperature T. The coordinates are P, V, $\mu_0\mathcal{H}$, $\mathcal{M}$, and T, only three of which are independent because of the two equations of state: the ideal-gas equation $PV = nRT$ and



(*a*) (*b*)

FIGURE 3-9
(*a*) A composite system composed of gas that is also paramagnetic. The gas may be connected to different heat reservoirs that hold the composite system at the same temperature as the reservoir. The thermodynamic coordinates are P, V, $\mu_0\mathcal{H}$, $\mathcal{M}$, and T. (*b*) A graph of the independent coordinates $V, \mathcal{M}$, and T.

Curie's law $\mathcal{M} = C_C\mathcal{H}/T$. Since the work done in any infinitesimal process is

$$đW = -P\,dV + \mu_0\mathcal{H}\,d\mathcal{M},$$

the most convenient independent coordinates are T, V, and $\mathcal{M}$, which are plotted along rectangular axes in Fig. 3-9(*b*). *Any* vertical line would represent a process in which no work is done.

In general, a five-coordinate system using Y, X, Y', X', and T as coordinates has work expressed as

$$đW = Y\,dX + Y'\,dX'.$$

The most convenient coordinates of this system are T, X, and X'.

PROBLEMS

3.1. A thin-walled metal container of volume V contains a gas at high pressure. Connected to the container is a capillary tube and stopcock. When the stopcock is opened slightly, the gas leaks slowly into a cylinder equipped with a nonleaking, frictionless piston, where the pressure remains constant at the atmospheric value P_0.
(*a*) Show that, after as much gas as possible has leaked out, an amount of work

$$W = -P_0(V_0 - V)$$

has been done, where V_0 is the volume of the gas at atmospheric pressure and temperature.

(*b*) How much work would be done if the gas leaked directly into the atmosphere?

3.2. (*a*) Show that the work done by an ideal gas during the quasi-static, isothermal expansion from an initial pressure P_i to a final pressure P_f is given by

$$W = nRT \ln \frac{P_f}{P_i}.$$

(*b*) Calculate the work done when the pressure of 1 mol of an ideal gas is decreased quasi-statically from 20 to 1 atm, the temperature remaining constant at 20°C ($R = 8.31$ J/mol · deg).

3.3. An adiabatic chamber with rigid walls consists of two compartments, one containing a gas and the other evacuated; the partition between the two compartments is suddenly removed. Is the work done during an infinitesimal portion of this process (called an adiabatic *free expansion*) equal to $P\,dV$?

3.4. (*a*) Calculate the work done upon expansion of 1 mol of gas quasi-statically and isothermally from volume v_i to a volume v_f, when the equation of state is

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

where a and b are the van der Waals constants.

(*b*) If $a = 1.4 \times 10^9\ \mathrm{N \cdot m^4/mol}$ and $b = 3.2 \times 10^{-5}\ \mathrm{m^3/mol}$, how much work is done when the gas expands from a volume of 10 liters to a volume of 22.4 liters at 20°C?

3.5. During a quasi-static expansion of a gas in an adiabatic container, the pressure at any moment is given by the equation

$$PV^\gamma = K,$$

where γ and K are constants. Show that the work done in expanding from a state (P_i, V_i) to a state (P_f, V_f) is

$$W = -\frac{P_i V_i - P_f V_f}{\gamma - 1}.$$

If the initial pressure and volume are 10^6 Pa and $10^{-3}\ \mathrm{m^3}$, respectively, and the final values are 2×10^5 Pa and $3.16 \times 10^{-3}\ \mathrm{m^3}$, respectively, how much work is done on a gas having $\gamma = 1.4$?

3.6. A stationary vertical cylinder, closed at the top, contains a gas whose volume may be changed with the aid of a heavy, frictionless piston of weight w.

(*a*) How much work is done by the external force in compressing the gas by an amount dV by raising the piston a distance dy?

(*b*) If this device is used as part of an engine, what expression is appropriate to calculate the net work delivered to or received from the surroundings?

(*c*) If this device is used only to produce temperature changes of the gas, what expression for work would be appropriate?

3.7. The pressure on 100 g of nickel is increased quasi-statically and isothermally from 0 to 500 atm. Assuming the density and isothermal compressibility to remain constant at values of 8.90×10^3 kg/m^3 and 6.75×10^{-12} Pa^{-1}, respectively, calculate the work.

3.8. (*a*) The tension in a wire is increased quasi-statically and isothermally from $\mathcal{J}_i$ to $\mathcal{J}_f$. If the length, cross-sectional area, and isothermal Young's modulus of the wire remain practically constant, show that the work done is

$$W = \frac{L}{2AY}\left(\mathcal{J}_f^2 - \mathcal{J}_i^2\right).$$

(*b*) The tension in a copper wire 1 m long and 0.001 cm^2 in area is increased quasi-statically and isothermally at 20°C from 10 to 100 N. How much work is done if the isothermal Young's modulus at 20°C is 1.23×10^{11} N/m^2?

3.9. The equation of state of an ideal elastic substance is

$$\mathcal{J} = KT\left(\frac{L}{L_0} - \frac{L_0^2}{L^2}\right),$$

where K is a constant and L_0 (the value of L at zero tension) is a function of temperature only. Calculate the work necessary to compress the substance from $L = L_0$ to $L = L_0/2$ quasi-statically and isothermally.

3.10. Show that the work required to blow a spherical soap bubble of radius r in an isothermal, quasi-static process in the atmosphere is equal to $8\pi\gamma r^2$.

3.11. An electrochemical cell, in which the reaction

$$\mathrm{Cu} + \mathrm{Hg_2SO_4} \rightarrow 2\mathrm{Hg} + \mathrm{CuSo_4}$$

takes place, is connected to a motor having a back emf only slightly smaller than the emf of the cell. The emf of this cell is given by Eq. (2.14), with $\mathcal{E}_{20} = 0.3497$ V, $\alpha = -6.35 \times 10^{-4}$ V/deg, $\beta = -2.4 \times 10^{-6}$ V/deg^2, and $\gamma = 0$. If the cell is kept at a constant temperature of 25°C and 0.1 mol of copper reacts, then how much work is done on the motor?

3.12. A dielectric has an equation of state $\mathcal{P} = \chi E V$, where χ is a function of temperature only. Show that the work done in an isothermal, quasi-static change of state is given by

$$W = \frac{1}{2V\chi}\left(\mathcal{P}_f^2 - \mathcal{P}_i^2\right) = \frac{V\chi}{2}\left(E_f^2 - E_i^2\right).$$

3.13. Prove that the work done during a quasi-static isothermal change of state of a paramagnetic substance obeying Curie's law is given by

$$W = \frac{\mu_0 T}{2C_C}\left(\mathcal{M}_f^2 - \mathcal{M}_i^2\right) = \frac{\mu_0 C_C}{2T}\left(\mathcal{H}_f^2 - \mathcal{H}_i^2\right),$$

where C_C is the Curie constant.

3.14. A volume of 200 cm^3 of a paramagnetic substance is maintained at constant temperature. The magnetic field is increased quasi-statically and isothermally from 0 to

10^6 A/m. Assume the Curie law to hold and the Curie constant per unit volume to be 1.885 K/m^3.

(*a*) How much work would have to be done if no material were present?

(*b*) How much work is done to change the total magnetization of the material when the temperature is 300 K and when it is 1 K?

(*c*) How much work is done to change the total magnetization by the generator supplying the current?

CHAPTER 4

Heat and the First Law of Thermodynamics

4.1
WORK AND HEAT

It was shown in Chap. 3 how a system could be transferred from an initial to a final state by means of a quasi-static process and how the work done during the process could be calculated. There are, however, other means of changing the state of a system that do not necessarily involve the performance of work. Consider the four processes shown in Fig. 4-1, which involve *closed* systems, where a closed system is a system in which no matter passes between the system and surroundings.† In Fig. 4-1(*a*), the system is a composite one consisting of water and a paddle wheel, which is caused to rotate and churn the water by means of a falling weight. As a result, the temperature of the water rises from room temperature to a slightly higher temperature. In Fig. 4-1(*b*), the water and the resistor constitute the composite system, the electric current in the resistor being maintained by a generator turned by means of a falling weight. Again, the temperature of the water rises. In both cases, the state of the system is caused to change; and since the agency for changing the state of the system is a falling weight, both processes involve the performance of work.

In Figs. 4-1(*c*) and 4-1(*d*), however, the situation is quite different. The system in both these cases is water in a diathermic container. In Fig. 4-1(*c*), the system is in contact with the burning gases at a high temperature; whereas, in Fig. 4-1(*d*), the system is near but not in contact with a lamp whose temperature is much higher than that of the water. In both cases, the system is caused to change, but in neither case can the agency of change be described by mechanical means.

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† In Chap. 11, we shall consider systems *open* to the exchange of matter.

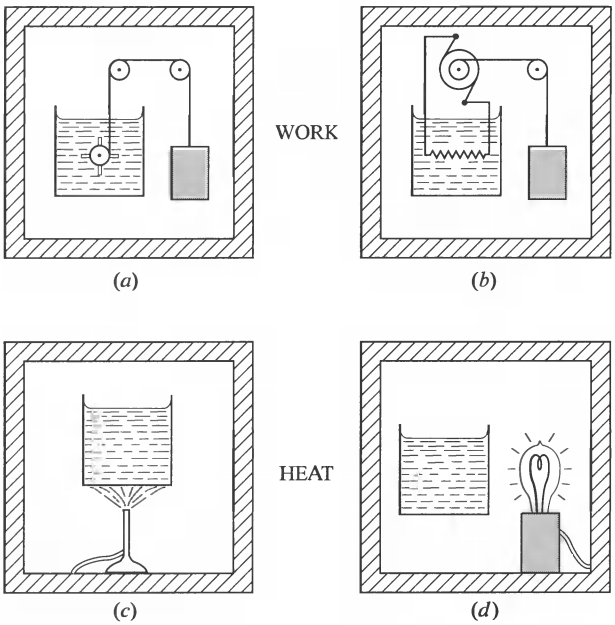

FIGURE 4-1
Distinction between work and heat: (*a*) and (*b*) show work being done on the system by means of a falling body, whereas (*c*) and (*d*) show heat entering the system from a hotter substance.

The results of placing two systems at different temperatures together is one of our most familiar sensory experiences. It is well known that the final temperature reached by both systems is intermediate between the two starting temperatures. Up to the beginning of the nineteenth century, such phenomena, which comprise the subject of *calorimetry*, were explained by postulating the existence of a substance termed *caloric*, or, more commonly, heat, a supposed elastic fluid found in every body. It was believed that a body at a high temperature contained much caloric and that one at a low temperature had only a little caloric. When the two bodies were brought together, the body rich in caloric lost some to the other, and, thus, the final temperature of the two bodies was intermediate. Although we now know that heat is not a fluid whose total amount remains constant, nevertheless, there is a grain of truth in the idea that the changes occurring in Figs. 4-1(*c*) and 4-1(*d*) are the result of the transfer of "something" from the body at the higher temperature to the one at the lower temperature, and this "something" we call heat. Therefore, we adopt as a *calorimetric* definition the following: *heat is that which is transferred between a system and its surroundings by virtue of a temperature difference only*. Whether heat is a fluid or a form of energy cannot be decided yet, but it will be shown in Secs. 4.4 and 4.5 that heat is a form of energy. It is obvious that an adiabatic wall, commonly called a *heat insulator*, is impervious to heat; whereas a diathermic wall, commonly called a *heat conductor*, transmits heat. Notice that an adiabatic wall prevents heating from occurring, just as a rigid wall prevents the performance of work in a hydrostatic system from occurring; similarly, a diathermic wall allows heating to occur, just as a movable (or deformable) wall allows the performance of work to occur.

It is important to observe that the decision as to whether a particular change of state is the result of work or heat requires first an unequivocal answer to these questions: "What is the system?" and "What are the surroundings?" For example, in Fig. 4-1(*b*), if the resistor is regarded as the system and the water as the surroundings, then there is a process of heating done by the hotter resistor by virtue of the difference in temperature between the resistor and the water. Also, if a small part of the water is regarded as the system, with the rest of the water being the hotter surroundings, then, again, there is a process of heating. Regarding, however, the composite system comprising both the water and the resistor, we find that the surroundings do not contain any object whose temperature differs from that of the system, and, hence, no heating occurs between *this composite system* and its surroundings.

4.2
ADIABATIC WORK

When a closed system is completely surrounded by an adiabatic boundary, the system may still be coupled to the surroundings so that work may be done. Four examples of different systems experiencing the process of working in an adiabatic container, so-called *adiabatic work*, are shown in Fig. 4-2. It was a series of experiments using a paddle wheel, like the one in Fig. 4-1(*a*), that established the important fact that the state of a system may be caused to change from a given initial state to the same final state by the performance of adiabatic work *only*.

Mechanical systems are not easily controlled in changing the state of a system, so let us consider a composite *electrical* system composed of a resistor immersed in water. The initial state i is characterized by the thermodynamic coordinates $P_i = 1\,\text{atm}$ and $T_i = 287.7\,\text{K}$ (14.5°C) and the final state f is characterized by the coordinates $P_f = 1\,\text{atm}$ and $T_f = 288.7\,\text{K}$ (15.5°C), as shown in Fig. 4-3. To cause the system to proceed from i to f along path I by the performance of adiabatic work only, it would be necessary to surround the water with an adiabatic wall, keep the water at atmospheric pressure, and maintain a current in the resistor for a suitable interval of time.

But, path I is not the only path by which the system may be changed from i to f by the performance of adiabatic work only. We might compress the water adiabatically from i to a, then use a current in a resistor from a to b, and then expand from b to f, the whole series of processes being designated by

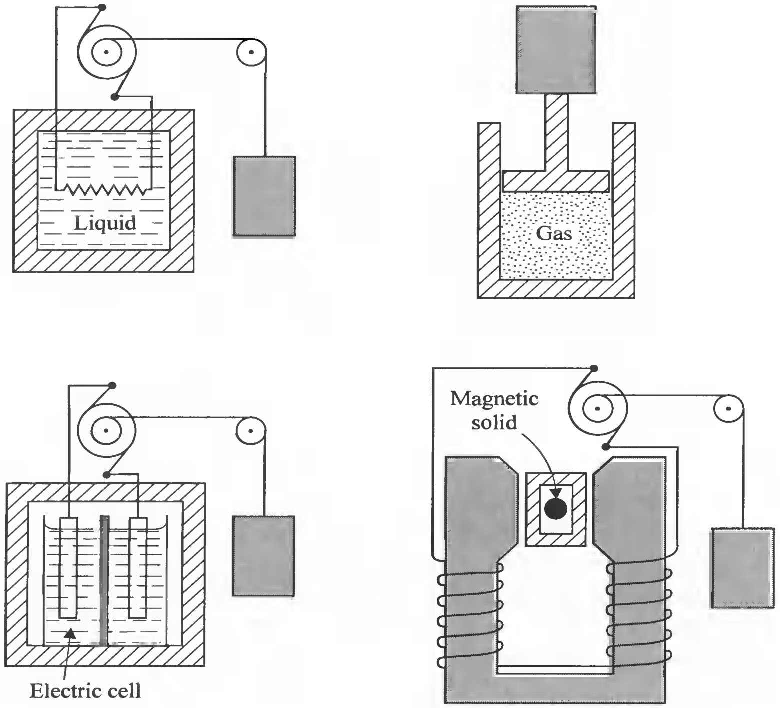

FIGURE 4-2
Adiabatic work for different types of systems.

path II. Or, we might make use of a similar adiabatic path III. There are an infinite number of paths by which a system may be transferred from an initial state to a final state by the performance of adiabatic work only. Although further measurements of adiabatic work along different paths between the same two states were not made after Joule's pioneering work, indirect experiments and the validity of subsequent results indicate that the adiabatic work is the *same* along all such paths. The generalization of this result is a restricted statement of the *first law of thermodynamics*:

> *If a closed system is caused to change from an initial state to a final state by adiabatic means only, then the work done on the system is the same for all adiabatic paths connecting the two states.*

Whenever a quantity is known to depend only on the initial and final states, and not on the path connecting them, an important conclusion can be drawn. Recall from mechanics that, in moving an object from one point in a gravitational field to another point, in the absence of friction, the work done

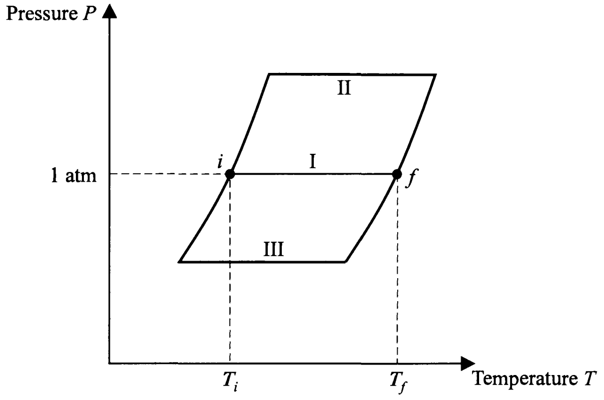

FIGURE 4-3
Changing the state of a system from the initial state i to the final state f along three different adiabatic paths.

depends only on the positions of the two points and not on the path through which the body was moved. It was concluded that, for a conservative force, there exists a function of the space coordinates of the body whose final value minus its initial value is equal to the work done. This function was called the *potential-energy function.* Similarly, the work done in moving an electric charge from one point in a conservative electric field to another point is also independent of the path and, therefore, is also expressible as the value of the *electric potential function* at the final state minus its value at the initial state. Therefore, it follows from the restricted statement of the first law of thermodynamics that there exists a function of the coordinates of a thermodynamic system whose value at the final state minus its value at the initial state is equal to the adiabatic work in going from one state to the other. This function is known as the *internal-energy function.*

Denoting the internal-energy function by U, we have

$$\boxed{W_{i\to f}(\text{adiabatic}) = U_f - U_i,} \tag{4.1}$$

where the signs are such that, if positive work is done *on* the system, U_f will be greater than U_i. It is found by experiment that it is not always possible to take a system from an initial state i to *any* final state f by the performance of adiabatic work only. It will be shown later, when entropy is discussed, that if f cannot be reached in this way, then it is always possible to go from f to i by adiabatic means, in which case the change in internal energy from i to f, instead of being $+W_{i\to f}$, is $-W_{f\to i}$. The importance of Eq. (4.1) is that thermodynamic work, which is generally path-dependent, becomes path-independent for an adiabatic process.

4.3
INTERNAL-ENERGY FUNCTION

The physical interpretation of the difference $U_f - U_i$ is the increase in internal energy of the system. The equality, therefore, of the increase of internal energy and the adiabatic work expresses the law of the conservation of energy. It should be emphasized, however, that Eq. (4.1) expresses more than the law of the conservation of energy. It states that *there exists an energy function*, whose difference between two values is the energy change of the system.

The internal energy is a function of as many thermodynamic coordinates as are necessary to specify the state of a system. The equilibrium states of a closed hydrostatic system, which is describable by means of three thermodynamic coordinates P, V, and T, are completely determined by only two coordinates, since the third is fixed by the equation of state. Therefore, the internal energy may be thought of as a function of only two (any two) of the three thermodynamic coordinates. This is true for each of the simple systems described in Chap. 2. It is not always possible to write the internal-energy function in simple mathematical form, especially if one deals with real materials instead of ideal ones. Very often, the exact form of the function U is unknown. It must be understood, however, that it is not necessary to know the exact form of the internal-energy function, but only that such a function exists because of the results of experiments on adiabatic work.

If the coordinates characterizing the two states differ from each other only infinitesimally, then the change of internal energy is dU, where dU is an exact differential, since it is the differential of a state function. In other words, the integral of dU is independent of the path between the initial and final states. In the case of a hydrostatic system, if U is regarded as a function of T and V, then

$$dU(T, V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

or, regarding U as a different function of T and P,

$$dU(T, P) = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP.$$

Notice that the two partial derivatives $(\partial U/\partial T)_V$ and $(\partial U/\partial T)_P$ are not equal, because the function U is not the same in both cases. The first partial derivative is a function of T and V, and the second partial derivative is a function of T and P. They are different mathematically and also have different physical meanings.

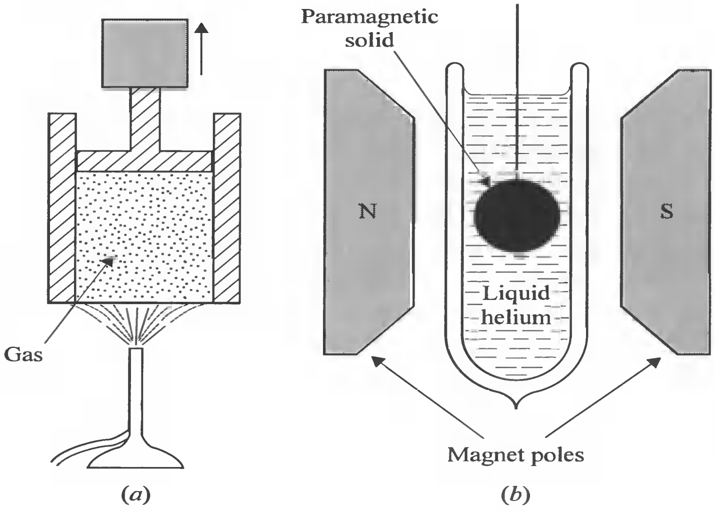

FIGURE 4-4
Nonadiabatic processes.

4.4
MATHEMATICAL FORMULATION OF THE FIRST LAW

We have been considering processes during which a system undergoes a change of state through the performance of adiabatic work only. Such experiments must be performed in order to measure the change in the internal-energy function of a system, but they are not the usual processes that are carried out in the laboratory. In Fig. 4-4, there are depicted two examples of processes involving changes of state that take place nonadiabatically; specifically, with diathermic walls. In Fig. 4-4(*a*), the gas is in thermal contact with a flame whose temperature is higher than that of the gas; and, at the same time, the gas is forced to contract, so diathermic work is performed on the system. In Fig. 4-4(*b*), the total magnetization of a paramagnetic solid is increased while it is in contact with liquid helium, the temperature of which is lower than that of the solid. As a matter of fact, some of the helium boils away during the magnetization.

Let us now imagine two different experiments performed on the same closed system. In one experiment, we measure the adiabatic work necessary to change the state of the system from i to f in order to obtain $U_f - U_i$. In the other experiment, we cause the system to undergo the *same* change of state, so we have the same $U_f - U_i$, but the process is diathermic, and we measure the diathermic work W done. The result of all such experiments is that the *nonadiabatic work* W *is* **not** *equal to* $U_f - U_i$. In order that this result shall be consistent with the law of the conservation of energy, we are forced to conclude that energy has been transferred by means *other than* the performance of work. This energy, whose transfer between the system and its surroundings is required by the law of the conservation of energy and which has taken place only by virtue of the temperature difference between the system and its surroundings, is what we previously called heat. Therefore, we give the following as our *thermodynamic* definition of heat: *When a closed system whose surroundings are at a different temperature and on which diathermic work may be done undergoes a process, then the energy transferred by nonmechanical means, equal to the difference between the change of internal energy and the diathermic work, is called heat.* Denoting heat by Q, we have

$$Q = (U_f - U_i) - W\,\text{(diathermic)},$$

or

$$\boxed{U_f - U_i = Q + W,} \tag{4.2}$$

where the sign convention has been adopted that Q is positive when it enters a system and negative when it leaves a system. Like internal energy and work, heat is measured in joules in the SI system. Equation (4.2) is known as the *mathematical formulation of the first law of thermodynamics.*

It should be emphasized that the mathematical formulation of the first law contains three related ideas: (1) the existence of an internal-energy function; (2) the principle of the conservation of energy; (3) the definition of heat as *energy* in transit by virtue of a temperature difference.

It was many years before it was understood that heat is related to energy. The first really conclusive evidence that heat could not be a fluid within a body was given by Benjamin Thompson, an American from Woburn, Massachusetts, who later became Count Rumford of Bavaria. In 1798, Rumford observed the rise in temperature of the brass chips produced during the boring of a cannon, and concluded that the process of boring was responsible for the production of heat, not some inherent caloric. One year later, the English chemist Sir Humphry Davy tried to show that two pieces of ice could be melted by rubbing them together. His idea was to show that heat is a manifestation of energy, but his experiment was highly inconclusive.

The idea that heat is a form of energy was put forward in 1839 by M. Séguin, a French engineer. In 1842, Mayer, a German physician, discovered the equivalence of heat and work and made the first announcement of the principle of the conservation of energy (the first law of thermodynamics). No conclusive experiments were performed by either Séguin or Mayer. It remained for Joule, an Englishman with a private laboratory, in the period from 1840 to 1849, to convince the world by performing a series of admirable experiments, in which brass paddle wheels were turned steadily by slowly falling weights. Joule also performed experiments with mercury or sperm oil in place of water, and with iron paddles in place of brass paddles. He found that the performance of a definite amount of adiabatic work always produced the same change of state of the system, regardless of the material performing the work or the substance used for the system.

Helmholtz, a surgeon in the Prussian army, recognized the epoch-making importance of Joule's work and wrote a brilliant paper in 1847, in which he applied Joule's ideas to the sciences of physical chemistry and physiology. William Thomson (Lord Kelvin) collaborated with Joule to refine the experiments.

Heating is a process by which there is an exchange of energy between system and surroundings because of a difference in temperature. But what is the energy that is exchanged? The question cannot be answered until the conditions for the process of heating are determined. In any process of heating, there is always a difference in temperature across the diathermic boundary between the system and its surroundings. But, for a specific system, more conditions must be specified. For example, consider the hydrostatic system. If the diathermic boundary of a hydrostatic system is held rigid, then the volume of the system does not change and the *isochoric* heat transferred is simply the internal energy. If the diathermic boundary of a hydrostatic system is movable (a piston), then the pressure of the system does not change and the *isobaric* heat transferred is known as the *enthalpy*, which is another type of energy to be introduced in Chap. 10.

4.5
CONCEPT OF HEAT

Heat is either internal energy or enthalpy in transit, depending on the experimental conditions. During the process of heating, energy flows from one part of a system to another, or from one system to another, by virtue of only a temperature difference. When the flow has ceased, there is no longer any occasion to use the word heat or the symbol Q, because the process is completed. All that remains after heating has been completed is a different state of the system, that is, a new value for the internal energy or enthalpy. Consequently, it is incorrect to refer to the "heat in a body," just as it is incorrect to speak of the "work in a body." The processes of working and heating are transient activities that lead to a change of the energy found in a system. All that endures is the new state of the energy. The energy of a system cannot be separated into a mechanical part and a thermal part, just as you cannot analogously identify some water in a lake as originating from this river and other water from that rain. The river and the rain have lost their meanings, but the new water level endures.

We have seen earlier that the work done on or by a system is not a function of the coordinates of the system, so the calculation of the work depends on the path of integration by which the system is brought from the initial to the final state. The same situation applies to the heat transferred in or out of a system. Heat Q is not a function of the thermodynamic coordinates, that is, not a state function, so the calculation of the heat depends on the path of integration. An infinitesimal amount of heat $đQ$, therefore, is an inexact differential and not the differential of an actual function of the thermodynamic coordinates.

Imagine two systems: a system A in thermal contact with a system B, and the composite system is surrounded by adiabatic walls. For system A alone,

$$U_f - U_i = Q + W;$$

and for system B alone,

$$U_f' - U_i' = Q' + W'.$$

Adding, we get

$$(U_f + U_f') - (U_i + U_i') = Q + Q' + W + W'.$$

Since $(U_f + U_f') - (U_i + U_i')$ is the change in energy of the composite system and $W + W'$ is the work done on the composite system, it follows that $Q + Q'$ is the heat transferred to the composite system. Since the composite system is surrounded by adiabatic walls,

$$Q + Q' = 0,$$

and

$$Q = -Q'. \tag{4.3}$$

In other words, *within an adiabatic boundary, the heat lost (or gained) by system A is equal to the heat gained (or lost) by system B.* Equation (4.3) is the basis of calculations of the intermediate temperature after a piece of hot metal has been dropped into a sample of cold water contained in a calorimeter. One is allowed to consider the quantity of heat to be conserved within the adiabatic container, but heat is generally not a conserved quantity, as Rumford's experiments showed.

4.6
DIFFERENTIAL FORM OF THE FIRST LAW

A process involving only infinitesimal changes in the thermodynamic coordinates of a system is known as an *infinitesimal process.* For such a process, the general statement of the first law becomes

$$\boxed{dU = đQ + đW.} \tag{4.4}$$

If the infinitesimal process is quasi-static, then dU and $đW$ can be expressed in terms of thermodynamic coordinates only. An infinitesimal quasi-static process is one in which the system passes slowly from an initial equilibrium state to a neighboring equilibrium state.

Equation (4.4) shows that the exact differential dU is the sum of two inexact differentials, $đQ$ and $đW$. It is surprising that the inexactness of the right side of the equation is not found on the left side. It should be recognized that dU refers to a property within the system (internal energy), whereas $đQ$

TABLE 4.1
The first law for simple systems

Simple system	First law	U is a function of *any* two of
Hydrostatic system	$dU = đQ - P\,dV$	P, V, T
Stretched wire	$dU = đQ + \mathcal{J}\,dL$	$\mathcal{J}, L, T$
Surface	$dU = đQ + \gamma\,dA$	γ, A, T
Electrochemical cell	$dU = đQ + \mathcal{E}\,dZ$	$\mathcal{E}, Z, T$
Dielectric slab	$dU = đQ + E\,d\mathcal{P}$	$E, \mathcal{P}, T$
Paramagnetic rod	$dU = đQ + \mu_0\mathcal{H}\,d\mathcal{M}$	$\mu_0\mathcal{H}, \mathcal{M}, T$

and $đW$ are *not* related to properties of the system; rather, they refer to the surroundings, where the surroundings interact with the system by means of *processes* of transferring energy. The quantity $đW$ was found in the last chapter to be expressible in terms of the product of an intensive generalized force and an extensive generalized displacement, as shown in Table 3.1. But, the quantity $đQ$ itself is not yet expressed in terms of thermodynamic (system) coordinates only. In this chapter, we begin the task of expressing heat in terms of system coordinates by introducing the quantity known as heat capacity of the system. After the second law of thermodynamics and the concept of entropy have been introduced in Chap. 8, we shall complete the discussion of heat and find that the first law can be written completely in terms of coordinates appropriate to the system only.

For an infinitesimal quasi-static process of a hydrostatic system, the first law can be written

$$đQ = dU + P\,dV, \tag{4.5}$$

where U is a function of any two of the three thermodynamic coordinates P, V, and T. The pressure P is, of course, a function of V and T from the equation of state. Notice that for a process restricted to constant volume, $đQ = dU|_V$, that is, heat is the flow of internal energy in an isochoric process. A similar equation may be written for each of the other simple systems, as shown in Table 4.1.

To deal with more complicated systems, it is merely necessary to replace $đW$ in the first law by two or more expressions. For example, in the case of a composite system consisting of two hydrostatic parts separated by a diathermic wall, we may express $đQ$ as follows:

$$đQ = dU + P\,dV + P'\,dV', \tag{4.6}$$

and U is a function of three of the variables P, V, P', V', and T. In the case of a paramagnetic gas,

$$đQ = dU + P\,dV - \mu_0\mathcal{H}\,d\mathcal{M}, \tag{4.7}$$

and U is a function of three of the coordinates P, V, $\mu_0\mathcal{H}$, $\mathcal{M}$, and T.

4.7
HEAT CAPACITY AND ITS MEASUREMENT

Equation (4.2) shows that the internal energy can be changed either by heat or work. As a practical matter, it is much easier to produce heat from combustion or electricity passing through a resistor than it is to produce work from falling weights or compressed springs. As a result, when systematic experiments were performed to measure the capability of a substance to store internal energy, heat rather than work was used, and the results came to be known as the *heat capacity* of the sample. The term "heat capacity" implies that a substance can hold heat, which is completely false. Heat is not a function of the thermodynamic state of a system; internal energy is! The proper expression should be *internal energy capacity*, but too much data have been gathered and too many books have been written to make this correction, so we are forced to use the oxymoron: heat capacity.

When heat is absorbed by a system, a change of temperature may or may not take place, depending on the state of the system. For example, a material at its melting temperature experiences no change of temperature when it is heated but a material at less than its melting temperature becomes hotter. If a system experiences a change of temperature from T_i to T_f during the transfer of Q units of heat, the *average heat capacity* of the system is defined as the ratio:

$$\text{Average heat capacity} = \frac{Q}{T_f - T_i}.$$

As both Q and $(T_f - T_i)$ become smaller, this ratio approaches a limiting value, known as the *heat capacity* C, thus:

$$C = \lim_{T_f \to T_i} \frac{Q}{T_f - T_i},$$

or, at temperature T_i,

$$\boxed{C = \frac{đQ}{dT}.} \tag{4.8}$$

where heat capacity is measured in joules per kelvin (J/K) in SI units. Notice that the right side of Eq. (4.8) is not a derivative of a function, but, rather, the ratio of two small experimental quantities $đQ$ and dT.

In dealing with extensive quantities (see Sec. 2.10), such as volume or internal energy, the mass of the system or sample affects the magnitude of the variable. Standardization occurs when an extensive quantity is divided by the mass of an arbitrary sample, resulting in the volume per unit mass or the internal energy per unit mass. These quantities are called *specific* quantities, the adjective "specific" meaning "per unit mass." Heat capacity is an extensive quantity, and the "specific heat capacity," abbreviated as "specific heat," is an intensive quantity measured in joules per kilogram-kelvin (J/kg·K). When the specific heat capacities of different substances are compared, no interesting regularities appear. When, however, the heat capacities are standardized to the same *amount of substance* (a different mass for each different substance) called a *mole*, wonderful regularities (to be explained in Sec. 9.5) occur.

A mole (abbreviated "mol") is defined as the amount of substance that contains as many elementary entities (atoms, molecules, ions, electrons, other particles) as there are atoms in 0.012 kg of ^{12}C. This number of atoms of ^{12}C is called Avogadro's number N_A and is equal to 6.022×10^{23} particles per mole. If the mass of an atom is m, then the mass of a mole of atoms is mN_A. This quantity, the *molar mass*, has also been called the "molecular weight." Designating the molar mass by M, we have

$$M = mN_A,$$

and the number of moles n is given by

$$n = \frac{\text{total mass}}{M}.$$

If C is the heat capacity of n moles, then the *molar heat capacity* c is given by

$$c = \frac{C}{n} = \frac{1}{n}\frac{đQ}{dT}$$

and is measured in units of joules per mole-kelvin (J/mol · K). Both the specific heat and the molar heat capacity are expressed as lower-case c, whereas the heat capacity of an arbitrary sample is expressed as capital C. All three quantities are state functions, because they are a measure of the change of internal energy in an isochoric process.

The heat capacity may be negative, zero, positive, or infinite, depending on the process the system undergoes during the heat transfer. Heat capacity has a definite value only for a definite process. In the case of a hydrostatic system, the ratio $đQ/dT$ has a unique value each time a measurement is made while the pressure is held constant. Under these conditions, C is called the *heat capacity at constant pressure* and is denoted by the symbol C_P, where

$$C_P = \left(\frac{đQ}{dT}\right)_P. \tag{4.9}$$

In general, C_P is a function of P and T. Similarly, the heat capacity *at constant volume* is the result of taking data while the volume is held constant; thus,

$$C_V = \left(\frac{đQ}{dT}\right)_V, \tag{4.10}$$

and depends on both V and T. In general, C_P and C_V are different. Both will be thoroughly discussed throughout this book. Each simple system has its own heat capacities as shown in Table 4.2.

Each heat capacity of a simple system is a function of two variables. Within a small range of variation of these coordinates, however, the heat capacity may be regarded as practically constant. Very often, one heat capa-

TABLE 4.2
Heat capacities of simple systems

Simple system	Heat capacity	Symbol
Hydrostatic system	At constant pressure	C_P
	At constant volume	C_V
Stretched wire	At constant tension	$C_{\mathcal{J}}$
	At constant length	C_L
Surface	At constant surface tension	C_γ
	At constant area	C_A
Electrochemical cell	At constant emf	$C_{\mathcal{E}}$
	At constant charge	C_Z
Dielectric slab	At constant electric field	C_E
	At constant total polarization	$C_{\mathcal{P}}$
Paramagnetic rod	At constant magnetic field	$C_{\mathcal{H}}$
	At constant total magnetization	$C_{\mathcal{M}}$

city can be set equal to another without much error. Thus, the $C_{\mathcal{H}}$ of a paramagnetic solid is in many situations very nearly equal to C_P.

The measurement of the heat capacity of solids was one of the most important experimental projects of physics at the beginning of the twentieth century, because numerical values of heat capacity provide one of the most direct means of assessing the validity of the assumptions used in statistical mechanics. An electrical method of measurement of heat capacities is used almost invariably. If a resistance wire is wound around a cylindrical sample of material and if both the wire and the sample are regarded as the system, then the electrical energy dissipated in the wire is interpreted as work. When the wire is not included as part of the system, however, the energy which is dissipated within the wire and which flows into the sample by virtue of the temperature difference between the wire and the sample (however small) is designated as heat. The wire is often called a *heating coil*. If the current in the wire is I and the potential difference across it is $\mathcal{E}$, then the heat $đQ$ that leaves the heating coil over a time dt is

$$đQ = \mathcal{E} I \, dt.$$

If $\mathcal{E}$ is measured in volts, I in amperes, and t in seconds, the heat will be expressed in joules. The shape, size, and construction of the *calorimeter* (the container of the system), heating coils, thermometers, etc., depend on the nature of the material to be studied and the temperature range desired. It is impossible to describe one calorimeter that suffices for all purposes.

In modern calorimetry, particularly in the case of solids at low temperatures, the sample is suspended in a highly evacuated space by means of fine threads of nylon or some other poorly conducting material. A heating coil is wound around the sample, and a thermocouple or a resistance thermometer (platinum, carbon, or germanium, depending on the temperature range) is

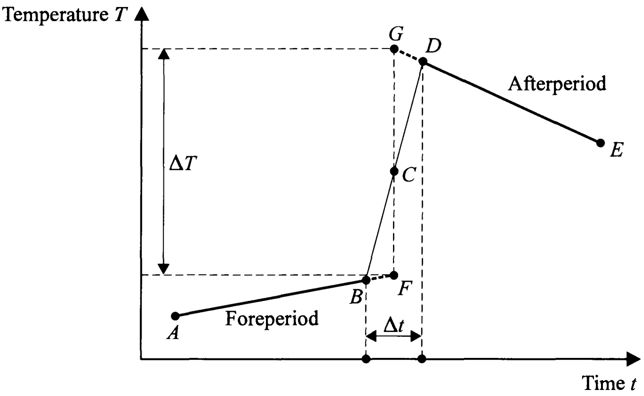

FIGURE 4-5
Temperature as a function of time in the measurement of heat capacity.

placed in a small hole drilled for that purpose. The connecting wires for the heater, for the current in the thermometer, and for the potential difference across the thermometer are made very thin so as not to allow much heat to be transferred between the sample and its surroundings through the connecting wires. The temperature of the sample is measured as a function of the time; when plotted as in Fig. 4-5, this gives the line AB, marked "foreperiod." At the time corresponding to point B, a switch is closed and a current is established in the heater at the same moment that an electronic timer is started. After a short interval of time Δt, the switch is opened and the timer is stopped. Then, the temperature is again measured as a function of time and is plotted as the line DE, marked "afterperiod" in Fig. 4-5.

As a rule, no reading of temperature or time is attempted while the timer is on, that is, from B to D. A vertical line is drawn through the center C of the line BD, and both the foreperiod and the afterperiod lines are extrapolated to this vertical line, giving the points F and G, as shown. The molar heat capacity c_P at the temperature corresponding to point C is then given by

$$c_P = \frac{\mathcal{E} I \,\Delta t}{n\,\Delta T}.$$

Sometimes ΔT is made as small as 0.001 deg. Strictly speaking, the graph shown in Fig. 4-5 is not a graph of temperature T vs. time t, but of the resistance R' of the resistance thermometer vs. time t. Typically, the entire $R'(t)$ curve is digitized and the molar heat capacities are calculated by computer.

4.8
SPECIFIC HEAT OF WATER; THE CALORIE

When the subject of calorimetry was developed in the middle of the eighteenth century, measurements were confined to the temperature range between the freezing and boiling points of water. The unit of heat found most convenient was called the *calorie* (abbreviation cal) and was defined as the amount of heat required to raise the temperature by 1°C in a system of 1 g of water. To measure the amount of heat transferred from the surroundings to the sample of water, it was necessary merely to make two measurements: the mass of water and change of temperature of the water. Later, as measurements became more precise and corrections were made, it was discovered that the heat necessary to change 1 g of water from 0 to 1°C was different from the heat required to go from, say, 30 to 31°C. The calorie was then defined to be the heat needed to go from 14.5 to 15.5°C (the "15-degree calorie").

The amount of work that had to be dissipated in water — either by maintaining a current in a resistor immersed in water or by churning the water in an irregular manner — per unit mass of water in going from 14.5 to 15.5°C was called the *mechanical equivalent of heat*, which was measured to be 4.1860 J/cal. In the 1920s, it was recognized that the measurement of this mechanical equivalent of heat was really a measurement of the specific heat of water, with the joule as the unit of heat. Since heat is a form of energy and the joule is the universal unit of energy, the calorie became superfluous. Among physicists and chemists today, the calorie has been dropped, and all thermal quantities are expressed in joules. There is no mechanical equivalent of heat, but instead there is the specific heat of water, whose temperature variation in the range of 0 to 100°C is shown in Fig. 4-6.

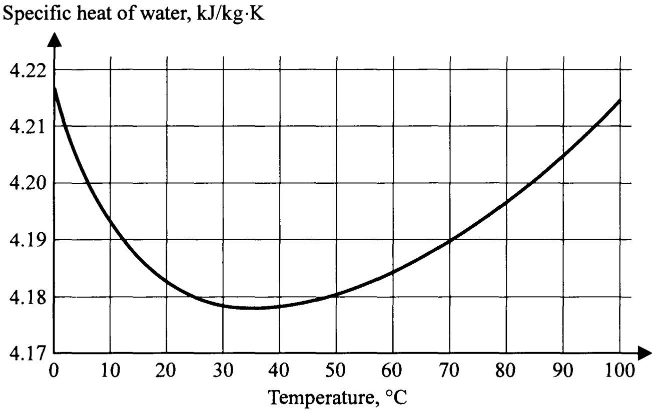

FIGURE 4-6
Specific heat of water at constant atmospheric pressure.

4.9
EQUATIONS FOR A HYDROSTATIC SYSTEM

The mathematical formulation of the first law for a hydrostatic system is

$$đQ = dU + P\,dV,$$

where U is a function of any two of P, V, and T. Choosing T and V, we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Therefore, the first law becomes

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \tag{4.11}$$

Dividing by dT, we get

$$\frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}. \tag{4.12}$$

This equation is true for *any* process involving any temperature change dT and any volume change dV.

1. If V is constant, then $dV = 0$, and

$$\left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

Notice that the term on the left is an experimental quantity—the measurement of a small amount of heat transferred due to a small difference in temperature between the system and the surroundings during a process in which the volume of the system is held constant. The term on the right is the derivative of the internal-energy function with respect to temperature while the variable volume is held constant during the differentiation.

The term on the left, by definition, is the heat capacity at constant volume C_V; therefore,

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V.} \tag{4.13}$$

The importance of Eq. (4.13) is that an experimental quantity on the left side of the equation is related to a partial derivative of thermodynamic coordinates on the right side. For example, if U is calculated from first principles by making special assumptions about the atoms or molecules of a particular material, then one of the first methods of checking these assumptions is to differentiate U with respect to T at constant V and to compare the resulting quantity with the experimentally measured value of C_V. However, the measurement of C_V can be very difficult, because the volume must be held fixed while the temperature is being raised. Recall, in Sec. 2.4, the pressure needed to hold a sample of mercury at constant volume for a temperature increase of only 10°C.

2. If P is constant, then Eq. (4.12) becomes

$$\left(\frac{đQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P.$$

But, by definition $(đQ/dT)_P = C_P$ and also $(\partial V/\partial T)_P = V\beta$ from Eq. (2.3). Hence,

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\beta,$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V\beta} - P. \tag{4.14}$$

Although this equation is not important in its present form, it is a good example of an equation that relates a quantity $(\partial U/\partial V)_T$, which is ordinarily not measured, with state functions such as C_P, C_V, and β, which can be measured.

4.10
QUASI-STATIC FLOW OF HEAT; HEAT RESERVOIR

It was shown in Chap. 3 that a process caused by a finite unbalanced force or torque is attended by phenomena such as acceleration or turbulence, which cannot be handled by means of thermodynamic coordinates that refer to the system as a whole. A similar situation exists when there is a finite difference between the temperature of a system and that of its surroundings. A nonuniform temperature distribution is set up in the system, and the calculation of this distribution and its variation with time is in most cases an elaborate mathematical problem. During a quasi-static process, however, the difference between the temperature of a system and that of its surroundings is infinitesimal. As a result, the temperature is at any moment uniform throughout the system, and its changes are infinitely slow. The flow of heat is also infinitely slow and may be calculated in a simple manner in terms of thermodynamic coordinates referring to the system as a whole.

Suppose that a system is in good thermal contact with a body of extremely large mass and that a quasi-static process is performed. A finite amount of heat flow during this process will not bring about an appreciable change in the temperature of the surrounding body if the mass is large enough. For example, an ice cube of ordinary size, if thrown into the ocean, will not produce a drop in temperature of the ocean. Or, another example, the flow of heat from an ordinary campfire into the air will not produce a rise of temperature of the atmosphere. The ocean and the atmosphere are approximate examples of an ideal body called a *heat reservoir. A heat reservoir is a body of such a large mass that it may absorb or reject an unlimited quantity of heat without experiencing an appreciable change in temperature or in any other thermodynamic coordinate.* Do not make the mistake of concluding that there is absolutely no change in the thermodynamic coordinates of a heat reservoir when a finite amount of heat flows in or out of the reservoir. There is a change in the reservoir, but an extremely small one, too small to be measured.

Any quasi-static process of a system in contact with a heat reservoir is bound to be isothermal. To describe a quasi-static flow of heat involving a change of temperature, one could conceive of a system placed in contact successively with a series of reservoirs. Thus, we imagine a series of reservoirs ranging in temperature from T_i to T_f placed successively in contact with a system at constant pressure in such a way that the difference in temperature between the system and the reservoir with which it is in contact is infinitesimal. The flow of heat will be quasi-static and can be calculated as follows from the definition of C_P:

$$C_P = \left(\frac{đQ}{dT}\right)_P,$$

and, therefore, for a quasi-static isobaric process, a path of integration is prescribed, so

$$Q_P = \int_{T_i}^{T_f} C_P\, dT. \tag{4.15}$$

For example, the heat absorbed by water from a series of reservoirs varying in temperature from T_i to T_f during a quasi-static isobaric process is calculated from Eq. (4.15). Assume C_P remains practically constant, integrate, and then

$$Q_P = C_P(T_f - T_i).$$

For a quasi-static isochoric process, another path of integration is prescribed, so

$$Q_V = \int_{T_i}^{T_f} C_V\, dT. \tag{4.16}$$

Similar considerations hold for other systems during quasi-static processes.

4.11
HEAT CONDUCTION

When two parts of a material substance are maintained at different temperatures and the temperature of each small volume element of the intervening substance is measured, experiment shows a continuous distribution of temperature. The transport of energy between neighboring volume elements by virtue of the temperature difference between them is known as *heat conduction.* The fundamental law of heat conduction is a generalization of the results of experiments on the linear flow of heat through a slab perpendicular to the faces. A piece of material is made in the form of a slab of thickness Δx and of area A. One face is maintained at the temperature T and the other at $T + \Delta T$. The heat Q that flows perpendicular to the faces for a time t is measured. The experiment is repeated with other slabs of the same material but with different values of Δx and A. The results of such experiments show that, for a given value of ΔT, the conducted heat Q is proportional to the time and to the area. Also, for a given time and area, Q is proportional to the ratio $\Delta T/\Delta x$, provided that both ΔT and Δx are small. These results may be written

$$\frac{Q}{t} \propto A\,\frac{\Delta T}{\Delta x},$$

which is only approximately true when ΔT and Δx are finite but which is rigorously true in the limit as ΔT and Δx approach zero. If we generalize this result for an infinitesimal slab of thickness dx, across which there is a temperature difference dT, and introduce a constant of proportionality K, the fundamental law of heat conduction becomes

$$\boxed{\frac{đQ}{dt} = -KA\,\frac{dT}{dx}.} \tag{4.17}$$

The derivative dT/dx is called the *temperature gradient.* The minus sign is introduced in order that the positive direction of the flow of heat should coincide with the positive direction of x. For heat to flow in the positive direction of x, this must be the direction in which temperature T decreases. The letter K is called the *thermal conductivity.* A substance with a large thermal conductivity is known as a *thermal conductor* and one with a small value of K as a *thermal insulator.* It will be shown in the next section that the numerical value of K depends upon a number of factors, one of which is the temperature. Volume elements of a conducting material may, therefore, differ in thermal conductivity. If the temperature difference between parts of a substance is small, however, K can be considered practically constant throughout the substance. This simplification is usually made in practical problems.

4.12
THERMAL CONDUCTIVITY AND ITS MEASUREMENT

When the substance to be investigated is a metal, it is made into the form of a bar, and one end is heated electrically while the other end is cooled with a stream of water. The surface of the bar is thermally insulated, and the heat loss through the insulation is calculated by subtracting the rate at which heat enters the water from the rate at which electrical energy is supplied. In the case of most metals, the heat lost from the surface is very small in comparison with that which flows through the bar. The temperature is measured with suitable thermocouples at two places a distance L apart, and the equation

$$K = \frac{L}{A(T_1 - T_2)} \frac{đQ}{dt}$$

is used to determine the average thermal conductivity within the given temperature range. If $T_1 - T_2$ is small, K is practically equal to the thermal conductivity at the mean temperature. K has units of watts per meter-kelvin (W/m · K).

When the substance to be investigated is a nonmetal, it is made into the form of a thin disk or plate, and the same general method is used. The substance is contained between two copper blocks, one of which is heated electrically and the other cooled by running water. In most cases, the rate at which heat is supplied is almost equal to the rate at which heat enters the water, showing that there is little loss of heat through the edges.

Experiments show that the thermal conductivity of a metal is quite sensitive to impurities. The slightest trace of arsenic in copper reduces the thermal conductivity by a factor of 3. A change in internal structure brought about by continued heating or a large increase in pressure also affects the value of K. No appreciable change in the K of solids and liquids takes place, however, under moderate changes of pressure. Liquefaction always produces a decrease in the thermal conductivity, and the thermal conductivity of a liquid usually increases as the temperature is raised. Nonmetallic solids behave in a manner similar to that of liquids. At room temperature, these are poor conductors of heat; in general, the thermal conductivity decreases as the temperature is raised. In the low-temperature range, however, the behavior is quite different, as shown in Fig. 4-7, where it may be seen that the thermal conductivity of sapphire rises to a maximum of approximately 6000 W/m · K at 35 K (about 15 times the conductivity of silver at room temperature). The thermal conductivity of some metals remains quite constant over a wide temperature range. Thus, silver, copper, and gold have thermal conductivities that remain practically constant in the temperature range from 100 to 1000 K. As a general rule, the thermal conductivity of metals increases as the temperature is lowered, until a maximum is reached. Further reduction of temperature causes a decrease toward zero, as shown in the case of copper in Fig. 4-7.

Gases are by far the poorest heat conductors. At pressures above a certain value, depending on the nature of the gas and the dimensions of the containing vessel, the thermal conductivity is independent of the pressure. Under the usual laboratory conditions, this limiting pressure is considerably below atmospheric pressure. The thermal conductivity of a gas always increases as the temperature is raised, as indicated by He (gas) in Fig. 4-7.

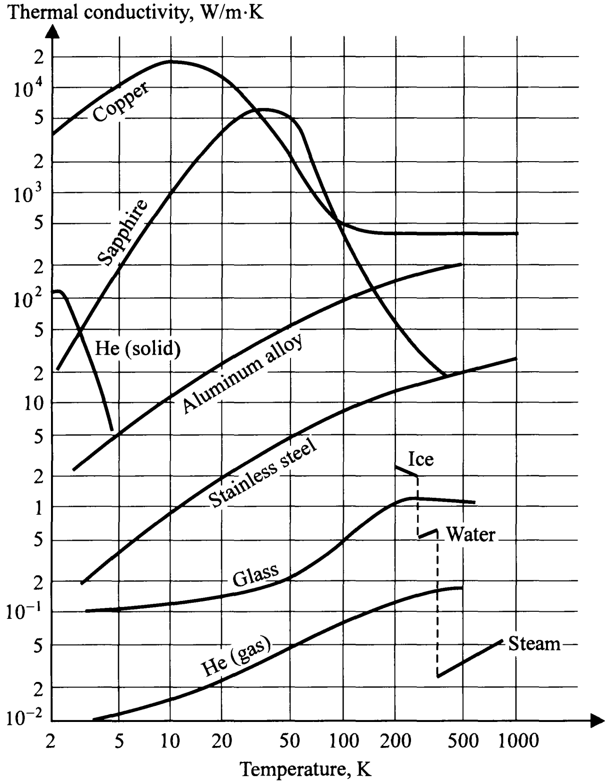

FIGURE 4-7
Typical curves showing temperature dependence of thermal conductivity.

4.13 HEAT CONVECTION

A flow of liquid or gas that absorbs heat at one place and then moves to another place, where it mixes with a cooler portion of the fluid and rejects heat, is called a *convection current*. If the motion of the fluid is caused by a difference in density that accompanies a temperature difference, the phenomenon is called *natural convection*. If the fluid is made to move by the action of a pump or a fan, it is called *forced convection*.

Consider a fluid in contact with a flat or curved wall whose temperature is higher than that of the main body of the fluid. Although the fluid may be in notion, there is a relatively thin layer of stagnant fluid next to the wall, the thickness of the layer depending upon the character of the motion of the main body of fluid. The more turbulent the motion, the thinner the layer. Heat is transferred from the wall to the fluid by a combination of conduction through the layer and convection in the fluid. Neglecting the transfer of heat by radiation (which will be taken into account in Sec. 4.15), we may define a *convection* *coefficient h* that includes the combined effect of conduction through the layer and convection in the fluid. Thus,

$$\boxed{\frac{đQ}{dt} = hA\,\Delta T,} \tag{4.18}$$

where A is the area of the wall, and ΔT is the temperature difference between the surface of the wall and the main body of the fluid. The fundamental problem of heat convection is to find the value of h that is appropriate to a particular piece of equipment.

Experiment shows that the convection coefficient depends on the following factors:

1. Whether the wall is flat or curved.
2. Whether the wall is horizontal or vertical.
3. Whether the fluid in contact with the wall is a gas or a liquid.
4. The density, viscosity, specific heat, and thermal conductivity of the fluid.
5. Whether the speed of the fluid is small enough to give rise to laminar flow or large enough to cause turbulent flow.
6. Whether evaporation, condensation, or formation of scale takes place.

Since the physical properties of the fluid depend upon temperature and pressure, it is clear that the rigorous calculation of a convection coefficient appropriate to a given wall and fluid is an enormously complicated problem. Solutions of the problem for particular situations are achieved by numerical integration.

4.14
THERMAL RADIATION; BLACKBODY

Thermal radiation is important in thermometry, since it is the basis of precisely measured high temperatures above the range of gas thermometers. As an example of the effects of thermal radiation, consider placing your hand near a hot object and experiencing the warming that occurs before the object is touched. Evidently, heat is transmitted across the space between the object and the hand. That this can occur without the intervention of matter is proved by the fact that heat comes to us from the sun across 93 million miles of empty space. By conduction and convection, the transfer of heat is accomplished through the medium of matter, and heat can be transferred in this way only as far as matter extends or can itself be transported. By the process of radiation, however, heat is separated from its association with matter and can travel as radiation as far as empty space extends. Originally, the waves of radiation were called "radio waves." But, as the nature of radiation came to be understood, the term was replaced by the term "electromagnetic waves."

A substance may be stimulated to emit electromagnetic radiation in a number of ways:

1. An electric conductor carrying a high-frequency alternating current emits radio waves.
2. Electrons oscillating in a magnetron-type tube emit microwaves.
3. A hot solid or liquid emits *thermal radiation*, that is, infrared radiation.
4. A gas experiencing an electric discharge may emit visible or ultraviolet radiation.
5. A substance exposed to ultraviolet radiation from an external source may emit fluorescent light.
6. A metal target bombarded by high-speed electrons emits x-rays.
7. A substance whose atoms are radioactive may emit gamma rays.

All these radiations are electromagnetic waves, differing only in frequency (or wavelength) in vacuum. We shall be concerned in this section only with thermal radiation, namely, the radiation emitted by a solid or a liquid by virtue of its temperature. The radiation characteristics of gases require special treatment. In this section, we shall assume that gases are transparent to thermal radiation.

When thermal radiation is dispersed by a prism or diffraction grating, one obtains a continuous spectrum of the visible spectrum and the invisible infrared radiation. The distribution of energy among the various wavelengths is such that, at temperatures below about 500°C, the energy is infrared radiation; at higher temperatures, increasingly more visible light is emitted. In general, the higher the temperature of a body, the greater the total energy emitted.

The loss of energy due to the emission of thermal radiation may be compensated in a variety of ways. The emitting body may be a source of energy itself, such as the sun; or, there may be a constant supply of electrical energy from the surroundings, as in the case of a lamp. Energy may be supplied also by heat conduction or by the performance of work on the emitting body. In the absence of these sources of supply, the only other way in which a body may receive energy is by the absorption of radiation from its surroundings. In the case of a body that is immersed in radiation, the internal energy of the body will remain constant when the rate at which radiant energy is emitted equals the rate at which radiant energy is absorbed; in other words, the exiting radiant power equals the incident radiant power.

Experiment shows that the radiant power leaving a body as thermal radiation depends on the temperature, on the area of the surface, and on the nature of the surface of the body. The total radiant power exiting an infinitesimal element of surface, divided by the area of that surface, is called the *radiant exitance* $\mathcal{R}$ of the body (formerly, radiant emittance). For example, the radiant exitance of tungsten at 1000 K is 6.46 kW/m^2, at 2000 K is 236 kW/m^2, and at 3000 K is 1534 kW/m^2.

When thermal radiation is incident upon a body equally from all directions, the radiation is said to be *isotropic*. Some of the radiation may be absorbed, some reflected, and some transmitted. In general, the incident isotropic radiation of all wavelengths that is *absorbed* depends on the temperature and the nature of the surface of the absorbing body. The fraction of the total incident radiant power that is absorbed is called the *absorptivity*. In thermal equilibrium, the processes of absorption and emission of radiant power are equal and opposite. So, the *total emissivity* ϵ, equal to the absorptivity, is defined as the fraction of the power provided to a real body that is emitted through a material surface as thermal radiation, where the word "total" includes all wavelengths of electromagnetic radiation. As a practical matter, it is easier to measure emissivity than absorptivity. To summarize:

Radiant exitance $\mathcal{R}$ = total radiant power emitted per unit area;

and

Total emissivity ϵ = fraction of the total radiant power that is emitted as thermal radiation.

The emissivity depends on both the temperature and the nature of the emitting surface. The emissive nature of surfaces is revealed by comparing emissivities at the same temperature. At 300 K, when all bodies emit only infrared radiation, the emissivity of polished steel is 0.09, rough oxidized steel is 0.81, and ocean water is 0.96. There are some substances, such as lampblack or carbon soot, whose emissivity is very nearly unity, that is, almost an ideal emitter. For theoretical purposes, it is useful to conceive of an *ideal substance* capable either of absorbing *all* the thermal radiation falling on it or of emitting *all* the energy provided to it in the form of thermal radiation. Such a substance is called a *blackbody*. If a blackbody is indicated by the subscript *bb*, we have

$$\epsilon_{bb} = 1.$$

A very good experimental approximation to a blackbody is provided by a cavity enclosed by high-temperature opaque walls. The interior walls, which are maintained at a uniform temperature, permit thermal radiation to pass through a hole small in comparison with the dimensions of the cavity. Any radiation entering the hole is completely absorbed by the walls after repeated reflections at the walls, with only a negligible amount eventually finding its way out the hole. *This is true regardless of the composition of the materials of the interior walls.*

The radiation emitted by the interior walls is similarly absorbed or diffusely reflected a large number of times, so that the cavity is filled with isotropic blackbody radiation. Let us define the *irradiance* as the radiant power per unit area incident upon a surface within the cavity. Suppose a blackbody whose temperature is the same as that of the walls is introduced into the cavity. Then, denoting the irradiance by H,[†]

$$\text{Radiant power absorbed per unit area} = \epsilon_{bb} H = H,$$

and

$$\text{Radiant power emitted per unit area} = \mathcal{R}_{bb}.$$

Since the temperature of the blackbody remains constant, the radiant power per unit area that is absorbed must equal the radiant power per unit area that is leaving; whence,

$$\boxed{H = \mathcal{R}_{bb},} \tag{4.19}$$

or *the irradiance within a cavity whose walls are at the temperature T is equal to the radiant exitance of a blackbody at the same temperature.* For this reason, the radiation enclosed within a cavity is called *blackbody radiation.* Such radiation, which provides standard radiation in terms of wavelengths and intensities, is a function only of temperature and is studied by allowing a small amount to escape from a small hole in the cavity. Since H is independent of the materials of which the interior walls are composed, it follows that the *radiant exitance of a blackbody is a function of the temperature only.*

4.15
KIRCHHOFF'S LAW; RADIATED HEAT

The radiant exitance of a *non-blackbody* depends as much on the nature of the surface as on the temperature, according to a simple law that we may derive as follows. Suppose that a non-blackbody at the temperature T, with radiant exitance $\mathcal{R}$, and emissivity ϵ, is introduced into a cavity whose interior walls are at the same temperature and where the irradiance is H. Then,

$$\text{Radiant power absorbed per unit area} = \epsilon H,$$

and

$$\text{Radiant power emitted per unit area} = \mathcal{R}.$$

Since the non-blackbody is in equilibrium,

$$\mathcal{R} = \epsilon H$$

But, from Eq. (4.19), $H = \mathcal{R}_{bb}$; hence,

$$\boxed{\mathcal{R} = \epsilon \mathcal{R}_{bb},} \tag{4.20}$$

[†] In books on radiometry, the radiant exitance is given the symbol M and the irradiance the symbol E. Here, we adopt the symbols $\mathcal{R}$ and H to avoid confusion with the molar mass and electric field intensity.

TABLE 4.3
Total emissivities of various surfaces, as compiled by Hottel
(Values at intermediate temperatures may be obtained by linear interpolation)

Material	Temperature range, K	Emissivity ϵ
Polished metals:		
Aluminum	525–875	0.039–0.057
Brass	525–675	0.033–0.037
Chromium	325–825	0.08–0.26
Copper	375	0.018
Iron	425–1275	0.05–0.37
Nickel	300–625	0.045–0.087
Zinc	525–625	0.045–0.053
Filaments:		
Molybdenum	1025–2875	0.096–0.29
Platinum	300–1475	0.036–0.19
Tantalum	1575–3275	0.19–0.31
Tungsten	300–3575	0.032–0.35
Other materials:		
Asbestos	325–625	0.93–0.95
Ice (wet)	273	0.97
Lampblack	300–625	0.95
Rubber (gray)	300	0.86

or *the radiant exitance of any body at any temperature is equal to a fraction of the radiant exitance of a blackbody at that temperature, this fraction being the emissivity at that temperature.*

This equation, known as *Kirchhoff's law* and named after the German physicist, shows that the emissivity of a body may be determined experimentally by measuring the radiant exitance of the body and dividing it by the exitance of a blackbody at the same temperature. Values of the emissivity of the surfaces of various materials, measured in this way, are given in Table 4.3. It should be emphasized that the tabulated values of emissivity refer to the thermal radiation appropriate to the temperature listed in the temperature-range column. Thus, the emissivity of ice is 0.97 not for visible radiation, but for the long infrared waves associated with matter at 0°C (273 K).

It should be noticed that the word "heat" has not appeared as yet. If there is a temperature difference between a body and its surroundings, then, in a given interval of time, the body loses an amount of internal energy equal to the energy radiated minus the energy absorbed, whereas the surroundings gain an amount of internal energy equal to the energy absorbed minus the energy radiated. The gain of the surroundings equals the loss of the body. *The gain or loss of internal energy of the body, equal to the difference between the energy of the thermal radiation which is absorbed and that which is radiated, is called heat.* This statement is in agreement with the original definition of heat, since a gain or loss of internal energy by radiation and absorption will take place *only if there is a difference in temperature* between a body and its surroundings. If the two temperatures are the same, there is no net gain or loss of internal energy of either the body or its surroundings, and there is, therefore, no transfer of heat.

Imagine a cavity whose interior walls are maintained at a constant temperature T_W. Suppose that a non-blackbody at a temperature T different from that of the walls is placed in the cavity. If the body is small compared with the size of the cavity, then the character of the radiation in the cavity will not be appreciably affected by the presence of the small body. Let H, as before, denote the irradiance within the cavity, and $\mathcal{R}$ and ϵ the radiant exitance and emissivity, respectively, of the body. Then, as before,

$$\text{Radiant power absorbed per unit area} = \epsilon H,$$

and

$$\text{Radiant power emitted per unit area} = \mathcal{R};$$

but now *these two powers per unit area are not equal.* The difference between them is the heat transferred by radiation per second per unit area. If $\text{đ}Q$ is the heat transferred in time dt to the non-blackbody whose area is A, then

$$\frac{\text{đ}Q}{dt} = A(\epsilon H - \mathcal{R}), \tag{4.21}$$

where, it must be remembered, emissivity ϵ and exitance $\mathcal{R}$ are functions of the temperature of the body T; and irradiance H is a function of the temperature of the wall T_W; thus,

$$\mathcal{R} = \epsilon(T)\mathcal{R}_{bb}(T),$$

and

$$H = \mathcal{R}_{bb}(T_W).$$

Hence,

$$\frac{\text{đ}Q}{dt} = A\epsilon(T)[\mathcal{R}_{bb}(T_W) - \mathcal{R}_{bb}(T)], \tag{4.22}$$

or the rate at which heat is transferred by radiation is proportional to the difference between the radiant exitances of a blackbody at the two temperatures in question.

4.16
STEFAN-BOLTZMANN LAW

The first measurements of the heat transferred by radiation between a body and its surroundings were made by Tyndall. On the basis of these experiments, it was concluded by Stefan in 1879 that the heat radiated was proportional to the difference of the fourth powers of the absolute temperatures. This purely experimental result was later derived thermodynamically by Boltzmann, who showed that the radiant exitance of a blackbody at *any* temperature T is equal to

$$\boxed{\mathcal{R}_{bb}(T) = \sigma T^4.} \tag{4.23}$$

This law is now known as the *Stefan-Boltzmann law*, and σ (Greek letter sigma) is called the Stefan-Boltzmann constant.

Referring to Eq. (4.22), we have for the heat transferred by radiation between a body at the temperature T and walls at T_W,

$$\boxed{\frac{đQ}{dt} = A\epsilon\sigma(T_W^4 - T^4),} \tag{4.24}$$

where ϵ is a function of the temperature T.

Two simple methods may be employed for the determination of the Stefan-Boltzmann constant:

1. *Nonequilibrium method.* A blackened silver disk is placed in the center of a large blackened copper hemisphere. The silver disk is covered and shielded from radiation until the copper hemisphere achieves the temperature of condensing steam; this temperature is measured with a thermocouple. Then, the disk is uncovered, and its temperature T is measured as a function of the time t. From the resulting heating curve, the slope dT/dt is obtained. Assuming the silver disk to be a blackbody and putting $đQ = C_P\,dT$ in Eq. (4.24), where C_P is the heat capacity at constant pressure, we have

   $$\frac{C_P\,dT}{dt} = A\sigma(T_W^4 - T^4);$$

   whence,
   $$\sigma = \frac{C_P}{A(T_W^4 - T^4)}\,\frac{dT}{dt}.$$

2. *Equilibrium method.* A hollow blackened copper sphere is provided with an electric heater and a thermocouple and is suspended inside a vessel whose walls are maintained at a constant temperature T_W. Electrical energy is supplied at a constant rate $\mathscr{E}I$ until the sphere achieves an equilibrium temperature T at which the rate of supply of energy is equal to the rate of emission of radiation. Assuming the sphere to be a blackbody, we have, at equilibrium,

   $$\mathscr{E}I = A\sigma(T^4 - T_W^4);$$

   whence,
   $$\sigma = \frac{I}{4\pi r^2(T^4 - T_W^4)},$$

   where r is the radius of the sphere. The best measurements of the Stefan-Boltzmann constant to date have yielded the value

$$\boxed{\sigma = 5.67051 \times 10^{-8}\ \mathrm{W/m^2\cdot K^4}.} \tag{4.25}$$

PROBLEMS

4.1. A gas contained in a cylinder by a layer of styrofoam is quickly compressed, the temperature rising several hundred degrees. Has there been a transfer of heat? Has the "heat content" of the gas been increased?

4.2. A combustion experiment is performed by burning a mixture of fuel and oxygen in a constant-volume container surrounded by a water bath. During the experiment, the temperature of the water rises. If the system is the mixture of fuel and oxygen:
(*a*) Has heat been transferred?
(*b*) Has work been done?
(*c*) What is the sign of ΔU?

4.3. A liquid is irregularly stirred in a well-insulated container and thereby experiences a rise in temperature. If the system is the liquid:
(*a*) Has heat been transferred?
(*b*) Has work been done?
(*c*) What is the sign of ΔU?

4.4. The amount of water in a lake may be increased by action of underground springs, by inflow from a river, and by rain. It may be decreased by various outflows and by evaporation.
(*a*) Comment on the question: How much rain is there in the lake?
(*b*) Comment on the question: How much water in the lake is due to rain?
(*c*) What concept is analogous to "rain in the lake"?

4.5. A container with rigid well-insulated walls is divided into two parts by a partition. One part contains a gas, and the other is evacuated. If the partition suddenly breaks, show that the initial and final internal energies of the gas are equal. (*Note*: this process is called an adiabatic *free expansion.*)

4.6. When an electric current is maintained in an electrolytic cell of slightly acidic water and 1 mol of water is electrolyzed into hydrogen and oxygen, 2 F (faradays) of charge are transferred through a source of emf $\mathcal{E}$ ($1F \approx 96{,}500$ C/mol). The energy change of the system is +286,500 J, and 50,000 J of heat is absorbed. What is $\mathcal{E}$?

4.7. A cylinder with rigid well-insulated walls is divided into two parts by a rigid insulating wall with a small hole in it. A frictionless, insulated piston is held against the perforated partition, thus preventing the gas that is on the other side from seeping through the hole. The gas is maintained at a pressure P_i by another frictionless insulated piston. Imagine both pistons to move simultaneously in such a way that, as the gas streams through the hole, the pressure remains at a constant value P_i on one side of the dividing wall and at a constant lower value P_f on the other side, until all the gas is forced through the hole. (*Note*: this process is called a *throttling process.*) Prove that

$$U_i + P_i V_i = U_f + P_f V_f.$$

4.8. A container of volume V contains n moles of gas at high pressure. Connected to the container is a capillary tube through which the gas may leak slowly out to the atmosphere, where the pressure is P_0. Surrounding the container and capillary is a water bath, in which is immersed an electrical resistor. The gas is allowed to leak slowly through the capillary into the atmosphere while electrical energy is dissipated in the resistor at such a rate that the temperature of the gas, the container, the capillary, and the water is kept equal to that of the outside air. Show that, after as much gas as possible has leaked out during time interval t, the change in internal energy is

$$\Delta U = \mathcal{E} It - P_0(nv_0 - V),$$

where v_0 is the molar volume of the gas at atmospheric pressure, $\mathcal{E}$ is the potential difference across the resistor, and I is the current in the resistor.

4.9. A thick-walled insulated metal chamber contains n_i moles of helium at high pressure P_i. It is connected through a valve with a large, almost empty gasholder in which the pressure is maintained at a constant value P', very nearly atmospheric. The valve is opened slightly, and the helium flows slowly and adiabatically into the gasholder until the pressure on the two sides of the valve is equalized. Prove that

$$\frac{n_f}{n_i} = \frac{h' - u_i}{h' - u_f},$$

where n_f = number of moles of helium left in the chamber,
u_i = initial molar internal energy of helium in the chamber,
u_f = final molar internal energy of helium in the chamber, and
$h' = u' + P'v$ (where u' = molar internal energy of helium in the gasholder;
v' = molar volume of helium in the gasholder).

4.10. Regarding the internal energy of a hydrostatic system to be a function of T and P, derive the following equations:

(a) $$\text{đ}Q\left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP.$$

(b) $$\left(\frac{\partial U}{\partial T}\right)_P = C_P - PV\beta.$$

(c) $$\left(\frac{\partial U}{\partial P}\right)_T = PV\kappa - (C_P - C_V)\frac{\kappa}{\beta}.$$

4.11. Taking U to be a function of P and V, derive the following equations:

(a) $$\text{đ}Q = \left(\frac{\partial V}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right]dV.$$

(b) $$\left(\frac{\partial U}{\partial P}\right)_V = \frac{C_V\kappa}{\beta}.$$

(c) $$\left(\frac{\partial U}{\partial V}\right)_P = \frac{C_P}{V\beta} - P.$$

4.12. Derive the equations listed in the accompanying table.

System	Heat capacity at constant extensive variable	Heat capacity at constant intensive variable
Stretched wire	$C_L = \left(\frac{\partial U}{\partial T}\right)_L$	$C_{\mathcal{J}} = \left(\frac{\partial U}{\partial T}\right)_{\mathcal{J}} - \mathcal{J}L\alpha$
Paramagnetic solid obeying Curie's law	$C_{\mathcal{M}} = \left(\frac{\partial U}{\partial T}\right)_{\mathcal{M}}$	$C_{\mathcal{H}} = \left(\frac{\partial U}{\partial T}\right)_{\mathcal{H}} + \frac{\mathcal{M}^2}{C_C}$

Note: C_C is the Curie constant, not a heat capacity.

4.13. Consider using the apparatus shown in Fig. 4-1(*a*), known as the Joule paddle wheel, to determine the specific heat at constant atmospheric pressure. The paddle wheel is driven by a slowly falling weight, and both have a temperature of 14.5°C. As a result of the work done by the 0.427 kg mass that falls 1.00 m, the temperature of 1 kg of water rises 1°C. Calculate c_P.

4.14. One mole of a gas obeys the van der Waals equation of state:

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

and its molar internal energy is given by

$$u = cT - \frac{a}{v},$$

where a, b, c, and R are constants. Calculate the molar heat capacities c_V and c_P.

4.15. The equation of state for a monatomic solid is

$$Pv + f(v) = \Gamma u,$$

where v is the molar volume, Γ is the Grüneisen constant, and u is the molar internal energy due to lattice vibrations. Prove that

$$\Gamma = \frac{\beta v}{c_V \kappa},$$

where κ is the isothermal compressibility. This equation, known as the Grüneisen relation, plays an important role in solid-state theory.

4.16. The molar heat capacity at constant pressure C_P/n of a gas varies with the temperature according to the equation

$$\frac{C_P}{n} = a + bT - \frac{c}{T^2},$$

where a, b, and c are constants. How much heat is transferred during an isobaric process in which n moles of gas experience a temperature rise from T_i to T_f?

4.17. The molar heat capacity at constant volume of a metal at low temperatures varies with the temperature according to the equation

$$\frac{C_V}{n} = \left(\frac{124.8}{\Theta}\right)^3 T^3 + \gamma T,$$

where Θ is the Debye temperature, γ is a constant, and C_V/n is measured in units of mJ/mol · K. The first term on the left is the contribution attributable to lattice vibrations and the second term is due to the contribution of free electrons. For copper, Θ is 343 K and γ is 0.688 mJ/mol · K^2. How much heat per mole is transferred during a process in which the temperature changes from 2 to 3 K?

4.18. Suppose that heat conduction occurs at a constant rate $\text{đ}Q/dt$ in a hollow sphere with an inner radius r_1 at temperature T_1 and an outer radius r_2 at temperature T_2. Show that for constant thermal conductivity K, the temperature difference between the two surfaces is given by

$$T_1 - T_2 \frac{\text{đ}Q/dt}{4\pi K}\left(\frac{1}{r_2} - \frac{1}{r_1}\right).$$

4.19. Two thin concentric spherical shells of radius 0.05 m and 0.15 m, respectively, have their annular cavity filled with charcoal. When energy is supplied at the steady rate of 10.8 W to a heater at the center, a temperature difference of 50°C is set up between the spheres. Find the thermal conductivity of charcoal.

4.20. The air above the surface of a freshwater lake is at a temperature T_A, while the water is at its freezing point T_i, where $T_A < T_i$. After a time t has elapsed, ice of thickness y has formed. Assuming that the heat, which is liberated when the water freezes, flows up through the ice by conduction and then into the air by natural convection, prove that

$$\frac{y}{h} + \frac{y^2}{2K} = \frac{T_i - T_A}{\rho L} t,$$

where h is the convection coefficient per unit area and is assumed constant while ice forms, K is the thermal conductivity of ice, l is the latent heat of fusion of ice, and ρ is the density of ice. (*Hint*: The temperature of the upper surface is variable. Assume that the ice has a thickness y and imagine an infinitesimal thickness dy to form in time dt.)

4.21. A solid cylindrical copper rod 0.10 m long has one end maintained at a constant temperature of 20 K. The other end is blackened and exposed to thermal radiation from a body at 300 K, with no energy lost or gained through the sides of the cylinder. When equilibrium is reached, what is the temperature difference between the two ends? (*Hint*: Refer to Fig. 4.7.)

4.22. A cylindrical metal can, blackened on the outside, 0.10 m high and 0.05 m in diameter, contains liquid ^{4}He at its normal boiling point of 4.22 K, at which its heat of vaporization is 20.4 kJ/kg. Completely surrounding the helium can are walls maintained at the temperature of liquid nitrogen (77.35 K), and the intervening space is continuously evacuated to a very low pressure. How much helium is lost per hour?

4.23. The operating temperature of a tungsten filament in an incandescent lamp is 2460 K, and its total emissivity is 0.30. Find the surface area of the filament of a 100-W lamp.

4.24. A copper wire of length 1.317 m and diameter 3.26×10^{-4} m is blackened and placed along the axis of an evacuated glass tube. The wire is connected to a battery, a rheostat, an ammeter, and a voltmeter, and the current is increased until, at the moment the wire is about to melt, the ammeter reads 12.8 A and the voltmeter reads 20.2 V. Assuming that all the energy supplied was radiated and that the radiation from the glass tube is negligible, calculate the melting temperature of copper.

4.25. The *solar constant* is the incident energy per unit of time on a unit area of a surface placed at right angles to a sunbeam just outside the earth's atmosphere. The value of the solar constant is 1.37 kW/m^2. The area of a sphere with radius 93,000,000 miles is 2.79×10^{23} m^2, and the surface area of the sun is 6.09×10^{18} m^2. Assuming that the sun is a blackbody, calculate its surface temperature.

4.26. (*a*) A small body with temperature T and emissivity ϵ is placed in a large evacuated cavity with interior walls kept at temperature T_W. When $T_W - T$ is small, show that the rate of heat transfer by radiation is

$$\frac{đQ}{dt} = 4T_W^3 A\epsilon\sigma(T_W - T).$$

(*b*) If the body remains at constant pressure, show that the time for the temperature of the body to change from T_1 to T_2 is given by

$$t = \frac{C_P}{4T_W^3 A\epsilon\sigma} \ln \frac{T_W - T_1}{T_W - T_2}.$$

(*c*) Two small blackened spheres of identical size, one of copper and the other of aluminum, are suspended by silk threads within a large hole in a block of melting ice. It is found that it takes 10 min for the temperature of the aluminum to drop from 276 to 274 K, and 14.2 min for the copper to drop the same interval of temperature. What is the ratio of specific heats of aluminum and copper? (The densities of Al and Cu are 2.70×10^3 kg/m^3 and 8.96×10^3 kg/m^3 at 25°C, respectively.)

4.27. A blackened solid copper sphere with radius of 0.02 m is placed in an evacuated enclosure with walls kept at 100°C. In what time does its temperature change from 103 to 102°C? ($c_P = 0.395$ kJ/kg·K; $\rho = 8.96 \times 10^3$ kg/m^3 at 25°C.)

4.28. In the case of a paramagnetic gas:

(*a*) Derive the equation

$$đQ = \left(\frac{\partial U}{\partial T}\right)_{V,\mathcal{M}} dT + \left[\left(\frac{\partial U}{\partial V}\right)_{\mathcal{M},T} + P\right] dV + \left[\left(\frac{\partial U}{\partial \mathcal{M}}\right)_{T,V} - \mu_0 \mathcal{H}\right] d\mathcal{M}.$$

(*b*) Derive expressions for $C_{V,\mathcal{M}}$, $C_{V,\mathcal{H}}$, $C_{P,\mathcal{M}}$, and $C_{P,\mathcal{H}}$.

CHAPTER 5

Ideal Gas

5.1
EQUATION OF STATE OF A GAS

It was emphasized in Chap. 1 that a gas is the best-behaved thermometric substance because of the fact that the ratio of the pressure P of a gas at any temperature to the pressure P_{TP} of the same gas at the triple point, as both P and P_{TP} approach zero, approaches a value independent of the nature of the gas. The limiting value of this ratio, multiplied by 273.16 K, was defined to be the ideal-gas temperature T of the system at whose temperature the gas exerts the pressure P. The reason for this regular behavior may be found by investigating the way in which the product PV of a gas depends on P.

Suppose that the pressure P and the volume V of n moles of gas held at any constant temperature are measured over a wide range of values of the pressure, and the product Pv, where the molar volume $v = V/n$, is plotted as a function of P. Experiments of this sort were first performed by Amagat in France in 1870 and later by Holborn and Otto in Berlin and by Kamerlingh-Onnes and Keesom in Leiden. The relation between Pv and P may be expressed for a real gas by means of a power series (or *virial expansion*) of the form

$$Pv = A(1 + BP + CP^2 + \cdots), \tag{5.1}$$

where A, B, C, etc., are called *virial coefficients* (A being the first virial coefficient, B the second, etc.) and depend on the temperature and on the nature of the gas. In the pressure range from 0 to about 40 standard atmospheres, the relation between Pv and P is practically linear, so that only the first two terms in the expansion are significant. In general, the greater the pressure range, the larger the number of terms in the virial expansion.

The remarkable property of gases that makes them so valuable in thermometry is displayed in Fig. 5-1, where the product Pv is plotted against P for four different gases, all at the temperature of boiling water in the top graph, all at the triple point of water in the middle graph, and all at the temperature of solid CO_2 in the bottom graph. In each case, it is seen that, as the pressure approaches zero, the product Pv approaches the same value for all gases at the same temperature. It follows from this that the *first virial coefficient A is independent of the nature of the gas and depends only on temperature.* Thus,

$$\lim_{P\to 0}(Pv) = \mathrm{A} = \begin{cases} \text{function of temperature only,} \\ \text{independent of gas.} \end{cases} \tag{5.2}$$

The ideal-gas temperature T is defined in Eq. (1.7) as

$$T = 273.16\,\mathrm{K} \lim_{P_{TP}\to 0}\left(\frac{P}{P_{TP}}\right) \qquad \text{(const. } V\text{)},$$

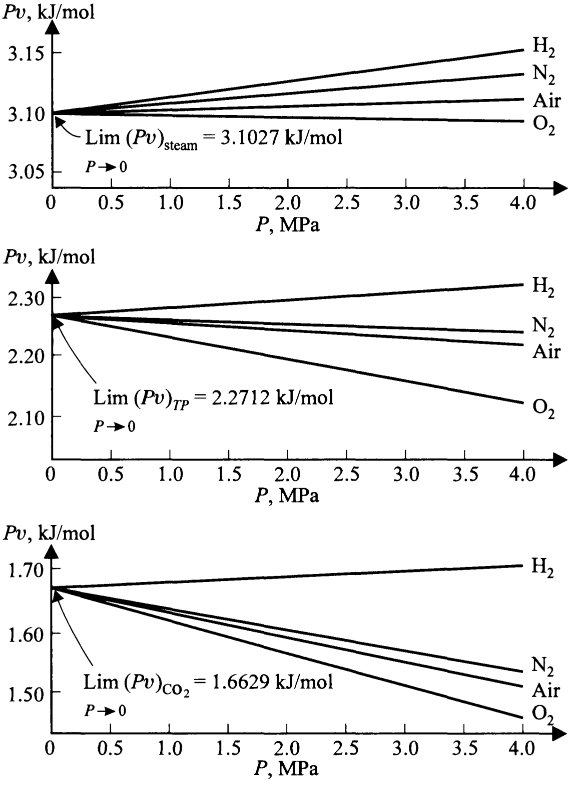

FIGURE 5-1

A fundamental property of gases is that $\lim (Pv)_T$ is independent of the species of chemical and depends only on the temperature of the gas.

so that $$T = 273.16\,\mathrm{K} \lim \frac{PV/n}{P_{TP}V/n} = 273.16\,\mathrm{K} \frac{\lim(Pv)}{\lim(Pv)_{TP}},$$

and $$\lim(Pv) = \left[\frac{\lim(Pv)_{TP}}{273.16\,\mathrm{K}}\right] T.$$

The bracketed term is called the *molar gas constant* and is denoted by R. Thus,

$$R = \frac{\lim(Pv)_{TP}}{273.16\,\mathrm{K}}. \tag{5.3}$$

In 1972, Batuecas determined $\lim(Pv)_{0^\circ\mathrm{C}}$ for oxygen to be 22.4132 liter · atm/mol (2.27102 kJ/mol). Hence, the gas constant R was determined to have the value of 8.31441 J/mol · K with an uncertainty of 31 parts per million in the 1973 recommendations of physical constants by the international Committee on Data for Science and Technology (CODATA). However, measurements of volume in the determination of R by the method of limiting density are beset with the problem of adsorption of gas on the walls of the container. Furthermore, the uncertainty in the normal melting temperature of ice is greater than the uncertainty of the triple-point temperature of water. For these reasons, an improved method for determining a more precise value of the molar gas constant R will be presented in Sec. 5.7.

Finally, substituting for v its value V/n, we may write the equation of state of a gas in the limit of low pressures in the form

$$\boxed{\lim(PV) = nRT,} \tag{5.4}$$

which is the experimental equation of state for the ideal gas. Since $\lim(Pv) = A = RT$, Eq. (5.1) becomes

$$\frac{Pv}{RT} = 1 + BP + CP^2 + DP^3 + \cdots.$$

The virial coefficients play an important role, not only in practical thermodynamics, but also in theoretical physics, where they are related to molecular properties. Except at very low temperatures, the virial coefficients are quite small, as shown in Table 5.1, where the virial coefficients are given for nitrogen in the temperature range 150 to 500 K.

5.2
INTERNAL ENERGY OF A REAL GAS

Imagine a thermally insulated vessel with rigid walls, divided into two compartments by a partition. Suppose that there is a gas in one compartment and that the other contains a vacuum. If the partition is removed, the gas will undergo what is known as an adiabatic *free expansion* in which no work is done and no heat is transferred. From the first law, since both Q and W are zero, it follows that *the internal energy remains unchanged during a free expan-*

TABLE 5.1
Virial coefficients for nitrogen

T, K	B, 10^{-9} Pa^{-1}	C, 10^{18} Pa^{-2}	D, 10^{27} Pa^{-3}
150	−55.13	−2425	−9992
200	−20.97	−7.80	55,050
250	−7.79	229	14,270
300	−1.81	203	2860
350	1.18	152	−202
400	2.75	111	−932
450	3.59	81.6	−990
500	4.03	60.7	−856

sion. The question of whether or not the temperature of a gas changes during a free expansion and, if it does, of the magnitude of the temperature change has engaged the attention of scientists for about a hundred years. Starting with Joule in 1843, many attempts have been made to measure either the quantity $(\partial T/\partial V)_U$, which is called the *Joule coefficient*, or related quantities that are all a measure, in one way or another, of the effect of an adiabatic free expansion, or as it is often called, *Joule expansion.*

In order to study the free expansion of a gas and to measure $(\partial T/\partial V)_U$, Joule connected two vessels by a short tube and stopcock, which were immersed in a water bath. One vessel contained air at high pressure, and the other was evacuated. The temperature of the water was measured before and after the expansion, the idea being to measure indirectly the drop in temperature of the gas from the decrease in temperature of the water. Since the heat capacity of the vessels and the water was approximately 1000 times as large as the heat capacity of the air, Joule was unable to detect any temperature change of the water, although, in the light of our present knowledge, the air must have undergone a temperature decrease of several degrees. A direct measurement of the temperature change associated with a free expansion is so difficult that it is necessary to give up directly measuring the Joule coefficient $(\partial T/\partial V)_U$. Instead of measuring a temperature change during a free expansion for which the internal energy is constant, consider measuring a change of internal energy for constant temperature.

In general, the internal energy of any gas is a function of any two of the coordinates P, V, and T. The differential of U as a function of T and V is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

If no temperature change ($dT = 0$) takes place in a free expansion ($dU = 0$), then it follows that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0;$$

or, in other words, U does not depend on V. Considering U to be a function of T and P, we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP.$$

If no temperature change ($dT = 0$) takes place in a free expansion ($dU = 0$), then it follows that

$$\left(\frac{\partial U}{\partial P}\right)_T = 0;$$

or, in other words, U does not depend on P. Then, it is apparent that, if no temperature change takes place in a free expansion of a gas, U is independent of V and of P, and, therefore, *U is a function of T only.* Thus, to determine if the internal energy is a function of temperature, one must perform an experiment where the temperature is constant and measure whether either $(\partial U/\partial V)_T$ or $(\partial U/\partial P)_T$ is zero.

Later methods of attacking the question of the temperature dependence of the internal energy of a gas involved the measurement of the quantity $(\partial u/\partial P)_T$, where u is the molar internal energy, by having the gas undergo an isothermal expansion in which heat is transferred and work is done. The most extensive series of measurements of this kind was performed by Rossini and Frandsen in 1932 at the National Bureau of Standards. The apparatus is shown in Fig. 5-2. A container B holds n moles of gas at a pressure P and communicates with the atmosphere through a long coil wrapped around the

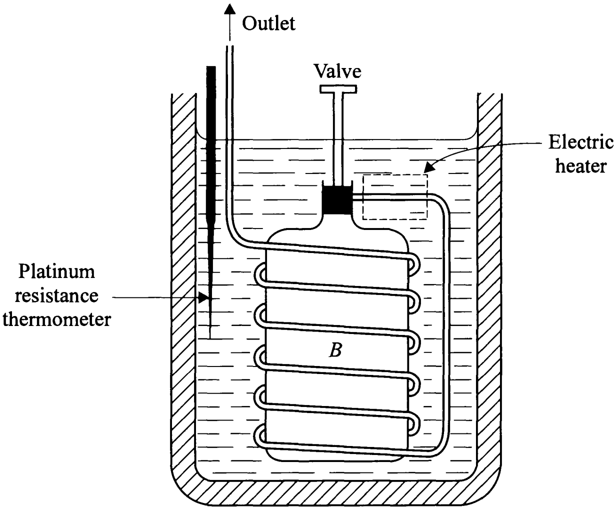

FIGURE 5-2
Apparatus for measuring $(\partial u/\partial P)_T$ of a gas. (F. D. Rossini and M. Frandsen: *Journal of Research of the National Bureau of Standards*, vol. 9, pp. 733–747, 1932.)

container. The whole apparatus is immersed in a water bath whose temperature can be maintained constant at exactly the same value as that of the surrounding atmosphere.

The experiment is performed as follows. When the valve is opened slightly, the gas flows slowly through the long coil and out into the air. At the same time, the temperature of the gas, the container, the coils, and the water is maintained constant by an electric heating coil immersed in the water. The electrical energy supplied to the water is, therefore, the heat Q absorbed by the gas during the expansion. The work done by the gas is evidently

$$W = -P_0(nv_0 - V),$$

where P_0 is atmospheric pressure, v_0 is the molar volume at atmospheric temperature and pressure, V is the volume of the container, and nv_0 is larger than V.

If $u(P, T)$ is the molar internal-energy at pressure P and temperature T and if $u(P_0, T)$ is the molar internal-energy at atmospheric pressure and the same temperature, then, from the first law, the change of molar internal-energy can be expressed in terms of the measured quantities Q and W as

$$u(P, T) - u(P_0, T) = \frac{Q + W}{n},$$

provided that corrections have been made to take account of the energy changes due to the contraction of the walls of the container. In this way, the change of molar internal-energy Δu was measured for various values of the initial pressure P at constant temperature T. The values of Δu were plotted against the corresponding pressure P, as shown in Fig. 5-3. Since $u(P_0, T)$ is constant, the slope of the resulting curve is equal to $(\partial u/\partial P)_T$ at any value of P. Within the pressure range of 1 to 40 standard atmospheres, the experimental points fall on a straight line, meaning that $(\partial u/\partial P)_T$ has the same value at every pressure; that is, $(\partial u/\partial P)_T$ *is independent of the pressure*, depending only on the temperature. Thus,

$$\left(\frac{\partial u}{\partial P}\right)_T = f(T).$$

Rossini and Frandsen's experiments with air, oxygen, and mixtures of oxygen and carbon dioxide led to the conclusion that the internal energy of a real gas is a function of both temperature and pressure. They found no pressure or temperature range in which the quantity $(\partial u/\partial P)_T$ was equal to zero. In other words, their real gases did not reach the low-pressure limit of the ideal gas.

Their experiment has somewhat the same disadvantage as Joule's original experiment, in that the heat capacity of the gas is much smaller than that of the calorimeter and water bath. To keep the temperature of the gas constant within reasonable limits, the temperature of the water must be kept constant to within less than a thousandth of a degree. In Rossini and Frandsen's measurements, the final precision was estimated to be $2\frac{1}{2}$ percent.

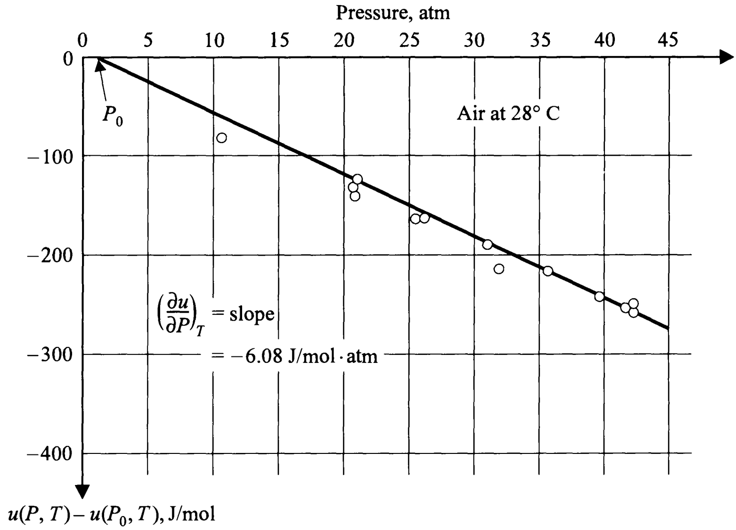

FIGURE 5-3
Dependence of change of molar internal energy of a real gas on pressure, where P_0 is atmospheric pressure.

5.3
IDEAL GAS

We have seen that, in the case of a real gas, only in the limit as the pressure approaches zero does the equation of state assume the simple form $PV = nRT$. Furthermore, the internal energy of a real gas is a function of pressure as well as temperature. It is convenient at this point to define the *ideal gas* whose properties, while not corresponding to those of any existing gas, are approximately those of a real gas at low pressures. By definition, the ideal gas satisfies the equations

$$\boxed{\begin{aligned} &PV = nRT \\ &\left(\frac{\partial U}{\partial P}\right)_T = 0 \end{aligned}} \qquad \text{(ideal gas).} \tag{5.5}$$

The requirement that $(\partial U/\partial P)_T = 0$ may be written in other ways. Thus,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T,$$

and since $(\partial P/\partial V)_T = -nRT/V^2 = -P/V$, and, therefore, is not zero, while $(\partial U/\partial P)_T$ is zero, it follows that for the ideal gas

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0} \qquad \text{(ideal gas).} \tag{5.6}$$

Finally, since both $(\partial U/\partial P)_T$ and $(\partial U/\partial V)_T$ are zero,

$$U = f(T) \text{ only.} \tag{5.7}$$

Whether a real gas may be treated as the ideal gas depends upon the error that may be tolerated in a given calculation. A real gas at pressures below about twice standard atmospheric pressure may be treated as the ideal gas without introducing an error greater than a few percent. Even in the case of a saturated vapor in equilibrium with its liquid, the ideal-gas equation of state may be used with only a small error if the vapor pressure is low.

For an infinitesimal quasi-static process of a hydrostatic system, the first law is

$$đQ = dU + P\,dV,$$

and the heat capacity at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

In the special case of the ideal gas, U is a function of T only; therefore, the partial derivative with respect to T is the same as the total derivative. Consequently,

$$C_V = \frac{dU}{dT},$$

and

$$\boxed{đQ = C_V\,dT + P\,dV.} \tag{5.8}$$

Now, all equilibrium states are represented by the ideal-gas equation,

$$PV = nRT,$$

and, for an infinitesimal quasi-static process,

$$P\,dV + V\,dP = nR\,dT.$$

Substituting the above in Eq. (5.8), we get

$$đQ = (C_V + nR)dT - V\,dP,$$

and dividing by dT yields

$$\frac{đQ}{dT} = C_V + nR - V\frac{dP}{dT}.$$

At constant pressure, the left-hand member becomes C_P and $dP = 0$; therefore,

$$\boxed{C_P = C_V + nR} \qquad \text{(ideal gas).} \tag{5.9}$$

We have the result, therefore, that the heat capacity of an ideal gas at constant pressure is always larger than the heat capacity at constant volume, the difference remaining constant and equal to nR. The reason that C_P is always larger than C_V is the following: As heat is supplied to a system at constant pressure, the gas expands and works against the external pressure, which, of course, is equal to the pressure of the gas in a quasi-static process. Thus, C_P includes work of expansion, which is not found in the constant volume ($\int P\,dV = 0$) heat capacity C_V.

Since U is a function of T only for an ideal gas, it follows that

$$C_V = \frac{dU}{dT} = \text{a function of } T \text{ alone,}$$

and so

$$C_P = C_V + nR = \text{a function of } T \text{ alone.}$$

One more useful equation can be obtained. Since

$$đQ = (C_V + nR)dT - V\,dP,$$

we find

$$\boxed{đQ = C_P\,dT - V\,dP.} \tag{5.10}$$

5.4
EXPERIMENTAL DETERMINATION OF HEAT CAPACITIES

The heat capacities of real gases are measured by the electrical method. To measure C_V, the gas is contained in a thin-walled steel flask with a heating wire wound around it. By maintaining an electric current in the wire, an equivalent amount of heat is supplied to the gas, and the heat capacity at constant volume is obtained by measuring the temperature rise of the gas. The same method is used to measure C_P except that, instead of confining the gas to a constant volume, the gas is allowed to flow at constant pressure through a calorimeter, where it receives electrically a known equivalent heat per unit of time. From the initial (inlet) and final (outlet) temperatures, the rate of supply of heat, and the rate of flow of gas, the value of C_P is calculated.

The results of such measurements on gases at *low pressures*, that is, ideal gases, can be stated in a simple manner in terms of *molar* heat capacities.

1. *All ideal gases:*
   (*a*) c_V is a function of T only.
   (*b*) c_P is a function of T only, and is greater than c_V.
   (*c*) $c_P - c_V$ is *not* a function of T, but equal to R.
   (*d*) the ratio $c_P/c_V = \gamma$ is a function of T only, and is greater than 1.
2. *Monatomic gases*, such as He, Ne, and A, and most metallic vapors, such as the vapors of Na, Cd, and Hg:

  - (*a*) c_V is constant over a wide temperature range and is very nearly equal to $\frac{3}{2}R$.
  - (*b*) c_P is constant over a wide temperature range and is very nearly equal to $\frac{5}{2}R$.
  - (*c*) the ratio $c_P/c_V = \gamma$ is constant over a wide temperature range and is very nearly equal to $\frac{5}{3}$.

3. *So-called permanent diatomic gases*, namely, air, H_2, D_2, O_2, N_2, NO, and CO:
   - (*a*) c_V is constant at ordinary temperatures, being equal to about $\frac{5}{2}R$, and increases as the temperature is raised.
   - (*b*) c_P is constant at ordinary temperatures, being equal to about $\frac{7}{2}R$, and increases as the temperature is raised.
   - (*c*) the ratio $c_P/c_V = \gamma$ is constant at ordinary temperatures, being equal to about $\frac{7}{5}$, and decreases as the temperature is raised.
4. *Polyatomic gases and gases that are chemically active*, such as CO_2, NH_3, CH_4, Cl_2, and Br_2:

   c_P, c_V, and c_P/c_V vary with the temperature, the variation being different for each gas.

These experimental results indicate that the molar gas constant $R = 8.315\,\mathrm{J/mol\cdot K}$ is a natural unit with which to express the molar heat capacity of a gas. It is a very interesting consequence of theory that the universal gas constant is also the natural unit for solids. In the remainder of this book, we shall specify not the molar heat capacities themselves but the ratios c_V/R and c_P/R.

The behavior of hydrogen gas (H_2) is quite exceptional, as shown in Fig. 5-4. At very low temperatures, c_P/R drops to a value of $\frac{5}{2}$, appropriate to a *monatomic* gas, even though hydrogen is a diatomic gas. At room temperature, c_P/R for hydrogen has its expected value of $\frac{7}{2}$. For all other diatomic gases, c_P/R may always be written

$$\frac{c_P}{R} = \frac{7}{2} + f(T),$$

where $f(T)$ is often one or more functions of the type

$$\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{(e^{b/T} - 1)^2}.$$

Exact equations of the above type are difficult to handle and are not suitable for the practical calculations of the laboratory scientist; consequently, approximate empirical equations are used. Empirical equations for c_P/R of some of the most important gases, compiled by H. M. Spencer, are given in Table 5.2, within the temperature range 300 to 1500 K.

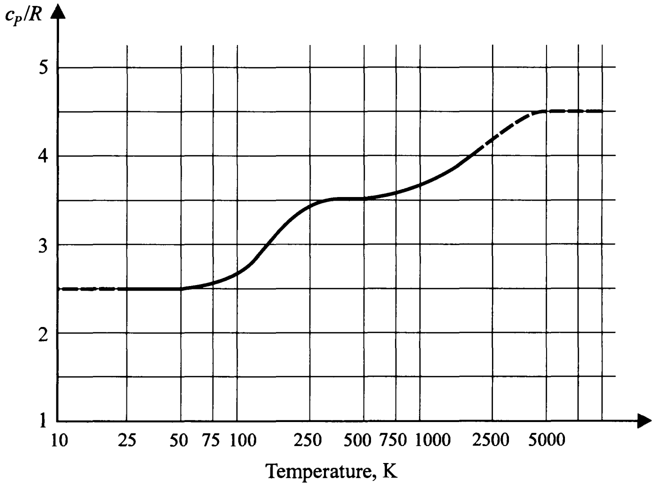

FIGURE 5-4
Experimental values of c_P/R for hydrogen as a function of temperature, plotted on a logarithmic scale.

TABLE 5.2
c_P/R of important gases
$c_P/R = a + bT + cT^2$ (from 300 to 1500 K)

Gas	a	b, $10^{-3}\,\mathrm{K}^{-1}$	c, $10^{-6}\,\mathrm{K}^{-2}$
H_2	3.495	−0.101	0.243
O_2	3.068	1.638	−0.512
Cl_2	3.813	1.220	−0.486
Br_2	4.240	0.490	−0.179
N_2	3.247	0.712	−0.041
CO	3.192	0.924	−0.141
HCl	3.389	0.218	0.186
HBr	3.311	0.481	0.079
CO_2	3.206	5.082	−1.714
H_2O	3.634	1.195	0.135
NH_3	3.116	3.970	−0.366
H_2S	3.214	2.871	−0.608
CH_4	1.702	9.083	−2.164

5.5
QUASI-STATIC ADIABATIC PROCESS

When an ideal gas undergoes a quasi-static adiabatic process, the pressure, volume, and temperature change in a manner that is described by a relation between P and V, T and V, or P and T. In order to derive the relation between P and V, we start with Eqs. (5.8) and (5.10). Thus,

$$đQ = C_V\,dT + P\,dV,$$

and

$$đQ = C_P\,dT - V\,dP.$$

In an adiabatic process, $đQ = 0$, so

$$V\,dP = C_P\,dT,$$

and

$$P\,dV = -C_V\,dT.$$

Dividing the first equation by the second, we obtain

$$\frac{dP}{P} = -\frac{C_P}{C_V}\frac{dV}{V},$$

and denoting the ratio of the heat capacities by the symbol γ, we have

$$\frac{dP}{P} = -\gamma\frac{dV}{V}.$$

This equation cannot be integrated until we know the structure of the gas, which determines γ. We have seen that for monatomic gases, γ is constant. For diatomic and polyatomic gases, γ varies with the temperature; a very large change of temperature produces an appreciable change in γ. For example, in the case of the carbon monoxide, a temperature rise from 300 to 3000 K produces a decrease in γ from 1.40 to 1.29. Most adiabatic processes that we encounter do not involve such a large temperature change. Therefore, in an adiabatic process that involves only a moderate temperature change, we are entitled to neglect the small accompanying change in γ. Regarding γ, therefore, as constant, and integrating, we obtain

$$\ln P = -\gamma \ln V + \ln \text{const.},$$

or

$$\boxed{PV^{\gamma} = \text{const.}} \tag{5.11}$$

This equation of state holds at all equilibrium states through which the ideal gas passes during a *quasi-static* adiabatic process. It is important to understand that a free expansion is an adiabatic process but is not quasi-static, because the gas rushing into the vacuum passes through nonequilibrium states before finally achieving equilibrium. Therefore, Eq. (5.11) cannot be applied to the states traversed by the ideal gas during a free expansion or any adiabatic process that is not quasi-static.

A family of curves representing quasi-static adiabatic processes may be plotted on a *PV* diagram by assigning different values to the constant in Eq. (5.11). The slope of any adiabatic curve is

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma\,\text{const.}\ V^{-\gamma-1}$$

or

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma\frac{P}{V}, \tag{5.12}$$

where the subscript S is used to denote a reversible adiabatic process.

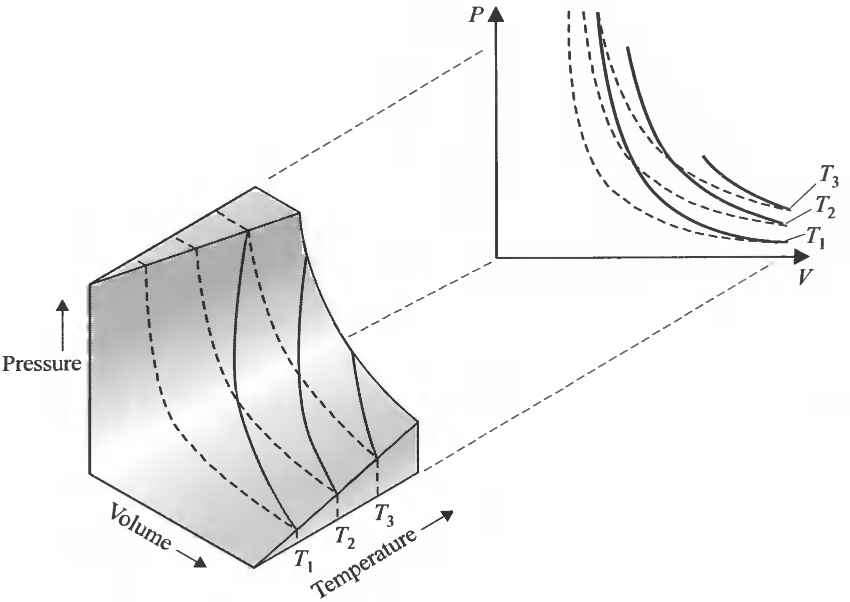

FIGURE 5-5
The *PVT* surface for the ideal gas and its projection onto a *PV* diagram. (Isotherms are shown as dashed curves, and adiabatics as full curves.)

Quasi-static isothermal processes are represented by a family of equilateral hyperbolas obtained by assigning different values to T in the equation $PV = nRT$. Since

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}, \tag{5.13}$$

it follows that an adiabatic curve has a steeper negative slope than does an isothermal curve at the same point, since $\gamma > 1$.

The isothermal curves and adiabatic curves of the ideal gas may be shown in a revealing way on a *PVT* surface. If P, V, and T are plotted along rectangular axes, the resulting surface is shown in Fig. 5-5, where it may be seen that the adiabatic curves cut across the isotherms.

5.6
RÜCHHARDT'S METHOD OF MEASURING γ

An ingenious method of measuring γ, developed by Rüchhardt in 1929, makes use of elementary mechanics, rather than thermodynamics. The gas is contained in a large jar of volume V. Fitted to the jar (see Fig. 5-6) is a glass tube with an accurate bore of cross-sectional area A, into which a metal ball of mass m fits snugly like a piston. Since the gas is slightly compressed by the

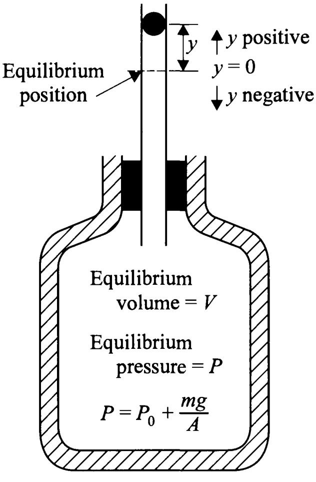

FIGURE 5-6
Mechanical apparatus for measuring the ratio of heat capacities γ. (E. Rüchhardt: *Physikalische Zeitschrift*, vol. 30, pp. 58–59, 1929.)

steel ball in its equilibrium position, its pressure P is slightly larger than atmospheric pressure P_0. Thus, neglecting friction,

$$P = P_0 + \frac{mg}{A}.$$

If the ball is given a slight downward displacement and then let go, it will oscillate with a period τ. Friction will cause the ball to come to rest eventually. Let the displacement of the ball from its equilibrium position at any moment be denoted by y, where y is positive when the ball is above the equilibrium position and negative below. A small positive displacement causes an increase in volume which is very small compared with the equilibrium volume V and which, therefore, can be denoted by dV, where

$$dV = yA.$$

Similarly, a small positive displacement causes a decrease in pressure which is very small compared with the equilibrium pressure P and which, therefore, can be denoted by dP, where dP is a negative quantity. The resultant force F acting on the ball is equal to $A\,dP$ if we neglect friction, or

$$dP = \frac{F}{A}.$$

Notice that, when y is positive, dP is negative and, therefore, F is negative; that is, F is a restoring force.

Now, as the ball oscillates fairly rapidly, the variations of P and V are adiabatic, because there is not enough time for appreciable heat transfer. Since the variations are also quite small, the states through which the gas passes can be considered to be approximately states of equilibrium. Therefore, we may assume that the changes of P and V represent an approximately quasi-static adiabatic process, and we may write

$$PV^{\gamma} = \text{const.},$$

and
$$\gamma P V^{\gamma-1}\, dV + V^{\gamma}\, dP = 0.$$

Substituting for dV and dP, we get

$$F = -\frac{\gamma P A^2}{V} y.$$

This equation expresses the fact that the restoring force is directly proportional to the displacement and is in the opposite direction, which is Hooke's law. This is precisely the condition for *simple harmonic motion*, for which the period τ is

$$\tau = 2\pi \sqrt{\frac{m}{-F/y}}.$$

Consequently,
$$\tau = 2\pi \sqrt{\frac{mV}{\gamma P A^2}},$$

and, as a result,

$$\gamma = \frac{4\pi^2 m V}{A^2 P \tau^2}. \tag{5.14}$$

The mass of the ball, the volume, the cross-sectional area of the tube, and the pressure are all known beforehand, and only the period has to be measured to obtain γ. The values obtained by Rüchhardt's mechanical measurements for air and for CO_2 were in good agreement with those obtained from calorimetric measurements of heat capacities.

Rüchhardt's method involves errors due to three simplifying assumptions: (1) that the gas is ideal; (2) that there is no friction; and (3) that volume changes are strictly adiabatic. It is estimated that the second assumption is responsible for the largest error, amounting to about 3 percent.

A modification of Rüchhardt's experiment in which accurate account is taken of the real equation of state of the gas, the friction present, and the departure from strict adiabatic conditions, was achieved by Clark and Katz in 1940. The method was adapted for an undergraduate teaching laboratory by D. G. Smith in 1979. A steel piston at the center of a cylindrical tube divides the gas into two equal parts, as shown in Fig. 5-7. It is set in vibration at any desired frequency by external coils in which an alternating current of suitable frequency is maintained. The cylinder is kept in a horizontal position, and friction between the piston and the cylinder is reduced by balancing the weight of the piston by the attraction of an electromagnet.

The amplitude of vibration of the piston is measured, using a microscope equipped with a micrometer eyepiece, at a number of values of the frequency of the impressed alternating current, and the resonance curve is plotted. From the resonance frequency and very elaborate calculations not involving the assumptions made by Rüchhardt, the value of γ is calculated. Since friction

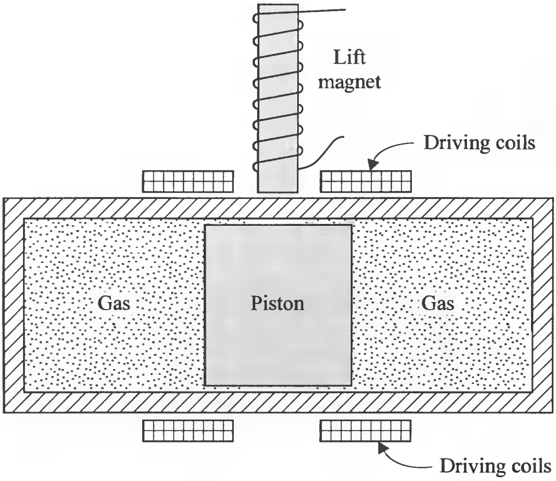

FIGURE 5-7
Resonance method of measuring the ratio of heat capacities γ of a real gas as a function of pressure. (A. L. Clark and L. Katz: *Canadian Journal of Research*, ser. A, vol. 21, pp. 1–17, 1943.)

TABLE 5.3
Pressure variation of γ ($\gamma = a + bP + cP^2$)

Gas	Temp., K	a	b, 10^{-9} Pa^{-1}	c, 10^{-12} Pa^{-2}	γ extrapolated to zero pressure (ideal gas)
He	296.25	1.6669	−1.97	0	1.667
Ar	297.35	1.6667	34.8	0	1.667
H_2	296.55	1.4045	2.47	0	1.405
N_2	296.15	1.4006	21.8	0	1.401
CO_2	303.05	1.2857	62.1	0	1.286
N_2O	298.45	1.2744	22.2	0.0948	1.274
CH_4	298.25	1.3029	−10.4	0.0472	1.303

was reduced to a great extent by the lift magnet, the corrections amounted to only about 1 percent. The authors measured γ at various pressures from 1 to 25 standard atmospheric pressures and expressed the results in the form of empirical equations, as shown in Table 5.3.

5.7
VELOCITY OF A LONGITUDINAL WAVE

Let us consider a gas enclosed in a cylinder and held in place by a piston exerting pressure P, as shown in the upper part of Fig. 5-8. If a compression is produced by moving the piston to the right at constant velocity w_0, the wave

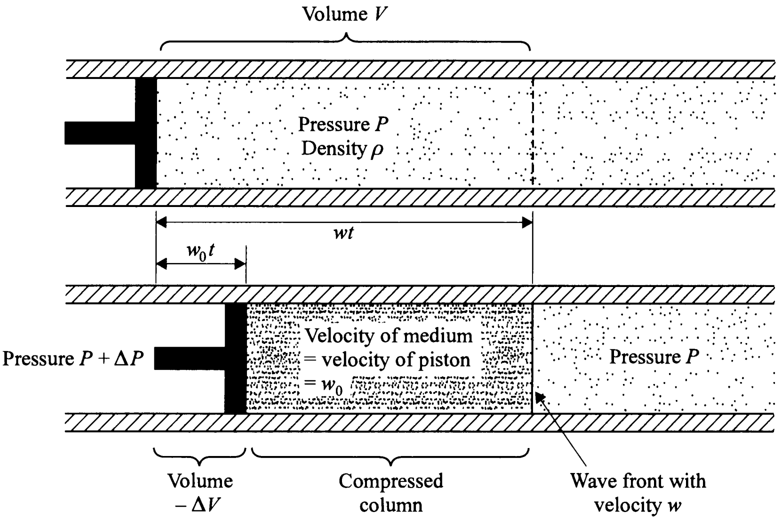

FIGURE 5-8
Propagation of a compression with constant velocity w through a gas caused by the motion of a piston with constant velocity w_0. Upper diagram at the start; lower diagram after time t.

front of the pressure pulse will travel with a different constant velocity w, depending on properties of the gas that we shall now proceed to determine. The "free body" for Newton's second law is volume V of the gas whose initial uncompressed length is wt and whose uncompressed volume $V = Awt$, where A is the cross-sectional area of the cylinder. If ρ is the density of the normal or uncompressed gas, the mass of the free body is ρAwt.

Let us suppose that the piston shown in the lower part of Fig. 5-8 exerts a force $A(P + \Delta P)$ as the piston moves to the right with a constant velocity w_0. The compression moves with constant velocity w, so that in time t the compression has traveled a distance wt while the piston has traveled a distance w_0t. At time t,

$$\left.\begin{array}{r}\text{Rate of increase of mass}\\ \text{of the compressed column}\end{array}\right\} = \frac{\rho Awt}{t} = \rho Aw.$$

The entire compressed column has a velocity w_0 equal to that of the piston. Therefore,

$$\left.\begin{array}{c}\text{Rate of increase of momentum}\\ \text{of the compressed column}\end{array}\right\} = \rho Aww_0.$$

The free body is acted on by a force $A(P + \Delta P)$ to the right and a force AP to the left. Therefore,

$$\left.\begin{array}{c}\text{Unbalanced force on the}\\ \text{compressed column}\end{array}\right\} = A\,\Delta P.$$

From Newton's second law, the unbalanced force is equal to the rate of change of momentum,

$$A\,\Delta P = \rho A w w_0,$$

or

$$\Delta P = \rho w^2 \frac{w_0}{w}.$$

The "uncompressed free body" of volume $V = Awt$ has undergone a compression $(-\Delta V) = Aw_0 t$. That is,

$$-\frac{\Delta V}{V} = \frac{Aw_0 t}{Awt} = \frac{w_0}{w}.$$

Therefore,

$$\Delta P = \rho w^2 \left(-\frac{\Delta V}{V}\right),$$

which may be written

$$w^2 = \frac{-1}{\dfrac{\rho}{V}\left(\dfrac{\Delta V}{\Delta P}\right)}. \tag{5.15}$$

This formula was first obtained by Newton, who regarded the quantity $(1/V)(\Delta V/\Delta P)$ as the isothermal compressibility. It was shown later by Laplace that the expression is really the adiabatic compressibility. To see why this is so, let us consider a column of gas of cross section A, bounded by two planes, one at the center of a compression and the other at the center of a rarefaction, a distance $\lambda/2$ apart, where λ is the wavelength. Let us suppose that the temperature at the center of the compression exceeds the temperature at the center of the rarefaction by an amount ΔT. Then, the heat conducted a distance $\lambda/2$ in the time $\lambda/2w$ (time for the wave to travel the distance $\lambda/2$) is given by

$$\left.\begin{array}{c}\text{Heat conducted in the time for the}\\ \text{wave to travel a distance } \lambda/2\end{array}\right\} = KA\frac{\Delta T}{\lambda/2}\frac{\lambda}{2w} = KA\frac{\Delta T}{w},$$

where K is the thermal conductivity of the medium. The mass of material between the compression and rarefaction is $\rho A\lambda/2$, and the heat necessary to raise the temperature of this mass by the amount ΔT is

$$\left.\begin{array}{c}\text{Heat necessary to raise temperature}\\ \text{of mass } \rho \mathrm{A}\lambda/2 \text{ by } \Delta T\end{array}\right\} = \rho A\frac{\lambda}{2}c_V\Delta T,$$

where c_V is the molar heat capacity at constant volume.

The propagation of the wave would be adiabatic if the conducted heat were much too small to raise the temperature of the mass $\rho A\lambda/2$ by the amount ΔT, or

$$\frac{KA\Delta T}{w} \ll \rho A \frac{\lambda}{2} c_V \Delta T \qquad \text{(adiabatic condition).}$$

This may be written

$$\frac{2K}{w\rho c_V} \ll \lambda \qquad \text{(adiabatic condition).}$$

The usual range of wavelengths of compressional waves is from a few centimeters to a few hundred centimeters. Let us compare these values with $2K/w\rho c_V$. Taking a gas like air as a typical case, we have, roughly,

$$\begin{aligned} K &= 0.02\,\text{W/m}\cdot\text{K}, \\ w &= 3 \times 10^2\,\text{m/s}, \\ \rho &= 1\,\text{kg/m}^3, \\ c_V &= 0.4\,\text{kJ/kg}\cdot\text{K}, \end{aligned}$$

and

$$\begin{aligned} \frac{2K}{w\rho c_V} &= \frac{2(0.02\,\text{W/m}\cdot\text{K})}{(3 \times 10^2\,\text{m/s})(1\,\text{kg/m}^3)(0.4\,\text{kJ/kg}\cdot\text{K})} \\ &= 330 \times 10^{-9}\,\text{m} \\ &= 330\,\text{nm} \end{aligned}$$

In the case of a metal, K would be much larger, but this would be compensated by the much larger values of w and ρ, and the quantity $2K/w\rho c_V$ would be still smaller than 330 nm. This quantity is, therefore, seen to be so much smaller than the usual value of a wavelength of a compressional wave (330 nm is the wavelength of ultraviolet light) that the adiabatic condition is well fulfilled. Therefore, we conclude that, in view of the properties of ordinary matter, *the volume changes which take place under the influence of a longitudinal wave at ordinary frequencies are adiabatic*, not isothermal.

Returning now to Eq. (5.15) for the velocity of a longitudinal wave and identifying $(-1/V)(\Delta V/\Delta P)$ as the *reversible adiabatic* compressibility κ_S,† we have, finally,

$$w^2 = \frac{1}{\rho \kappa_S}. \tag{5.16}$$

The adiabatic compressibility can be calculated for the ideal gas using Eq. (5.12); thus,

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{\gamma P}.$$

Since the density is

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† The compressibility introduced in Eq. (2.4) is the *isothermal* compressibility.

$$\rho = \frac{M}{v},$$

where M is the molar mass and the v is the molar volume, Eq. (5.16) becomes

$$w^2 = \frac{\gamma P v}{M},$$

or

$$w^2 = \frac{\gamma R T}{M}. \tag{5.17}$$

Equation (5.17) allows us to calculate γ from experimental measurements of w and T. For example, the speed of sound in air at 0°C is about 331 m/s. Therefore, using the values

$$\begin{aligned} w &= 331\,\mathrm{m/s} \\ T &= 273\,\mathrm{K}, \\ R &= 8.31\,\mathrm{J/mol\cdot K}, \\ M &= 0.029\,\mathrm{kg/mol}, \end{aligned}$$

we get

$$\begin{aligned} \gamma &= \frac{M w^2}{RT} \\ &= \frac{(0.029\,\mathrm{kg/mol})(331\,\mathrm{m/s})^2}{(8.31\,\mathrm{J/mol\cdot K})(273\,\mathrm{K})} \\ &= 1.40. \end{aligned}$$

The speed of a sound wave in a gas can be measured roughly by means of Kundt's tube. The gas is admitted to a horizontal cylinder tube, closed at one end and supplied at the other end with a movable piston capable of being set in vibration parallel to the axis of the tube. In the tube is a small amount of light powder. For a given frequency, a position of the piston can be found at which standing waves are set up. Under these conditions, small heaps of powder pile up at the nodes. The distance between any two adjacent nodes is one-half a wavelength, and the speed of the waves is the product of the frequency and the wavelength. Values of γ obtained by this mechanical method are in good agreement with those obtained from measurements of heat capacity.

Much greater accuracy is achieved by replacing Kundt's tube with an acoustic interferometer, at one end of which is a source of waves such as a piezoelectric crystal and at the other end a receiver. When the distance between source and receiver is kept constant and the frequency varied, the various resonances corresponding to different numbers of antinodes are noted. The frequency of the compressional waves can be varied from audible to ultrasonic frequency, but corrections for errors due to viscosity, heat conduction, and boundary layer absorption must be applied.

Equation (5.17) can be used to determine the molar gas constant R by plotting the square of the speed of sound as a function of pressure. Then, in the limit of zero pressure, which assures ideal-gas conditions, Eq. (5.17) becomes

$$R = \frac{M w_0^2}{\gamma T}, \tag{5.18}$$

where w_0^2 is the extrapolation of the square of the speed of sound to zero pressure. In 1984, A. R. Colclough and colleagues at the National Physical Laboratory in England used an acoustic interferometer operating at the only defined temperature, namely, the triple point of water at 273.16 K, to determine w_0^2 for argon, a monatomic gas for which $\gamma = \frac{5}{3}$. The Committee on Data for Science and Technology used the value of $w_0^2 = 94{,}756.75\,\mathrm{m^2/s^2}$ to calculate a new value of the molar gas constant R in its 1986 table of fundamental physical constants, namely, R equals 8.314510 J/mol · K, with an uncertainty of 8.4 parts per million. All the earlier data, including the 1973 recommendation based on Batuecas' measurement of R based on Eq. (5.3), were excluded in the determination of the latest value of the molar gas constant. Systematic errors were introduced by the presence of water adsorbed on the surface of the gas container, which could not be accounted for in an error analysis.

5.8
THE MICROSCOPIC POINT OF VIEW

We have emphasized that the point of view of classical thermodynamics is entirely macroscopic. Systems are described with the aid of their gross, or large-scale, properties. The first law of thermodynamics is a relation among the fundamental physical quantities of work, internal energy, and heat. When the first law is applied to a class of systems, a general relation is obtained which holds for *any* member of the class but which contains no quantities or properties of a particular system that would distinguish it from another. For example, Eq. (4.13),

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V,$$

is true for all hydrostatic systems, whether solid, liquid, or gas. It enables one to calculate C_V of a hydrostatic system, *provided that one knows the internal energy* as a function of T and V. The heat transferred during an isochoric process, Eq. (4.16), which is

$$Q_V = \int_{T_i}^{T_f} C_V\, dT,$$

may be calculated once the C_V of the particular system under consideration is known as a function of T. But there is nothing in classical thermodynamics that provides detailed information concerning U or C_V.

Another example of the limitation of classical thermodynamics is its inability to provide the equation of state of any desired system. To make use of any thermodynamic equation involving P, V, T, and the derivatives $(\partial P/\partial V)_T$, $(\partial V/\partial T)_P$, and $(\partial T/\partial P)_V$, one must have an equation of state. Experimental values are very often useful, but there are occasions when it is not feasible to perform the necessary experiments. If an experiment is performed on, let us say, oxygen, the numerical constants in the equation of state of oxygen only are obtained, and no clue is at hand concerning the values of the constants for any other gas.

To obtain detailed information concerning the thermodynamic coordinates and thermal properties of systems without having to resort to experimental measurements, we require calculations based on the properties and behavior of the particles of the system. There are two such microscopic theories: one is called *kinetic theory*, and the other is *statistical mechanics*. Both theories deal with particles, their internal and external motion, their collisions with one another and with any existing walls, and their forces of interaction. Making use of the laws of mechanics and statistics, kinetic theory concerns itself with the average motion of atoms and their collisions with walls and other objects in order to calculate the equation of state for the ideal gas. Statistical mechanics avoids the mechanical aspects of particles and deals with the energy aspects of aggregates or ensembles of particles. It relies heavily on statistics and quantum mechanics. Only equilibrium states can be handled — but in a uniform, straightforward manner, so that once the energy levels of the atom or of systems of atoms are understood, a program of calculations yields the equation of state, the energy, and other thermodynamic functions as well.

In this chapter, we shall limit ourselves to a small part of the kinetic theory of the ideal gas. Statistical mechanics will be presented in Chap. 12.

5.9
KINETIC THEORY OF THE IDEAL GAS

The kinetic theory of gases was the result of the early nineteenth century work of Avogadro and Loschmidt, who calculated the number of atoms or molecules in a molar volume of a gas. In unpublished work, Waterston recognized that temperature is a function of the motion of the particles of a gas, but Krönig is commonly recognized as the originator of the kinetic theory of gases in 1856. In order to formulate a microscopic theory of gases, which will be limited to *monatomic* gases, several simplifying assumptions about the behavior of atoms of the ideal gas are made:

1. Any small sample of gas consists of an enormous number of particles N. For any one chemical species, all atoms are identical and inert. If m is the mass of each atom, then the total mass is mN. If M denotes the molar mass

in kilograms per mole (formerly called the *atomic* or *molecular weight*), then the number of moles n is given by

$$n = \frac{mN}{M}.$$

The number of particles per mole of gas is called *Avogadro's number* N_A, where

$$N_A = \frac{N}{n} = \frac{M}{m} = 6.0221 \times 10^{23} \, \frac{\text{particles}}{\text{mole}}.$$

Since a mole of ideal gas at the freezing point of water and at standard atmospheric pressure occupies a volume of $22.4 \times 10^3\,\text{cm}^3$, there are approximately 3×10^{19} atoms in a volume of only $1\,\text{cm}^3$, 3×10^{16} atoms per cubic millimeter, and even a volume as small as a cubic micrometer contains as many as 3×10^7 atoms.

2. The atoms of an ideal gas are supposed to resemble small hard spheres that are in perpetual random motion. Within the temperature and pressure range of an ideal gas, the average distance between neighboring atoms is large compared with the size of an atom. The diameter of an atom is of the order of 2 or 3×10^{-10} m. Under standard conditions, the average distance between atoms is about 50 times their diameter.
3. The atoms of an ideal gas are assumed to exert no forces of attraction or repulsion on other atoms except when they collide with one another and with a wall. Between collisions, they therefore move with uniform rectilinear motion.
4. The portion of a wall with which an atom collides is considered to be smooth, and the collision is assumed to be perfectly elastic. If w is the speed of an atom approaching a wall, only the perpendicular component of velocity $w_\perp$ is changed upon collision with the wall, from $w_\perp$ to $-w_\perp$, or a total change of $-2w_\perp$.
5. When there is no external field of force, the atoms are distributed uniformly throughout a container. The *number density* N/V is assumed constant, so that in any small element of volume dV there are dN atoms, where

$$dN = \frac{N}{V} dV.$$

The infinitesimal dV must satisfy the same conditions in kinetic theory as in thermodynamics, namely, that it is small compared with V but large enough to make dN a large number. If, for example, a volume of 1 cm^3 contains 10^{19} atoms, then one-millionth of a cubic centimeter would still contain 10^{13} atoms and would qualify as a differential volume element.

6. There is no preferred direction for the velocity of any atom, so that at any moment there are as many atoms moving in one direction as in another.
7. Not all atoms have the same speed. A few atoms at any moment move slowly and a few move very rapidly, so that speeds may be considered to cover the

range from zero to the speed of light. Since most atomic speeds are so far below the speed of light, no error is introduced in integrating the speed from 0 to ∞. If dN_w represents the number of atoms with speeds between w and $w + dw$, it is assumed that dN_w remains constant at equilibrium, even though the atoms are perpetually colliding and changing their speeds.

Since the velocity vectors of the atoms of gas have no preferred direction, consider an arbitrary velocity vector $\mathbf{w}$ directed from the point O in Fig. 5-9 to the elementary area dA'. It is important to know how many atoms have velocity vectors in the neighborhood of $\mathbf{w}$. The calculation of this quantity involves the concept of a *solid angle*. Taking O as the origin of polar coordinates r, θ, and ϕ, we construct a sphere of radius r. The area dA' on the surface of this sphere, formed by two circles of latitude differing by $d\theta$ and two circles of longitude differing by $d\phi$, has the magnitude

$$dA' = (r\,d\theta)(r \sin\theta\,d\phi).$$

The solid angle $d\Omega$, formed by lines radiating from O and touching the edge of dA', is by definition

$$d\Omega = \frac{dA'}{r^2} = \frac{(r\,d\theta)(r \sin\theta\,d\phi)}{r^2}.$$

or

$$d\Omega = \sin\theta\,d\theta\,d\phi. \tag{5.19}$$

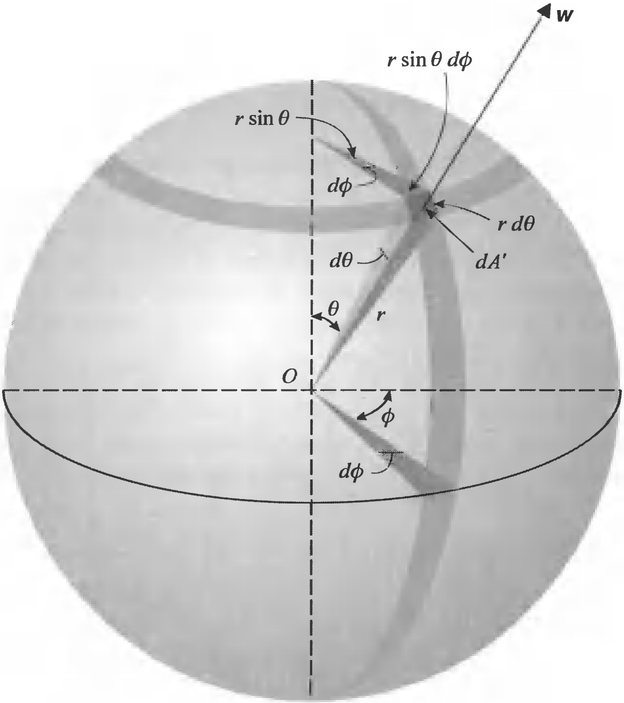

FIGURE 5-9
The solid angle $d\Omega = \sin\theta\,d\theta\,d\phi$.

Since the largest area on the surface of the sphere is that of the entire sphere $4\pi r^2$, the maximum solid angle is 4π sr (*steradians*).

The fraction of atoms with velocity vectors in the neighborhood of $\mathbf{w}$ will have speeds between w and $w+dw$ and directions within the solid angle $d\Omega$ about $\mathbf{w}$. If dN_w is the number of atoms with speeds between w and $w+dw$, then the fraction of *these* atoms whose directions lie within the solid angle $d\Omega$ is $d\Omega/4\pi$, so that the number of atoms within the speed range dw, in the θ range of $d\theta$ and the ϕ range of $d\phi$, is given by

$$d^3N_{w,\theta,\phi} = dN_w \frac{d\Omega}{4\pi}, \tag{5.20}$$

an equation expressing the fact that *atomic velocities have no preferred direction.*

Now consider this group of atoms approaching a small area dA of the wall of the containing vessel. Many of these atoms will undergo collisions along the way, but if we consider only those members of the group that lie within the cylinder (Fig. 5-10) whose side is of length $w\,dt$, where dt is such a short time interval that no collisions are made, then *all* the $d^3N_{w,\theta,\phi}$ atoms *within this cylinder* will collide with dA. The volume of the cylinder dV is

$$dV = w\,dt\,\cos\theta\,dA, \tag{5.21}$$

and if V is the total volume of the container, only the fraction dV/V of the atoms will be contained within the cylinder. Therefore the number of atoms (speed range, dw; θ range, $d\theta$; ϕ range, $d\phi$) striking dA in time dt is expressed as

$$\text{No. of } w,\theta,\phi \text{ atoms striking } dA \text{ in time } dt = d^3N_{w,\theta,\phi}\frac{dV}{V}, \tag{5.22}$$

which expresses the fact that *atoms have no preferred location.*

According to our fundamental assumptions, an atomic collision is perfectly elastic. It follows, therefore, that an atom moving with speed w in a direction making an angle θ with the normal to a wall will undergo a change only in its perpendicular component of velocity, as shown in Fig. 5-10. Furthermore, it follows that the total change in momentum per collision is

$$\text{Change of momentum per collision} = -2mv\cos\theta. \tag{5.23}$$

$$\begin{aligned}
\begin{array}{l}\text{Total change}\\ \text{of momentum}\end{array} &= \left[\begin{array}{c}\text{No. of atoms}\\ \text{of speed } w \text{ in}\\ \text{solid angle } d\Omega\end{array}\right] \left[\begin{array}{c}\text{Fraction of}\\ \text{these atoms}\\ \text{striking } dA\\ \text{in time } dt\end{array}\right] \left[\begin{array}{c}\text{Change in}\\ \text{momentum}\\ \text{per collision}\end{array}\right]\\
&= \left(dN_w\frac{d\Omega}{4\pi}\right) \qquad \left(\frac{dV}{V}\right) \qquad (-2mw\cos\theta)\\
&= \left(\frac{dN_w}{4\pi}\sin\theta\,d\theta\,d\phi\right)\left(\frac{1}{V}w\,dt\,\cos\theta\,dA\right)(-2mw\cos\theta)\\
&\qquad\quad [\text{Eq. (5.19)}] \qquad\qquad [\text{Eq. (5.21)}] \qquad\quad [\text{Eq. (5.23)}]
\end{aligned}$$

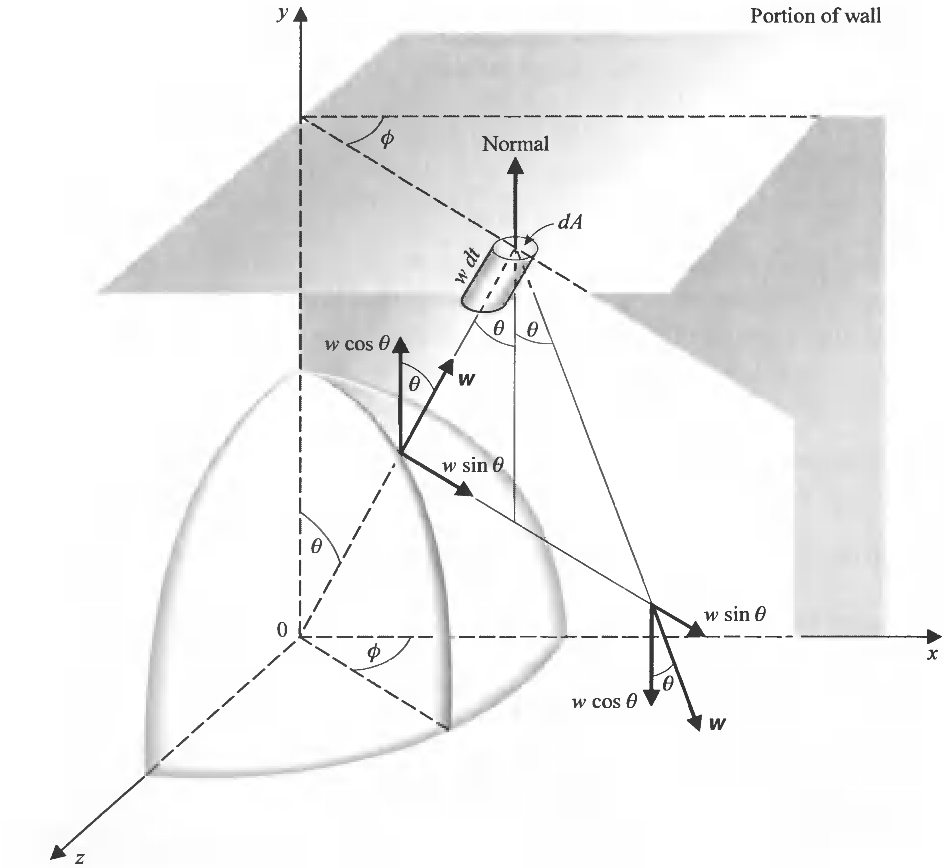

FIGURE 5-10
All the atoms in the cylinder of length $w\,dt$ strike the area dA at the angle θ to the normal. The perpendicular component of velocity $w\cos\theta$ is reversed, but the parallel component $w\sin\theta$ is unchanged.

The change in momentum per unit time and per unit area due to collisions from all directions is the pressure dP_w exerted by the wall on the dN_w gas atoms. Reversing the sign of the momentum change, we get the pressure dP_w exerted by the dN_w atoms *on the wall*:

$$dP_w = mw^2 \frac{dN_w}{V} \left(\frac{1}{2\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos^2 \theta \sin \theta \, d\theta \right). \tag{5.24}$$

The quantity in parentheses may be integrated at sight and is found to be $\frac{1}{3}$, so that the total pressure due to atoms of all speeds is given by

$$PV = \tfrac{1}{3} m \int_0^{\infty} w^2 \, dN_w.$$

The average of the square of the atomic speeds $\langle w^2 \rangle$ is defined to be

$$\langle w^2 \rangle = \frac{1}{N} \int_0^\infty w^2 \, dN_w, \tag{5.25}$$

so that we have

$$PV = \frac{Nm}{3} \langle w^2 \rangle. \tag{5.26}$$

From the macroscopic point of view, at the beginning of this chapter, we saw that the experimental equation of state of the ideal gas is given by Eq. (5.4),

$$PV = nRT.$$

From the microscopic point of view of the kinetic theory of the ideal gas, we found Eq. (5.26). A comparison of these two equations leads to

$$\frac{Nm}{3} \langle w^2 \rangle = nRT.$$

The *average kinetic energy* of the gas atoms is $\frac{1}{2} m \langle w^2 \rangle$. Solving for T, we find

$$T = \frac{2N}{3nR} \left(\tfrac{1}{2} m \langle w^2 \rangle \right). \tag{5.27}$$

Equation (5.27) provides an interpretation of temperature based on kinetic theory: *Temperature is proportional to the average kinetic energy of the atoms in the **ideal gas**.*

In kinetic theory, it is assumed that atoms behave as noninteracting particles, so the potential energy of their interaction may be neglected. The only form of energy these particles may possess is translational kinetic energy. They may not possess, for example, rotational or vibrational energies. Therefore, the internal energy U of the ideal monatomic gas is the sum of the kinetic energies of all its atoms:

$$U = \sum_j \tfrac{1}{2} m w_j^2 = N \left(\tfrac{1}{2} m \langle w^2 \rangle \right).$$

Using Eq. (5.27) to replace the kinetic energy, we obtain a calculated expression for the internal energy of a monatomic ideal gas,

$$\boxed{U = \tfrac{3}{2} nRT.} \tag{5.28}$$

The interpretation of Eq. (5.28) is that the internal energy of the ideal monatomic gas, calculated from the kinetic theory of gases, is proportional to the thermodynamic temperature T only, in agreement with the experimental result expressed in Eq. (5.7). In the kinetic theory of gases, the concept of temperature is primarily a foreign element, since, in fact, the individual atoms are characterized by their speed alone. But, it is suggestive that we should define the ideal-gas temperature T in terms of the mean kinetic energy. The importance of Eq. (5.28) is that it has been derived from the laws of physics and statistics, rather than being formulated from experimental data.

As a result of Eq. (5.28), there is an explicit calculated function for $U(T)$ for an ideal monatomic gas. One can now calculate C_V from Eq. (4.13), with the result that $C_V = \frac{3}{2}nR$, that is, C_V is independent of temperature. From Eq. (5.9), C_P is also independent of temperature and, for a monatomic gas, $C_P = \frac{5}{2}nR$.

Equation (5.28) can be rewritten using the relation of the number of particles per mole, $n = N/N_A$, where N_A is Avogadro's number; thus,

$$k = \frac{R}{N_A} = 1.3807 \times 10^{-23}\ \mathrm{J/K},$$

where k is *Boltzmann's constant*, given by

$$U = \tfrac{3}{2}\frac{N}{N_A}RT = \tfrac{3}{2}NkT.$$

So, we can rewrite Eq. (5.27) for the average kinetic energy per particle,

$$\tfrac{1}{2}m\langle w^2\rangle = \tfrac{3}{2}kT. \tag{5.29}$$

In this derivation, the average energy per atom, $\frac{1}{2}m\langle w^2\rangle$, is wholly kinetic energy of translation. This is the only kind of energy that a hard, spherical atom, uninfluenced by its neighbors or fields, can possess. Therefore, we have limited ourselves to a monatomic gas only. Diatomic and polyatomic molecules can also rotate and vibrate and may, therefore, be expected to possess energies of rotation and vibration, even though there are no forces between interacting molecules.

It is worthwhile, at this point, to compare the symbolism used in our treatment of kinetic theory with that used in thermodynamics. This is shown in Table 5.4. The equation of state for the ideal monatomic gas has a simple form, namely,

$$PV = nKT. \tag{5.30}$$

TABLE 5.4
Comparison of symbols

Thermodynamics	**Kinetic theory**
m = Mass of system	m = Mass of particle
n = Number of moles	N = Number of particles
M = Mass per mole = m/n (molar mass; molecular "weight")	N_A = Particles per mole = N/n (Avogadro's number)
R = Molar gas constant	k = Boltzmann's constant = R/N_A
V = Volume	V = Volume
ρ = Mass density = m/V	Number density = N/V

Of course, the severe assumptions of point-mass atoms and noninteracting atoms in the earliest version of the kinetic theory of gases were recognized as shortcomings in a discussion of *real* gases. So, in 1881, van der Waals proposed an equation of state that accounted for the finite volume of the atoms themselves and interactions between atoms:

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

where the constant a accounts for cohesive forces between atoms, thereby decreasing the measured pressure P, and b accounts for the volume occupied by the atoms themselves inside the system volume V.

PROBLEMS

5.1. A stream of air moves with a speed w. Assume that a mass m of air is stopped adiabatically by an obstacle.

(*a*) Prove that the rise in temperature of this mass of air is given by

$$\Delta T=\frac{w^2M}{5R},$$

where M is the molar mass of air.

(*b*) Calculate ΔT when $w = 600$ miles/h.

(*c*) Apply the equation in part (*a*) to a meteor moving through a stationary atmosphere at a speed of 20 miles/s. What would happen?

5.2. A vertical tank of length greater than 0.76 m has its top end closed by a tightly fitting frictionless piston of negligible weight. The air inside the cylinder is at an absolute pressure of 1 atm (1 atm = 101,325 Pa). The piston is depressed by pouring mercury on it slowly, so that the temperature of the air is maintained constant. What is the height of the air column when mercury starts to spill over the top of the cylinder?

5.3. Mercury is poured into the open end of a J-shaped glass tube, which is closed at the short end, trapping air in that end. How much mercury can be poured in before the mercury overflows? Assume air to act like an ideal gas. The long and short arms are 1 m and 0.5 m long, respectively, and effects due to the curvature of the bottom may be neglected. Take atmospheric pressure to be 76 cm Hg.

5.4. A cylindrical cocktail glass 15 cm high and 35 cm^2 in cross section contains water up to the 10-cm mark. A card is placed over the top and held there while the glass is inverted. When the support for the card is removed, what mass of water must leave the glass in order that the rest of the water will remain in the glass, if one neglects the weight of the card? (*Caution*: Try this over a sink.)

5.5. Two bulbs containing air, one of which has a volume three times the other, are connected by a tube of negligible volume and are initially at the same temperature. To what temperature must the air in the larger bulb be raised in order that the pressure be doubled? Neglect heat conduction through the air in the connecting tube.

5.6. Expand the following equations in the form

$$Pv = RT(1 + BP + CP^2 + \cdots),$$

and determine the second virial coefficient B in each case:

(*a*) $\left(P + \frac{a}{v^2}\right)(v - b) = RT$ (van der Waals equation of state).

(*b*) $\left(Pe^{a/RTv}\right)(v - b) = RT$ (Dieterici equation of state).

(*c*) $\left(P + \frac{a}{v^2 T}\right)(v - b) = RT$ (Berthelot equation of state).

(*d*) $\left[P + \frac{a}{(v + c)^2 T}\right](v - b) = RT$ (Clausius equation of state).

(*e*) $Pv = RT\left(1 + \frac{B'}{v} + \frac{C'}{v^2} + \cdots\right)$ (another type of virial expansion).

5.7. An ideal gas is contained in a cylinder equipped with a frictionless, nonleaking piston of area A. When the pressure is atmospheric P_0, the piston face is a distance l from the closed end. The gas is compressed by moving the piston a distance x. Calculate the spring constant $\mathcal{F}/x$ of the gas:

(*a*) Under isothermal conditions.
(*b*) Under adiabatic conditions.
(*c*) In what respect is a gas cushion superior to a steel spring?
(*d*) Using Eq. (4.14), show that $C_P - C_V = nR$ for the ideal gas.

5.8. The temperature of an ideal gas in a tube of very small, constant cross-sectional area varies linearly from one end ($x = 0$) to the other end ($x = L$) according to the equation

$$T = T_0 + \frac{T_L - T_0}{L}x.$$

If the volume of the tube is V and the pressure P is uniform throughout the tube, show that the equation of state for n moles of gas is given by

$$PV = nR\frac{T_L - T_0}{\ln(T_L/T_0)}.$$

Show that, when $T_L = T_0 = T$, the equation of state reduces to the obvious one, $PV = nRT$.

5.9. Prove that the work done *by* an ideal gas with constant heat capacities during a quasi-static adiabatic expansion is equal to:

(*a*) $W = -C_V(T_i - T_f)$.

(*b*) $W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$.

(*c*) $W = \frac{P_f V_f}{\gamma - 1}\left[1 - \left(\frac{P_i}{P_f}\right)^{(\gamma-1)/\gamma}\right].$

5.10. (*a*) Show that the heat transferred during an infinitesimal quasi-static process of an ideal gas can be written

$$đQ = \frac{C_V}{nR} V dP + \frac{C_P}{nR} P dV.$$

Applying this equation to an adiabatic process, show that $PV^\gamma = \text{const.}$

(*b*) An ideal gas of volume 0.05 ft^3 and pressure 120 lb/in^2 undergoes a quasi-static adiabatic expansion until the pressure drops to 15 lb/in^2. Assuming γ to remain constant at the value 1.4, calculate the final volume. Calculate the work.

5.11. (*a*) Derive the following formula for a quasi-static adiabatic process for the ideal gas, assuming γ to be constant:

$$TV^{\gamma-1} = \text{const.}$$

(*b*) At about 0.1 ms after detonation of a 20-kiloton nuclear fission bomb, the "fireball" consists of a sphere of gas with a radius of about 40 ft and a uniform temperature of 300,000 K. Making rough assumptions, estimate the radius at a temperature of 3000 K.

5.12. (*a*) Derive the following formula for a quasi-static adiabatic process for the ideal gas, assuming γ to be constant:

$$\frac{T}{P^{(\gamma-1)/\gamma}} = \text{const.}$$

(*b*) Helium ($\gamma = \frac{5}{3}$) at 300 K and 1 atm pressure is compressed quasi-statically and adiabatically to a pressure of 5 atm. Assuming that the helium behaves like the ideal gas, calculate the final temperature.

5.13. A horizontal, insulated cylinder contains a frictionless nonconducting piston. On each side of the piston is 54 liters of an inert monatomic ideal gas at 1 atm and 273 K. Heat is slowly supplied to the gas on the left side until the piston has compressed the gas on the right side to 7.59 atm.

(*a*) How much work is done on the gas on the right side?
(*b*) What is the final temperature of the gas on the right side?
(*c*) What is the final temperature of the gas on the left side?
(*d*) How much heat was added to the gas on the left side?

5.14. An evacuated bottle with nonconducting walls is connected through a valve to a large supply of gas, where the pressure is P_0 and the temperature is T_0. The valve is opened slightly, and helium flows into the bottle until the pressure inside the bottle is P_0. Assuming that the helium behaves like an ideal gas with constant heat capacities, show that the final temperature of the helium in the bottle is γT_0.

5.15. A thick-walled insulated chamber contains n_i moles of helium at high pressure P_i. It is connected through a valve with a large, almost empty container of helium at constant pressure P_0, very nearly atmospheric. The valve is opened slightly, and the helium flows slowly and adiabatically into the container until the pressures on the two sides of the valve are equal. Assuming the helium to behave like an ideal gas with constant heat capacities, show that:

(*a*) The final temperature of the gas in the chamber is

$$T_f = T_i\left(\frac{P_f}{P_i}\right)^{(\gamma-1)/\gamma}.$$

(*b*) The number of moles left in the chamber is

$$n_f = n_i\left(\frac{P_f}{P_i}\right)^{1/\gamma}.$$

(*c*) The final temperature of the gas in the container is

$$T_f = \frac{T_i}{\gamma}\,\frac{1 - P_f/P_i}{1 - (P_f/P_i)^{1/\gamma}}.$$

(*Hint*: See Prob. 4.9.)

5.16. (*a*) If y is the height above sea level, show that the decrease of atmospheric pressure due to a rise of dy is given by

$$\frac{dP}{P} = -\frac{Mg}{RT}dy,$$

where M is the molar mass of air, g is the acceleration of gravity, and T is the temperature at the height y.

(*b*) If the decrease of pressure in part (*a*) is due to an adiabatic expansion, show that

$$\frac{dP}{P} = \frac{\gamma}{\gamma - 1}\,\frac{dT}{T}.$$

(*c*) From parts (*a*) and (*b*), using some of the numerical data of Sec. 5.7, calculate dT/dy in kelvin per kilometer.

5.17. A steel ball of mass 10 g is placed in the tube of cross-sectional area 1 cm^2 in Rüchhardt's apparatus. The tube is connected to a jar of air having a capacity of 5 liters, the pressure of the air being 76 cm Hg.

(*a*) What is the period of vibration for the ball?

(*b*) If the ball is held initially at a position where the air pressure is exactly atmospheric and then allowed to fall, how far will the ball drop before it starts to come up?

5.18. Carbon dioxide is contained in Rüchhardt's apparatus, which has a volume of 5270 cm^3. A ball of mass 16.65 g, placed in the tube of cross-sectional area 2.01 cm^2, vibrates with a period of 0.834 s. What is γ when the barometer reads 72.3 cm?

5.19. Mercury is poured into a U-tube open at both ends until the total length of mercury is h.

(*a*) If the level of mercury on one side of the tube is depressed and the mercury is allowed to oscillate with small amplitude, show that, neglecting friction, the period τ_1 is given by

$$\tau_1 = 2\pi\sqrt{\frac{h}{2g}}.$$

(*b*) One end of the U-tube is now closed so that the length of the entrapped air column is L, and again the mercury is caused to oscillate. Assuming friction to be negligible, the air to be ideal, and the changes of volume to be adiabatic, show that the period τ_2 is now

$$\tau_2 = 2\pi\sqrt{\frac{h}{2g + \gamma h_0 g/L}},$$

where h_0 is the height of the barometric column.

(*c*) Show that

$$\gamma = \frac{2L}{h_0}\left(\frac{\tau_1^2}{\tau_2^2} - 1\right).$$

5.20. Prove that the expression for the speed of a longitudinal wave in an ideal gas may be written

$$w = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_S}.$$

5.21. What is the speed of a longitudinal wave in argon at 293 K?

5.22. A standing wave of frequency 1100 Hz in a column of methane at 293 K produces nodes that are 20 cm apart. What is γ?

5.23. The speed of a longitudinal wave in a mixture of helium and neon at 300 K was found to be 758 m/s. What is the composition of the mixture?

5.24 The molar mass of iodine is 127 g. A standing wave in iodine vapor at 400 K produces nodes that are 6.77 cm apart when the frequency is 1000 Hz. Is iodine vapor monatomic or diatomic?

5.25. An open glass tube of uniform cross-section is bent into the shape of an L. One arm is immersed in a liquid of density ρ, and the other arm of length l remains in the air in a horizontal position. The tube is rotated with constant angular speed ω about the axis of the vertical arm. Prove that the height y to which the liquid rises in the vertical arm is equal to

$$y = \frac{P_0(1 - e^{-\omega^2 L^2 M/2RT})}{g\rho},$$

where P_0 is atmospheric pressure, M is the molar mass of air, and g is the acceleration of gravity.

5.26. One mole of an ideal paramagnetic gas obeys Curie's law, with a Curie constant C_C. Assume that the internal energy U is a function of T only, so that $dU = C_{V,\mathcal{M}}\, dT$, where $C_{V,\mathcal{M}}$ is a constant heat capacity.

(*a*) Show that the equation of the family of adiabatic surfaces is

$$\frac{C_{V,\mathcal{M}}}{nR} \ln T + \ln V = \frac{\mu_0 \mathcal{M}^2}{2nRC_C} + \ln A,$$

where A is a constant for one surface.

(*b*) Sketch one of these surfaces on a $TV\mathcal{M}$ diagram.

5.27. The definition of the average speed of a particle in an ideal gas is

$$\langle w \rangle = \frac{\sum_j w_j}{N}.$$

Prove that the number of particles striking a unit area of the wall of the container in unit time is equal to

$$\frac{N\langle w \rangle}{4V}.$$

5.28. The root-mean-square speed w_{rms} is defined as $\sqrt{\langle w \rangle^2}$. Show that:

(*a*) $w_{\mathrm{rms}} = \sqrt{\dfrac{3kT}{m}}$.

(*b*) $w_{\mathrm{rms}} = \sqrt{3/\gamma}$ times the speed of sound.

CHAPTER 6

The Second Law of Thermodynamics

6.1
CONVERSION OF WORK INTO HEAT AND VICE VERSA

When two stones are rubbed together under water, the work done against the force of friction is transformed into internal energy tending to produce a rise of temperature of the stones. As soon as the temperature of the stones rises above that of the surrounding water, however, there is heating of the water. If the mass of water is large enough, then there will be no appreciable rise of temperature, and the water can be regarded as a heat reservoir, as discussed in Sec. 4.10. Since the state of the stones is the same at the end of the process as at the beginning, the net result of the process is merely the conversion of mechanical work into heat. Similarly, when an electric current is maintained in a resistor immersed either in running water or in a very large mass of water, there is also a conversion of electrical work into heat, without any change in the thermodynamic coordinates of the wire. In general, work of any kind W may be done on a system in contact with a reservoir, causing heat Q to leave the system without altering the state of the system. The system acts merely as an intermediary. It is apparent from the first law that the work is equal to the heat, $W = Q$; in other words, the transformation of work into heat is accomplished with 100 percent efficiency. Moreover, this transformation can be continued indefinitely.

To study the opposite process, namely, the conversion of heat into work, we must also have at hand a process, or series of processes, by means of which such a conversion may continue indefinitely without involving any resulting changes in the state of the system. At first thought, it might appear that the isothermal expansion of an ideal gas might be a suitable process to consider in discussing the conversion of heat into work. In this case, there is no change of internal energy, since the temperature remains constant, and, therefore,

$Q = W$, or heat has been converted completely into work. This process, however, involves a change of state of the gas. The volume increases and the pressure decreases until atmospheric pressure is reached, at which point the process stops. Therefore, the process of isothermal expansion cannot be used indefinitely.

What is needed is a *series* of processes in which a system is brought back to its initial state, that is, a *cycle*. Each of the processes that constitute a cycle involves either the performance of work or a flow of heat between the system and its surroundings, which consist of a heat reservoir at a higher temperature than the system (a "high-temperature reservoir") and a heat reservoir at a lower temperature than the system (a "low-temperature reservoir"). For one complete cycle, let

the symbol $|Q_H|$ represent the heat exchanged between the high-temperature reservoir and the system;

the symbol $|Q_L|$ represent the heat exchanged between the low-temperature reservoir and the system; and

the symbol $|W|$ represent the work exchanged between the system and the surroundings.

All three quantities $|Q_H|$, $|Q_L|$, and $|W|$, are expressed as *absolute values*, that is, *positive numbers* only. In all chapters of this book, *except this chapter and the next one*, the symbols Q and W are algebraic quantities that may take on positive or negative values. In these two chapters, we shall deal with engines and refrigerators, so we shall know at all times the direction of flow of Q and W and we are interested only in the absolute values of Q and W.

If $|Q_H|$ is larger than $|Q_L|$ and if $|W|$ is done by the system, then the machine that causes the system to undergo the cycle is called a *heat engine*. The purpose of a heat engine is to deliver work continuously to the surroundings by performing the same cycle over and over again. The net work in the cycle is the output, and the heat absorbed from the high-temperature reservoir by the system is the input. The *thermal efficiency* of the engine, symbolized by η (Greek letter eta), is defined as

$$\text{Thermal efficiency} = \frac{\text{work output}}{\text{heat input}},$$

or

$$\eta = \frac{|W|}{|Q_H|}, \tag{6.1}$$

where $|W|$ and $|Q_H|$ are meaasured in joules. Applying the first law to one complete cycle, remembering that there is no change of internal energy, we get

$$|Q_H| - |Q_L| = |W|,$$

and, therefore,

$$\eta = \frac{|Q_H| - |Q_L|}{|Q_H|},$$

or

$$\boxed{\eta = 1 - \frac{|Q_L|}{|Q_H|}.} \tag{6.2}$$

It is seen from this equation that η will be unity (efficiency 100 percent) if Q_L is zero. In other words, if an engine could be built to operate in a cycle in which there is no outflow of heat from the working substance to the low-temperature reservoir, then there would be 100 percent conversion of heat from the high-temperature reservoir into work. But, as we shall see in Sec. 6.6, there must always be an outflow of heat from an engine, so the efficiency of a heat engine is always less than 100 percent.

The transformation of heat into work is usually accomplished, in practice, by two general types of heat engine: the *internal-combustion engine*, such as the gasoline engine and the diesel engine; and the *external-combustion engine*, such as the steam engine and the Stirling engine. In both types of heat engine, a gas or a mixture of gases is contained in the space between a cylinder, closed at one end, and a piston. The gas in the confined space is the system, which undergoes a cycle, thereby causing a reciprocating piston to impart a motion of rotation to a shaft, which acts against an opposing force. It is necessary, in all engines, that the gas in the confined space, at some time in the cycle, be raised to a high temperature and a high pressure, the pressure providing the force that performs external work. In the gasoline and diesel engines, the rapid burning of the fuel and oxygen from the air takes place in the confined space called the *combustion chamber*, thereby raising the temperature and pressure of the system. In the steam and Stirling engines, the increase in temperature and pressure of the gas is accomplished by high-temperature surroundings that transfer heat to the system inside the chamber.

6.2
THE GASOLINE ENGINE

In the gasoline engine, the cycle involves the performance of six processes, four of which require vertical motion of the piston and are called *strokes*:

1. *Intake stroke.* The system is a mixture of gasoline vapor and air, which moves into the cylinder due to suction as the receding piston enlarges the accessible volume. The outside pressure is greater than the pressure in the cylinder, so the mixture is pushed into the combustion chamber.
2. *Compression stroke.* The mixture of gasoline vapor and air is compressed until its pressure and temperature rise considerably. This is accomplished by the advancing piston, which decreases the volume of the combustion chamber.
3. *Combustion.* Burning of the hot mixture occurs very rapidly after ignition by an electric spark. The resulting combustion products attain a very high pressure and temperature, but the volume remains unchanged during this

very short time interval. The piston remains essentially motionless during this very rapid process.

4. *Power stroke.* The hot combustion products expand and push the piston away, thus increasing the volume and decreasing the pressure and temperature. The system, acting through the piston, performs work on the surroundings (crankshaft, transmission, etc.).
5. *Exhaust.* The combustion products at the end of the power stroke are still at a higher pressure and temperature than the surroundings. An exhaust valve allows some gas to escape until the pressure drops almost to atmospheric pressure. The piston remains essentially motionless during this process.
6. *Exhaust stroke.* The piston pushes almost all the remaining combustion products out of the cylinder by exerting a pressure significantly larger than atmospheric pressure.

In the above processes, there are several phenomena that render an exact mathematical analysis quite difficult. Among these are friction, turbulence, loss of heat by conduction, and the chemical reaction between gasoline vapor and oxygen. A drastic but useful simplification is provided by neglecting these troublesome effects. When this is done, we have an idealized gasoline engine that performs a cycle known as an *Otto cycle.* The cycle is named after the German engineer Nikolaus Otto for his invention in 1876, but the idea for a four-stroke engine came from the Frenchman Alphonse Beau de Rochas in 1862.

The behavior of a gasoline engine can be approximated by assuming a set of ideal conditions as follows: (1) the working substance is at all times air, which behaves like an ideal gas with constant heat capacities; (2) all processes are quasi-static; (3) there is no friction or turbulence; (4) there is no loss of heat through the walls of the combustion chamber; and (5) the processes are reversible. These assumptions then lead to the idealized air-standard Otto cycle, which is composed of six simple processes of an ideal gas; these processes are plotted on a PV diagram in Fig. 6-1 and described below.

Process 5 → 1 represents a quasi-static intake stroke, isobaric at atmospheric pressure. The volume of the combustion chamber varies from zero to V_1 as the number of moles varies from zero to n, according to the equation

$$P_0 V = nRT_1,$$

where P_0 is atmospheric pressure and T_1 is the temperature of the outside air.

Process 1 → 2 represents a quasi-static, adiabatic compression stroke. There is no friction, and no loss of heat through the cylinder wall. The temperature rises from the ambient T_1 to T_2, according to the equation

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1},$$

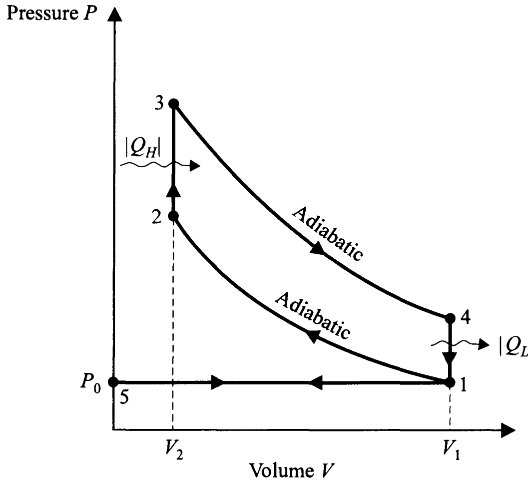

FIGURE 6-1
Idealized Otto cycle for gasoline engines shown on a PV diagram.

where V_1 is the larger volume when the piston is at the bottom of the compression stroke and V_2 the smaller volume when the piston is at the top. The ratio of heat capacities is assumed to be constant.

Process 2 → 3 represents a quasi-static isochoric increase of temperature and pressure of n moles of air, imagined to be brought about by an absorption of heat $|Q_H|$ from a *series* of external high-temperature reservoirs whose temperatures range from T_2 to T_3. If there were only one reservoir at the temperature T_3, then the flow of heat would not be quasi-static, because there would be a substantial difference in temperature between the system and the single reservoir at T_3. This process is meant to approximate the effect of the combustion in a gasoline engine when the piston is essentially motionless at the top of the stroke.

Process 3 → 4 represents a quasi-static adiabatic power stroke, involving a drop in temperature from T_3 to T_4, according to the equation

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1},$$

where V_1 is larger than V_2. This process represents the power stroke.

Process 4 → 1 represents a quasi-static isochoric drop in temperature and pressure of n moles of air, brought about by a rejection of heat $|Q_L|$ to a *series* of low-temperature external reservoirs ranging in temperature from T_4 to T_1, where T_1 is the temperature of the outside air. This process is meant to approximate the drop to atmospheric pressure upon opening the exhaust valve, but, in reality, the temperature does not actually drop to the temperature of the outside air as it leaves the exhaust port.

Process 1 → 5 represents a quasi-static exhaust stroke, isobaric at atmospheric pressure. The volume varies from V_1 to zero as the number of moles of exhaust gas varies from n to zero, the temperature remaining constant at the value T_1.

The two isobaric processes 5 → 1 and 1 → 5 obviously cancel each other and need not be considered further. Of the four remaining processes, only two involve a flow of heat. There is an absorption of $|Q_H|$ units of heat at high temperatures from 2 → 3, and a rejection of $|Q_L|$ units of heat at lower temperatures from 4 → 1, as indicated in Fig. 6-1.

Assuming C_V to be constant along the line 2 → 3, we find for heat entering the system,

$$|Q_H| = \int_{T_2}^{T_3} C_V\,dT = C_V(T_3 - T_2).$$

Similarly, for process 4 → 1, we find for heat leaving the system,

$$|Q_L| = -\int_{T_4}^{T_1} C_V\,dT = C_V(T_4 - T_1).$$

The thermal efficiency is, therefore,

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_4 - T_1}{T_3 - T_2}. \tag{6.3}$$

The two adiabatic processes during the compression stroke and power stroke are given by

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1},$$

and

$$T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1},$$

which yield, after division,

$$\frac{T_1}{T_4} = \frac{T_2}{T_3}. \tag{6.4}$$

Change signs and add unity to obtain

$$\frac{T_4 - T_1}{T_4} = \frac{T_3 - T_2}{T_3},$$

or

$$\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3}.$$

Combine this result with Eq. (6.4) and Eq. (6.3) to obtain the thermal efficiency η of an idealized gasoline engine,

$$\eta = 1 - \frac{T_1}{T_2}, \tag{6.5}$$

where T_1 and T_2 are the temperatures at the beginning and end of the compression stroke. This is the most important expression in connection with the gasoline engine. It shows that the thermal efficiency of a gasoline engine working in the Otto cycle depends on the temperature before and after compression. In a gasoline engine with temperatures $T_1 = 300\,\text{K}$ and $T_2 = 580\,\text{K}$, the efficiency is 48 percent.

This is the optimum efficiency for a gasoline engine operating in an idealized quasi-static Otto cycle for the temperatures cited. All the troublesome effects present in an actual gasoline engine, such as friction, turbulence, and heat conduction through the engine walls, are such that they make the efficiency much lower than that of the idealized Otto cycle. The actual operating thermal efficiency of a gasoline engine is in the range of 20–30 percent.

6.3
THE DIESEL ENGINE

In the diesel engine, only air is admitted on the intake stroke. The air is compressed adiabatically until the temperature is high enough to ignite oil that is sprayed into the cylinder after the compression. The rate of supply of oil is adjusted so that combustion takes place approximately isobarically, the piston moving out during combustion. The rest of the cycle, namely, power stroke, exhaust, and exhaust stroke, is exactly the same as in the gasoline engine. The usual troublesome effects take place in the diesel engine as in the gasoline engine. Eliminating these effects by making the same assumptions as before, we are left with an idealized diesel engine that performs a cycle known as the air-standard *Diesel cycle*, named after Rudolf Diesel who constructed the first successful diesel engine using liquid fuel in 1897. If the line 2 → 3 in Fig. 6-1 is imagined horizontal instead of vertical, the resulting cycle is shown in Fig. 6-2.

The line 2 → 3 in Fig. 6-2 represents the quasi-static isobaric absorption of heat from a *series* of external reservoirs ranging in temperature from T_2 to T_3. This process is meant to approximate the isobaric burning of the oil. All the other curves have the same meaning as in the case of the air-standard Otto cycle.

Assuming C_P to be constant along the line 2 → 3, we get

$$|Q_H| = \int_{T_2}^{T_3} C_P \, dT = C_P(T_3 - T_2),$$

and, as in the case of the Otto cycle,

$$|Q_L| = C_V(T_4 - T_1).$$

Therefore, the thermal efficiency of an idealized diesel engine is given by

$$\eta = 1 - \frac{1}{\gamma} \frac{(T_4 - T_1)}{(T_3 - T_2)}.$$

Notice that, unlike the thermal efficiency of the Otto cycle expressed in Eq. (6-3), the efficiency of the Diesel cycle depends upon γ, the ratio of heat capacities. This expression may be transformed into

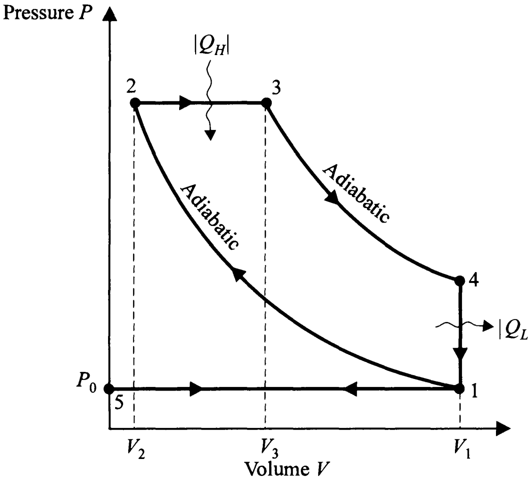

FIGURE 6-2
Idealized Diesel cycle for oil-fired engines shown on a PV diagram.

$$\eta = 1 - \frac{1}{\gamma}\frac{(r_E^\gamma - 1)}{(r_E - 1)} \cdot \frac{T_1}{T_2}, \tag{6.6}$$

where the *expansion ratio* r_E (also called the "cutoff ratio" in engineering) is given by

$$r_E = \frac{V_1}{V_3}$$

and T_1 and T_2 are the temperatures at the beginning and end of the compression stroke, respectively. Interestingly, the efficiency of the Diesel cycle expressed in Eq. (6.6) does not depend on the *compression ratio* r_C given by

$$r_C = \frac{V_1}{V_2}.$$

Taking, for example, $r_E = 5$, $\gamma = 1.4$, $T_1 = 300\,\text{K}$, and $T_2 = 990\,\text{K}$, we obtain

$$\begin{aligned}\eta &= 1 - \frac{(5^{1.4} - 1)}{(1.4)(5-1)} \cdot \frac{300\,\text{K}}{990\,\text{K}} \\ &= 54 \text{ percent.}\end{aligned}$$

The thermal efficiencies of actual diesel engines are, of course, lower, for the reasons mentioned in connection with the gasoline engine, typically being in the range of 30–35 percent.

In the diesel engine just considered, four strokes of the piston are needed for the completion of a cycle, and only one of the four is a power stroke. Since only air is compressed in the diesel engine, it is possible to eliminate the exhaust and intake strokes and thus complete the cycle in two strokes. In the two-stroke-cycle diesel engine, every other stroke is a power stroke, and thus the power is doubled. The principle is very simple: At the conclusion of the power stroke, when the cylinder is full of combustion products, the valve opens, exhaust takes place until the combustion products are at atmospheric pressure, and, then, instead of using the piston itself to exhaust the remaining gases, fresh air is blown into the cylinder, replacing the combustion products. A blower, operated by the engine itself, is used for this purpose, and thus it accomplishes in one simple operation what formerly required two separate piston strokes.

6.4

THE STEAM ENGINE

The steam engine is historically quite important, because it was the first engine driven by heat, rather than animals, water, or wind. The initial function of the steam engine was to pump water out of mines in England. The first practical and safe steam engine, a reciprocating piston–cylinder device, was invented by Thomas Newcomen in 1712 and had the greatest impact in bringing about the Industrial Revolution. James Watt greatly improved the steam engine in 1764, and William Rankine was the first to describe the thermodynamic cycle for adiabatic steam engines in 1859. Currently, steam engines are used in electric power plants, and in nuclear-powered aircraft carriers and submarines.

A schematic diagram of an elementary steam engine is shown in Fig. 6-3(*a*). The operation of such an engine can be understood by following the pressure and volume changes of a small constant mass of water as it is conveyed from the condenser, through the boiler, into the expansion chamber, and back to the condenser. The water in the condenser is at a pressure less than atmospheric and at a temperature less than the normal boiling point. By means of a pump, it is introduced into the boiler, which is at a much higher pressure and temperature. In the boiler, the water is first heated to its boiling point and then vaporized, both processes taking place approximately at constant high pressure. The steam is then raised to a temperature greater than the normal boiling point at the same pressure. It is then allowed to flow into a cylinder, where it expands approximately adiabatically against a piston or a set of turbine blades, until its pressure and temperature drop to that of the condenser. In the condenser, finally, the steam condenses into the water at the same temperature and pressure as at the beginning, and the cycle is complete.

In the actual operation of the steam engine, there are several processes that render an exact analysis difficult: turbulence caused by the pressure difference required to cause the flow of the steam from one part of the apparatus to another, friction, conduction of heat through the walls during expansion of the steam, and heat transfers due to a finite temperature difference between the furnace and the boiler.

A first approximation to the discussion of the steam engine may be made by introducing some simplifying assumptions which, although in no way realizable in practice, provide at least an upper limit to the efficiency of such a

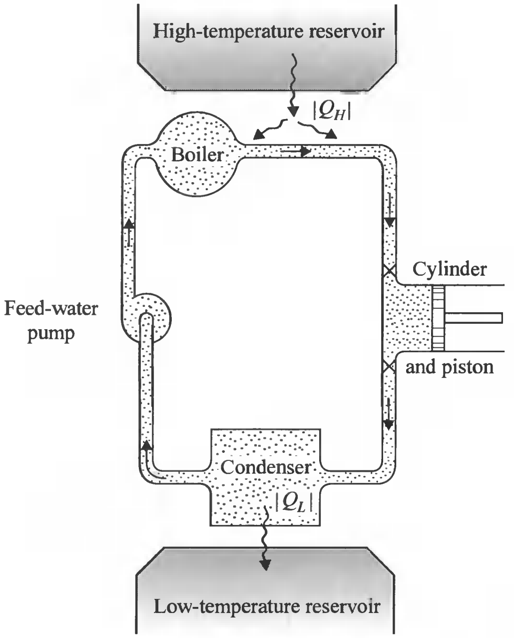

FIGURE 6-3(*a*)
Schematic diagram of a simple steam engine.

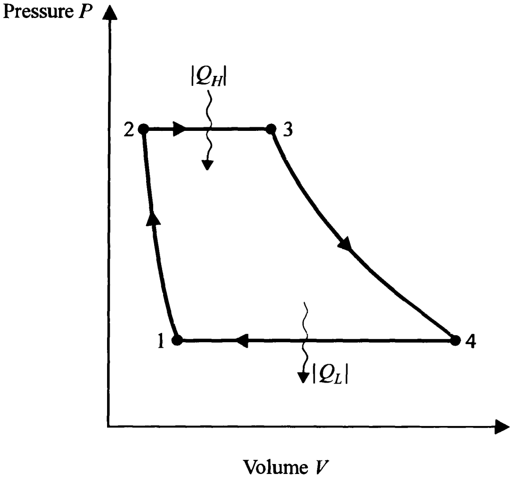

FIGURE 6-3(*b*)
PV diagram of the Rankine cycle for a steam engine. Process 1 → 2 is not an isochoric compression of steam, but an adiabatic compression of water, which yields a nearly vertical line. Process 3 → 4 is an adiabatic expansion of steam. For more detail, see Fig. 7-2.

plant and which define an idealized cycle, called the *Rankine cycle*, in terms of which the actual behavior of a steam plant may be discussed.

In the Rankine cycle, all processes are assumed to be well behaved; complications that arise from turbulence, friction, and heat losses are thus eliminated. Starting at point 1 in Fig. 6-3(*b*), we have liquid water at the temperature and pressure of the condenser. The Rankine cycle consists of the following four processes:

1 → 2 Adiabatic compression of water to the pressure of the boiler (only very small changes of temperature and volume of the liquid take place during this process).

2 → 3 Isobaric heating of water to the boiling point, vaporization of water into saturated steam, and superheating of steam to a temperature T_H higher than the boiling point.

3 → 4 Adiabatic expansion of superheated steam into wet steam.

4 → 1 Isobaric, isothermal condensation of steam into saturated water at the temperature T_L.

During the process 2 → 3, heat $|Q_H|$ enters the system from a hot reservoir; whereas during the condensation process 4 → 1, heat $|Q_L|$ is rejected by the system to the atmosphere, a reservoir at T_L. This condensation process *must* exist in order to bring the system back to its initial state 1. Since heat is always rejected during the condensation of water, $|Q_L|$ cannot be made equal to zero, and, therefore, the input $|Q_H|$ cannot be converted completely into work. So the efficiency of the idealized steam engine is always less than 100 percent. The efficiency of historic steam locomotives was quite low, which led to the development of diesel–electric locomotives. However, the actual operating thermal efficiency of a steam power plant is in the range 30–40 percent.

6.5
THE STIRLING ENGINE

In 1816, due to explosions of steam engines and loss of life, a minister of the Church of Scotland, named Robert Stirling, designed and patented a hot-air engine that could convert some of the energy liberated by a burning fuel into work. The Stirling engine remained useful and popular for many years in applications needing only a few horsepower, but, with the development of small internal-combustion engines, fell into disuse.

The steps in the operation of an idealized Stirling engine are shown schematically in Fig. 6-4(*a*). Two pistons, an expansion piston on the left and a compression piston on the right, are connected to the same shaft. As the shaft rotates, these pistons move out of phase, with the aid of suitable connecting linkages. The space between the two pistons is filled with a fixed amount of gas, usually hydrogen or helium, which is recycled from one cylinder to the other. The left-hand portion of the space is kept in contact with a high-tem-

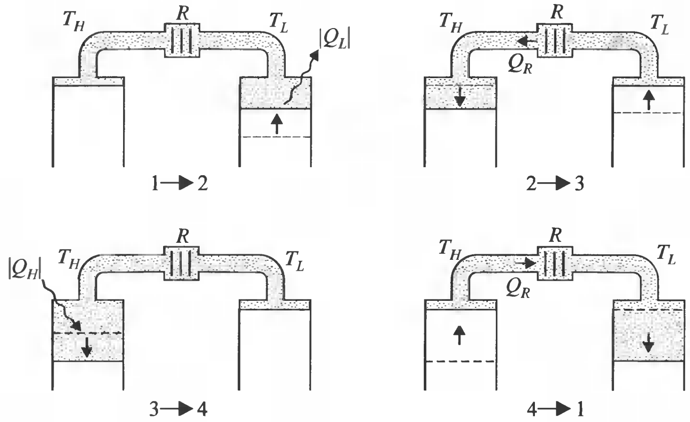

FIGURE 6-4(*a*)
Schematic diagram of the steps in the operation of an idealized Stirling engine. The numbers under each diagram refer to the processes shown in Fig. 6-4(*b*).

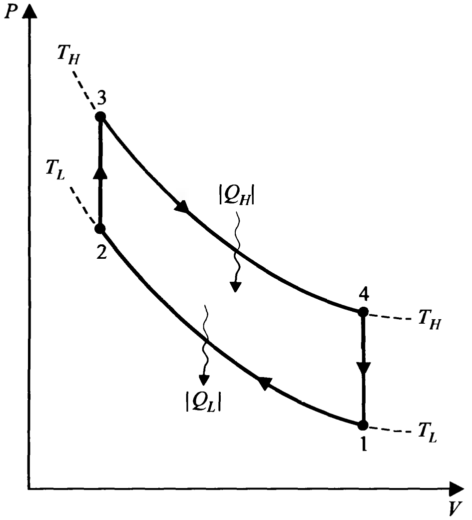

FIGURE 6-4(*b*)
PV diagram for a Stirling engine showing the heats exchanged between the system and the surroundings during the isothermal processes. During the isochoric processes, there are heats exchanged between the internal regenerator and the system, but these are not shown.

perature reservoir (burning fuel), while the right-hand portion is in contact with a low-temperature reservoir (atmosphere). Between the two cylinders is a device *R*, called a *regenerator*, consisting of a packing of fine wire screens to form a kind of metal sponge. The regenerator serves as an internal reservoir, which exchanges heat with the gas as it passes back and forth through the regenerator.

The *Stirling cycle* consists of four processes involving pressure and volume changes, plotted (as though ideal conditions existed) on the *PV* diagram of Fig. 6-4(*b*). During process 1 → 2, the left piston remains at the top of the cylinder. Meanwhile, the right piston moves halfway up its cylinder, compressing low-temperature gas that is in contact with the low-temperature reservoir and, therefore, causing heat $|Q_L|$ to leave. This is an approximately isothermal compression and is depicted as a rigorously isothermal process at the temperature T_L.

For process 2 → 3, the left piston moves down and the right piston up, so that there is no change in volume occupied by the gas. However, gas is forced through the regenerator from the low-temperature side to the high-temperature side and enters the left-hand side at the higher temperature T_H. To raise the temperature of the gas, the regenerator supplies heat $|Q_R|$ to the gas. Note that the process 2 → 3 in Fig. 6-4(*b*) is at constant volume.

In process 3 → 4, the right piston remains stationary. The left piston continues moving down while in contact with the high-temperature reservoir, which causes the gas to expand approximately isothermally. Additional heat $|Q_H|$ is absorbed from the outside at the temperature T_H.

During process 4 → 1, both pistons move in opposite directions, thereby forcing gas through the regenerator from the high-temperature to the low-temperature side and giving up approximately the same amount of heat $|Q_R|$ to the regenerator that is absorbed in the process 2 → 3, so the regenerator heats cancel each other during one cycle. This process takes place at practically constant volume.

The net result of the Stirling cycle is the absorption of heat $|Q_H|$ at the high temperature T_H, the rejection of heat $|Q_L|$ at the low temperature T_L, and the delivery of work $|W| = |Q_H| - |Q_L|$ to the surroundings, with no net heat transfer resulting from the two constant-volume processes. It must be emphasized that Fig. 6-4(*b*) is based on the assumptions that the gas is ideal, no leakage of gas takes place, no heat is lost or gained through cylinder walls, no heat is conducted from the regenerator to the surroundings, and there is no friction. Even if these idealizations could be realized, in practice, there would still be some heat $|Q_L|$ rejected at the lower temperature, and, therefore, all the input $|Q_H|$ could not be converted into work, rendering the efficiency less than 100 percent. The actual operating thermal efficiency of Stirling engines is in the range of 35–45 percent.

The Stirling engine has some unique advantages compared with other heat engines. The engine can use any heat source, from heating due to radioactivity to combustion of biomass waste products. Using open-air combustion, the engine does not produce toxic exhaust. Furthermore, it operates quietly. The Stirling engine can be used in automobiles, but internal-combustion engines are already quite good for this application. An interesting application is an implantable Stirling engine for artificial heart power, which is being developed at the Joint Center for Graduate Study, University of Washington.

A modification to the Stirling engine, called a *Ringbom* Stirling engine after its inventor Ossian Ringbom, uses only one reciprocating piston instead of two pistons. The regenerator or *displacer* oscillates between the closed end of the cylinder and the piston. As a result, the Ringbom Stirling engine is strikingly simpler than all the Stirling engines that had preceded it.

6.6
HEAT ENGINE; KELVIN-PLANCK STATEMENT OF THE SECOND LAW

In the preceding sections, four different heat engines have been briefly described. There are, of course, more types of heat engines and a tremendous number of structural details, methods of increasing thermal efficiency, mathematical analyses, etc., which constitute the subject matter of engineering thermodynamics. Thermodynamics owes its origin to the project of converting heat into work and of developing the theory of operation of machines for this purpose. Therefore, it is fitting that one of the fundamental laws of thermodynamics is based upon the operation of heat engines. Reduced to its simplest terms, the important characteristics of heat-engine cycles may be summed up as follows:

1. There is some process or series of processes during which there is an absorption of heat from an external reservoir at a higher temperature.
2. There is some process or series of processes during which heat is rejected to an external reservoir at a lower temperature.

This is represented schematically in Fig. 6-5. It is a fact of experience that no heat-engine has ever been developed that converts the heat extracted from a reservoir at a higher temperature into work *without* rejecting some heat to a reservoir at a lower temperature. This negative statement, which is the result of everyday experience, constitutes the *second law of thermodynamics* and has been formulated in several ways. The original statement of William Thomson (Kelvin) is, "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects." In the words of Max Planck, originator of quantum mechanics, "It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir." We may combine these statements into one equivalent statement, to which we shall refer hereafter as the *Kelvin-Planck statement of the second law*, thus:

> *It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.*

If the second law were not true, it would be possible to propel a ship across the ocean by extracting heat from the ocean or to run a power plant by extracting heat from the surrounding air. Notice that neither of these "impossibilities" violates the first law of thermodynamics. After all, both the ocean and the surrounding air contain an enormous store of internal energy, part of which you might hope could be extracted in the form of a flow of heat. There is nothing in the first law to preclude the possibility of converting this heat

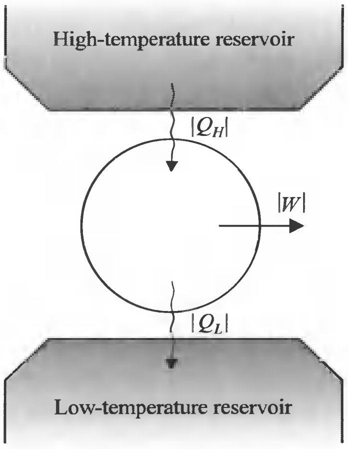

FIGURE 6-5
Schematic representation of the generalized heat engine.

completely into work. The second law, therefore, is not a deduction from the first law, but stands by itself as a separate law of nature, referring to an aspect of nature different from that described by the first law. The first law denies the possibility of creating or destroying energy; the second law denies the possibility of utilizing energy in a particular way. The continuous operation of a machine that creates its own energy and thus violates the first law is called a *perpetual motion machine of the first kind.* The operation of a machine that utilizes the internal energy of only one heat reservoir, thus violating the second law, is called a *perpetual motion machine of the second kind.*

6.7
REFRIGERATOR; CLAUSIUS' STATEMENT OF THE SECOND LAW

We have seen that a heat engine is a machine that takes a working substance through a cycle in such a sequence of processes that some heat is absorbed by the system from a high-temperature heat reservoir, a smaller amount of heat is rejected to a low-temperature heat reservoir, and a net amount of work is done by the system on the surroundings. If we imagine a cycle performed in a sequence of processes opposite to that of an engine, then some heat is absorbed by the system from a heat reservoir at a low temperature, a *larger* amount of heat is rejected to a heat reservoir at a high temperature, and a net amount of work is done *on* the system by the surroundings. A machine that performs a cycle in this direction is called a *refrigerator*, and the working substance (system) is called a *refrigerant.* Refrigerators used for climate control are the air-conditioner and the heat pump. Figure 6-6 represents a schematic diagram of a refrigerator.

Let the following notation (all positive quantities) refer to one complete cycle:

$|Q_H|$ represents the amount of heat rejected by the refrigerant to the high-temperature reservoir;

$|Q_L|$ represents the amount of heat absorbed by the refrigerant from the low-temperature reservoir; and

$|W|$ represents the net work done on the refrigerant by the surroundings.

Since the refrigerant undergoes a cycle, there is no change in internal energy, and the first law becomes

$$|Q_L| - |Q_H| = |W|,$$

or

$$|Q_H| = |Q_L| + |W|.$$

That is, the heat rejected to the high-temperature reservoir is larger than the heat extracted from the low-temperature reservoir by the amount of work done on the refrigerant.

The purpose of a refrigerator is to extract as much heat $|Q_L|$ as possible from the low-temperature reservoir with the expenditure of as little work $|W|$ as possible. Work is always necessary to transfer heat from a lower-temperature reservoir to a higher-temperature reservoir, because it is a fact of nature that heat does *not* flow spontaneously from a lower-temperature reservoir to a higher-temperature reservoir. This negative statement leads us to the *Clausius statement of the second law*:

> *It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher-temperature reservoir.*

At first sight, the Kelvin-Planck and the Clausius statements appear to be quite unconnected, but we shall see immediately that they are in all respects equivalent.

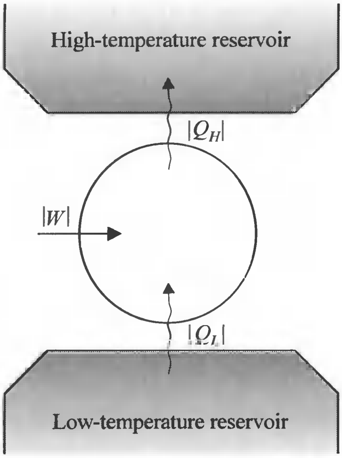

FIGURE 6-6
Schematic representation of the generalized refrigerator.

6.8

EQUIVALENCE OF THE KELVIN-PLANCK AND CLAUSIUS STATEMENTS

Let us adopt the following notation:

K = truth of the Kelvin-Planck statement;
$-K$ = falsity of the Kelvin-Planck statement;
C = truth of the Clausius statement;
$-C$ = falsity of the Clausius statement.

Two propositions or statements are said to be equivalent when the truth of one implies the truth of the second, and the truth of the second implies the truth of the first. Using the symbol $\supset$ to mean "implies" and the symbol $\equiv$ to denote "equivalence," we wish to prove that

$$K \equiv C,$$

when true statements imply each other, namely

$$K \supset C \qquad \text{and} \qquad C \supset K.$$

Alternatively, equivalence can be proven when false statements imply each other, namely,

$$-K \supset -C \qquad \text{and} - C \supset -K.$$

Thus, in order to demonstrate the equivalence of K and C, we use the latter strategy that the falsity of one statement implies the falsity of the second, and vice versa.

1. To prove that $-C \supset -K$, consider a refrigerator, shown in the left side of Fig. 6-7, that requires *no work* to transfer $|Q_L|$ units of heat from a low-temperature reservoir to a high-temperature reservoir and that, therefore, violates the Clausius statement. Suppose that a heat engine (on the right) also operates between the same two reservoirs in such a way that the same heat $|Q_L|$ is delivered to the low-temperature reservoir. The engine, of course, does not violate any law, but the refrigerator and engine *together* constitute a self-contained machine that takes heat $|Q_H| - |Q_L|$ from the high-temperature reservoir and converts *all* this heat into work without producing any change in the low-temperature reservoir. Therefore, the refrigerator and engine together constitute a violation of the Kelvin-Planck statement.
2. To prove that $-K \supset -C$, consider an engine, shown on the left side of Fig. 6-8, that rejects *no heat* to the low-temperature reservoir and that, therefore, violates the Kelvin-Planck statement. Suppose that a refrigerator (on the right) also operates between the same two reservoirs and uses up all the work performed by the engine. The refrigerator violates no law, but the engine and refrigerator *together* constitute a self-contained machine that

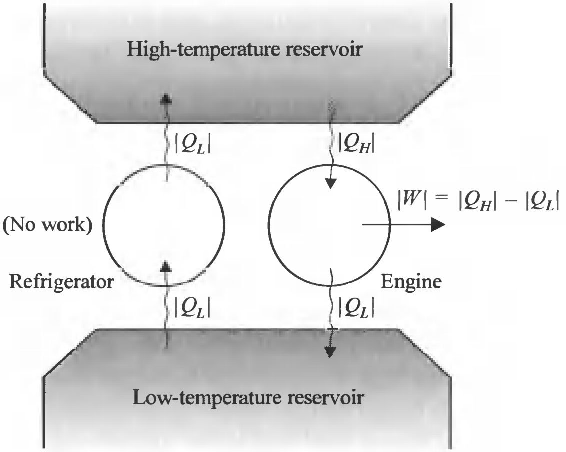

FIGURE 6-7
Proof that $-C \supset -K$. The refrigerator on the left is a violation of C; the refrigerator and the heat engine acting together violate K.

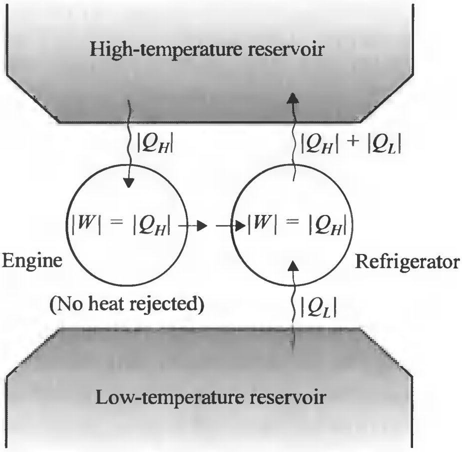

FIGURE 6-8
Proof that $-K \supset -C$. The heat engine on the left is a violation of K; the heat engine and refrigerator acting together violate C.

transfers heat $|Q_L|$ from the low-temperature reservoir to the high-temperature reservoir without producing any changes elsewhere. Therefore, the engine and refrigerator together constitute a violation of the Clausius statement.

Therefore, we arrive at the conclusion that both statements of the second law are equivalent. It is a matter of choice which one is used in a particular argument.

6.9
REVERSIBILITY AND IRREVERSIBILITY

In thermodynamics, work is a macroscopic concept. The performance of work may always be described in terms of the raising or lowering of an object or the winding or unwinding of a spring, that is, by the operation of a machine that serves to increase or decrease the potential energy of a mechanical system. Imagine, for the sake of simplicity, a suspended object coupled, by means of suitable pulleys, to a system so that any work done by or on the system can be described in terms of the raising or lowering of the object. Imagine, further, a series of reservoirs which may be put in contact with the system and in terms of which any flow of heat to or from the system may be described. We shall refer to the suspended object and the series of reservoirs as the *local surroundings* of the system. The local surroundings are, therefore, those parts of the surroundings which interact *directly* with the system. Other machines and reservoirs which are accessible and which *might* interact with the system constitute the *auxiliary surroundings* of the system or, for want of a better expression, the *rest of the universe.* The word "universe" is used here in a very restricted technical sense, with no cosmic or celestial implications. The universe merely means a finite portion of the world consisting of the system and those surroundings which may interact with the system.

Now, suppose that a process occurs in which: (1) the system proceeds from an initial state i to a final state f; (2) the suspended object is lowered to an extent that W units of work are performed on the system; and (3) a transfer of heat $|Q|$ takes place from the system to the series of reservoirs. If, at the conclusion of this process, the system may be restored to its initial state i, the object lifted to its former level, and the reservoirs caused to part with the same amount of heat $|Q|$, without producing any changes in any other mechanical device or reservoir in the universe, the original process is said to be *reversible.* In other words, *a reversible process is one that is performed in such a way that, at the conclusion of the process, both the system and the local surroundings may be restored to their initial states* **without producing any changes in the rest of the universe**. A process that does not fulfill these stringent requirements is said to be *irreversible.* The importance of the phrase in bold print is that *all* the initial states must be recoverable.

The question immediately arises as to whether natural processes, namely, the familiar processes of nature, are reversible or not. Since dissipation is present in all real processes, it follows that all natural processes are irreversible. By considering representative types of natural processes and examining the features that are responsible for irreversibility, we shall then be able to state the conditions necessary for a process to occur reversibly.

6.10
EXTERNAL MECHANICAL IRREVERSIBILITY

There is a large class of processes involving the *isothermal* transformation of work through a system (which remains unchanged) into internal energy of a reservoir. This type of process is depicted schematically in Fig. 6-9 and is illustrated by the following five examples:

1. Friction from rubbing two solids in contact with a reservoir.
2. Irregular stirring of a viscous liquid in contact with a reservoir.
3. Inelastic deformation of a solid in contact with a reservoir.
4. Transfer of charge through a resistor in contact with a reservoir.
5. Magnetic hysteresis of a material in contact with a reservoir.

In order to restore the system and its local surroundings to their initial states without producing changes elsewhere, $|Q|$ units of heat would have to be extracted from the reservoir and converted completely into work. Since this would involve a violation of the second law (Kelvin statement), all processes of the above type are irreversible.

Another set of processes involves the *adiabatic* transformation of work into internal energy of a system. This is depicted schematically in Fig. 6-10 and is illustrated by the following examples, similar to the preceding list:

1. Friction from rubbing two thermally insulated solids.
2. Irregular stirring of a viscous thermally insulated liquid.
3. Inelastic deformation of a thermally insulated solid.
4. Transfer of charge through a thermally insulated resistor.
5. Magnetic hysteresis of a thermally insulated material.

A process of this type is accompanied by a rise of temperature of the system from, say, T_i to T_f. In order to restore the system and its local surroundings to their initial states without producing changes elsewhere, the internal energy of the system would have to be decreased by extracting $U_f - U_i$ units of heat, thus lowering the temperature from T_f to T_i, and this heat would have to be completely converted into work. Since this violates the second law, all processes of the above type are irreversible.

The transformation of work into internal energy either of a system or of a reservoir is seen to take place through the agency of such phenomena as friction, viscosity, inelasticity, electric resistance, and magnetic hysteresis. These effects are known as *dissipative effects* and the work is said to be dissipated. Processes involving the dissipation of work into internal energy are said to exhibit *external mechanical irreversibility*. It is a matter of everyday experience that dissipative effects, particularly friction, are always present in machines. Friction, of course, may be reduced considerably by suitable lubrication, but experience has shown that it can never be completely eliminated. If friction could be eliminated, then a machine could run indefinitely without

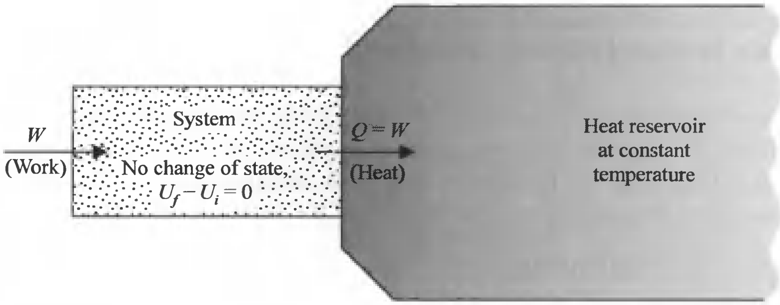

FIGURE 6-9
Isothermal transformation of work through a system (which remains unchanged) into internal energy of a reservoir.

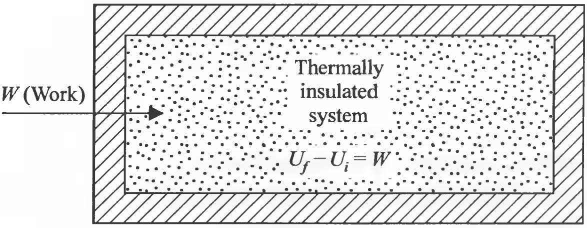

FIGURE 6-10
Adiabatic transformation of work into internal energy of a system.

violating either of the two laws of thermodynamics; that is, it would run but produce no work. The operation of a machine that has no dissipation of work and thus violates the fact that all natural processes are irreversible is called a *perpetual motion machine of the third kind.* Friction renders a process irreversible, since heat is produced by friction in whichever direction the process is traversed. For this reason, all the cycles discussed in this chapter are idealized by assuming frictionless processes.

This chapter is quite unusual in its use of negative statements to formulate the fundamental second law of thermodynamics. The Kelvin-Planck statement and Clausius statement each independently and equivalently establish the second law. Furthermore, the impossibility of creating three kinds of perpetual motion machines may be used to formulate the first and second laws of thermodynamics and the definition of reversibility. If we were to state the very broad laws of thermodynamics in a *positive* sense, then, in principle, it would require a very large number of experiments to verify the laws. On the other hand, by stating at least the second law in a negative sense, it is asserted that if a single, well-substantiated violation of the statement can be found, then the law is not valid. As a matter of fact, within their range of applicability, no violation of the laws of thermodynamics has been found.

6.11
INTERNAL MECHANICAL IRREVERSIBILITY

The following very important natural processes involve the transformation of internal energy of a system into mechanical energy and then back into internal energy again:

1. Ideal gas rushing into a vacuum (free expansion, i.e., Joule expansion).
2. Gas flowing through a porous plug (throttling process, i.e., Joule-Thomson expansion).
3. Snapping of a stretched wire after it is cut.
4. Collapse of a soap film after it is punctured.

We shall prove the irreversibility of only the first process.

During a free expansion, no interactions take place, and hence there are no local surroundings. The only effect produced is a change of state of an ideal gas from a volume V_i and temperature T to a larger volume V_f at the same temperature T. To restore the gas to its initial state, it would have to be compressed isothermally to the volume V_i. If the compression were performed quasi-statically and there were no friction between the piston and cylinder, an amount of work W would have to be done by some outside mechanical device, and an equal amount of heat would have to flow out of the gas into a reservoir at the temperature T. If the mechanical device and the reservoir are to be left unchanged, the heat would have to be extracted from the reservoir and converted completely into work. Since this last step is impossible, the process is irreversible.

In a free expansion, immediately after the valve is opened, there is a transformation of some of the internal energy into kinetic energy of "mass motion" or "streaming," and then this kinetic energy is dissipated through viscosity into internal energy again. Similarly, when a stretched wire is cut, there is first a transformation of internal energy into kinetic energy of irregular motion and of vibration, and then the dissipation of this energy through inelasticity into internal energy again. In all the processes, the first energy transformation takes place as a result of mechanical instability, and the second by virtue of some dissipative effect. A process of this sort is said to exhibit *internal mechanical irreversibility.*

6.12
EXTERNAL AND INTERNAL THERMAL IRREVERSIBILITY

Consider the following processes involving a transfer of heat between a system and a reservoir by virtue of a *finite* temperature difference:

1. Conduction or radiation of heat from a system to a cooler reservoir.

2. Conduction or radiation of heat through a system (which remains unchanged) from a hot reservoir to a cooler one.

If, at the conclusion of such a process, one attempts to restore both the system and its local surroundings to their initial states without producing changes elsewhere, heat would have to be transferred by means of a self-acting device from a cooler to a hotter body. Since this violates the second law (Clausius statement), all processes of this type are irreversible. Such processes are said to exhibit *external thermal irreversibility.*

A process involving a transfer of heat between parts of the same system, because of nonuniform temperatures, is also obviously irreversible by virtue of the Clausius statement of the second law. Such a process is said to exhibit *internal thermal irreversibility.*

6.13
CHEMICAL IRREVERSIBILITY

Some of the most interesting processes that go on in nature involve a spontaneous change of internal structure, chemical composition, density, crystal form, etc. Some important examples follow.

Formation of new chemical compounds:

1. All chemical reactions.

Mixing of two different substances:

2. Diffusion of two dissimilar inert ideal gases.
3. Mixing of alcohol and water.

Sudden change of phase:

4. Freezing of supercooled liquid.
5. Condensation of supersaturated vapor.

Transport of matter between phases in contact:

6. Solution of solid in water.
7. Osmosis.

Such processes are by far the most difficult to handle and must, as a rule, be treated by special methods. Such methods constitute what is known as chemical thermodynamics and are discussed in Chaps. 15, 16, and 17. It can be shown that the diffusion of two dissimilar inert ideal gases is equivalent to two independent free expansions. Since a free expansion is irreversible, it follows that diffusion is irreversible. At present, the statement that the other processes described above are irreversible is stated without proof. Processes that involve a spontaneous change of chemical structure, density, phase, etc., are said to exhibit *chemical irreversibility.*

6.14
CONDITIONS FOR REVERSIBILITY

Most processes that occur in nature are included among the general types of process listed in the preceding sections. Living processes, such as cell division, tissue growth, etc., are no exception. If one takes into account all the interactions that accompany living processes, such processes are irreversible. It is a direct consequence of the second law of thermodynamics that *all natural spontaneous processes are irreversible.*

A careful inspection of the various types of natural process shows that all involve one or both of the following features:

1. The conditions for mechanical, thermal, or chemical equilibrium, namely, thermodynamic equilibrium, are not satisfied.
2. Dissipative effects, such as friction, viscosity, inelasticity, electric resistance, and magnetic hysteresis, are present.

For a process to be reversible, it must *not* possess these features. If a process is performed quasi-statically, the system passes through states of thermodynamic equilibrium, which may be traversed just as well in one direction as in the opposite direction. If there are no dissipative effects, all the work done by the system during the performance of a process in one direction can be returned to the system during the reverse process. We are led, therefore, to the conclusion that a process will be reversible when: (1) it is performed quasi-statically; and (2) it is not accompanied by any dissipative effects.

Since it is impossible to satisfy these two conditions perfectly, it is obvious that a reversible process is purely an ideal abstraction, extremely useful for theoretical calculations (as we shall see) but quite devoid of reality. In this sense, the assumption of a reversible process in thermodynamics resembles the assumptions made so often in mechanics, such as those which refer to weightless strings, frictionless pulleys, and point masses.

A heat reservoir is defined as a body of very large mass capable of absorbing or rejecting an unlimited supply of heat without suffering appreciable changes in its thermodynamic coordinates. The changes that do take place are so very slow and so minute that dissipative actions never develop. *Therefore, when heat enters or leaves a reservoir, the changes that take place* **in the reservoir** *are the same as those which would take place if the same quantity of heat were transferred reversibly.*

It is possible, in the laboratory, to approximate the conditions necessary for the performance of reversible processes. For example, if a gas is confined in a cylinder equipped with a well-lubricated piston and is allowed to expand very slowly against an opposing force, provided either by an object suspended from a frictionless pulley or by an elastic spring, the gas undergoes an approximately reversible process. Similar considerations apply to a wire and to a surface.

A reversible transfer of charge from one electrode to the other electrode of an electrochemical cell (battery) may be imagined as follows. Suppose that a motor whose coils have a negligible resistance is caused to rotate until its back emf is only slightly different from the emf of the cell. Suppose further that the motor is coupled either to an object suspended from a frictionless pulley or to an elastic spring. If neither the cell itself nor the connecting wires to the motor have appreciable resistance, a reversible transfer of charge takes place.

In order to arrive at conclusions concerning the equilibrium states of thermodynamic systems, it is often necessary to invoke some sort of process in which the system passes through these states. To assume the process is quasi-static only, often is not sufficient; if dissipative effects are present, there may be heat flows or internal energy changes of neighboring systems (envelopes, containers, and surroundings) that limit the validity of the argument. In order to ensure that equilibrium states of the system *only* are considered, without having to take account of the effect of dissipated work in the system itself or in some other neighboring body, it is useful to invoke the concept of a *reversible process*, even though this assumption may at times seem a bit drastic. Notice that a quasi-static process is reversible only when dissipative effects are *not* present; otherwise, the quasi-static process with dissipative effects is irreversible. Thus, the processes in all four idealized cycles introduced in this chapter were assumed to be quasi-static without dissipation, that is, reversible.

Thermodynamics is by no means unique in introducing concepts using idealized systems. Mechanics deals with point masses and elastic collisions; electricity deals with wires having no resistance and batteries having constant voltages; quantum mechanics solves the hydrogen atom with coulombic interactions. A subject with idealized conditions is introduced for three reasons. First, the problems can be solved in simple, analytical forms. Next, the results are the optimum that can be achieved and serve as limiting cases. And, finally, the solutions to the ideal situations serve as the basis for approximation or perturbation methods in dealing with real situations as complications are introduced.

PROBLEMS

6.1. Show that the thermal efficiency of an ideal Otto cycle is given by

$$\eta = 1 - \frac{1}{\eta^{\gamma-1}},$$

where the ratio $r = V_1/V_2$ is called either the *compression ratio* or the *expansion ratio* for a gasoline engine. In practice, r cannot be made greater than about 10, because if r is larger, then the rise in temperature upon compression of the mixture of gasoline and air is great enough to cause combustion before the discharge of the spark. This is called *preignition*. Take r equal to 9 and γ equal to approximately 1.3 (because it is a mixture) and calculate the thermal efficiency.

6.2. Show that the thermal efficiency of an ideal Diesel cycle is given by

$$\eta = 1 - \frac{1}{\gamma}\frac{(1/r_E)^\gamma - (1/r_C)^\gamma}{(1/r_E) - (1/r_C)},$$

where the ratio $r_C = V_1/V_2$ is called the *compression ratio* and the ratio $r_E = V_3/V_2$ is called the *expansion ratio* for a diesel engine. The compression ratio of a diesel engine is much larger than that of a gasoline engine, because there is no preignition as only air is being compressed. Take $r_C = 20$, $r_E = 5$, and $\gamma = 1.4$ and calculate the thermal efficiency.

6.3. Figure P6-1 represents a simplified *PV* diagram of the Joule ideal-gas cycle. All processes are quasi-static, and C_P is constant. Prove that the thermal efficiency of an engine performing this cycle is

$$\eta = 1 - \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma}.$$

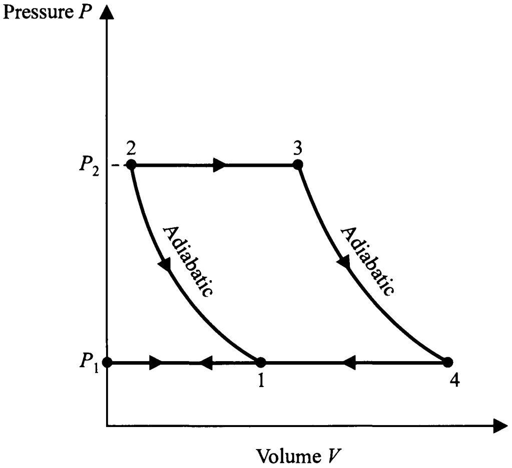

FIGURE P6-1
Joule ideal-gas cycle.

6.4. Figure P6-2 represents a simplified *PV* diagram of the Sargent ideal-gas cycle. All processes are quasi-static, and the heat capacities are constant. Prove that the thermal efficiency of an engine performing this cycle is

$$\eta = 1 - \gamma\frac{T_4 - T_1}{T_3 - T_2}.$$

6.5. Figure P6-3 represents an imaginary ideal-gas cycle. Assuming constant heat capacities, show that the thermal efficiency is

$$\eta = 1 - \gamma\frac{(V_1/V_2) - 1}{(P_3/P_2) - 1}.$$

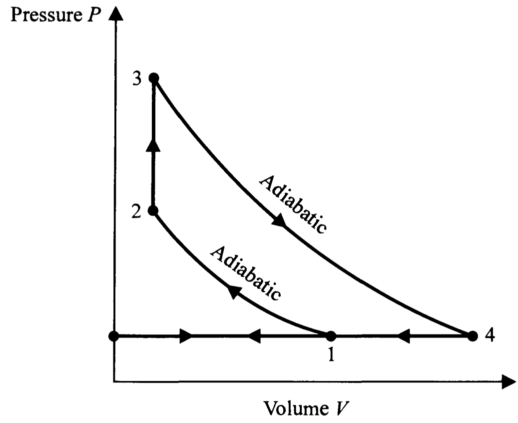

FIGURE P6-2
Sargent ideal-gas cycle.

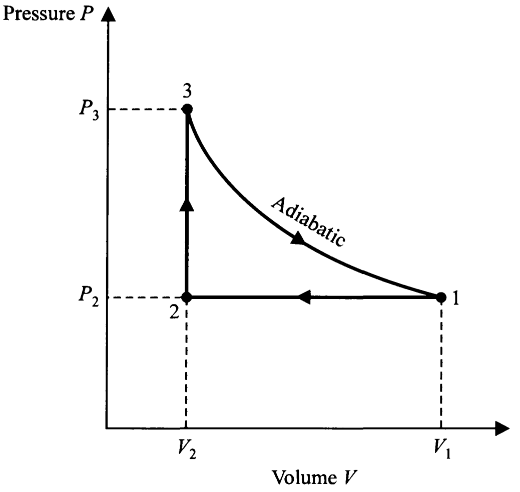

FIGURE P6-3
Imaginary ideal-gas cycle.

6.6. An imaginary ideal-gas engine operates in a cycle, which forms a rectangle with sides parallel to the axes of a PV diagram. Call P_1 and P_2 the lower and higher pressures, respectively; call V_1 and V_2 the lower and higher volumes, respectively.

(*a*) Calculate the work done in one cycle.

(*b*) Indicate which parts of the cycle involve heat flow into the gas, and calculate the amount of heat flowing into the gas in one cycle. (Assume constant heat capacities.)

(*c*) Show that the efficiency of this engine is

$$\eta = \frac{\gamma - 1}{\dfrac{\gamma P_2}{P_2 - P_1} + \dfrac{V_1}{V_2 - V_1}}.$$

6.7. A vessel contains $10^{-3}\,\text{m}^3$ of helium gas at 3 K and 10^3 Pa. Take the zero of internal energy of helium to be at this state.

(*a*) The temperature is raised at constant volume to 300 K. Assuming helium to behave like an ideal monatomic gas, how much heat is absorbed, and what is the internal energy of the helium? Can this energy be regarded as the result of heating or working?

(*b*) The helium is now expanded adiabatically to 3 K. How much work is done, and what is the new internal energy? Has heat been converted to work without compensation, thus violating the second law?

(*c*) The helium is now compressed isothermally to its original volume. What are the quantities of heat and work in this process? What is the thermal efficiency of the cycle? Plot the cycle on a PV diagram.

6.8. In the tropics, the water near the surface is warmer than the deep water. Would an engine operating between these two levels violate the second law? Why?

6.9. Would a nuclear power plant violate either the first law or the second law of thermodynamics? Explain.

6.10. A storage battery is connected to a motor, which is used to lift a weight. The battery remains at constant temperature by receiving heat from the outside air. Is this a violation of the second law? Why?

6.11. A convenient measure of the performance of a refrigerator is expressed by the *coefficient of performance* ω, which is the ratio of the heat extracted from the low-temperature resevoir to the work done on the refrigerant. Unlike the thermal efficiency η, ω may be considerably larger than unity. Derive an expression for the heat rejected to the *high-temperature* reservoir. Such a refrigerator is called a "heat pump" and can warm a house in winter by refrigerating the ground, outside air, or water supplied in the mains. Assume a value of 5 for the coefficient of performance and comment on the effectiveness of a heat pump.

6.12. There are many paramagnetic solids that have internal energies which depend only on temperature, like an ideal gas. In an isothermal decrease of the magnetic field, heat is absorbed from one reservoir and converted completely into work. Is this a violation of the second law? Explain.

6.13. Prove that it is impossible for two reversible adiabatics to intersect. (*Hint*: Assume that they do intersect and complete the cycle with an isothermal. Show that the performance of this cycle violates the second law.)

CHAPTER 7

The Carnot Cycle and the Thermodynamic Temperature Scale

7.1
CARNOT CYCLE

During a part of the cycle performed by the working substance in an engine, some heat is absorbed from a hotter reservoir; during another part of the cycle, a smaller amount of heat is rejected to a cooler reservoir. Therefore, the engine is said to operate between these two reservoirs. Since it is a fact of experience that some heat is always rejected to the cooler reservoir, the efficiency of an actual engine is never 100 percent. If we assume that we have at our disposal two reservoirs at given temperatures, it is important to answer the following questions: (1) What is the maximum thermal efficiency that can be achieved by an engine operating between these two reservoirs, inasmuch as 100 percent efficiency is not allowed by the second law? (2) What are the characteristics of such an engine? (3) Of what effect is the nature of the working substance?

The importance of these questions was recognized by Nicolas Léonard Sadi Carnot, a brilliant young French engineer who, in 1824, before the first law of thermodynamics was firmly established, described in a paper entitled "Réflexions sur la Puissance Motrice du Feu" ("Reflections on the Motive Power of Fire") an ideal engine operating in a particularly simple cycle known today as the *Carnot cycle.*

In describing and explaining the behavior of the idealized heat engine, Carnot made use of three terms: *feu*, *chaleur*, and *calorique*. By *feu*, he meant fire or flame, and, when the word is so translated, no misconceptions arise. Carnot gave, however, no definitions for *chaleur* and *calorique*, but in a footnote stated that they had the same meaning. If both of these words are translated as heat, then Carnot's reasoning is contrary to the first law of thermodynamics. There is, however, some evidence that, in spite of the unfortunate footnote, Carnot did not mean the same thing by *chaleur* and *calorique*. Carnot used *chaleur* when referring to heat in general, but when referring to the motive power of fire that is brought about when heat enters an engine at high temperature and leaves at low temperature, he used the expression *chute de calorique*, never *chute de chaleur*. It is the opinion of some scientists that Carnot had in the back of his mind the concept of entropy, for which he reserved the term *calorique*. This seems incredible, and yet it is a remarkable circumstance that, if the expression *chute de calorique* is translated as "fall of entropy," many of the objections to Carnot's work raised by Kelvin, Clapeyron, Clausius, and others are no longer valid. In spite of possible mistranslation, Kelvin recognized the importance of Carnot's ideas and put them in the form in which they appear today.

A Carnot cycle is a set of processes that can be performed by any thermodynamic system whatsoever, whether hydrostatic, chemical, electrical, magnetic, or otherwise. The system or working substance is imagined first to be in thermal equilibrium with a reservoir at the low temperature T_L. Four processes are then performed in the following order:

1. A reversible adiabatic process is performed in such a direction that the temperature rises to that of the high-temperature reservoir, T_H.
2. The working substance is maintained in contact with the reservoir at T_H, and a reversible isothermal process is performed in such a direction and to such an extent that heat $|Q_H|$ is absorbed from the reservoir.
3. A reversible adiabatic process is performed in a direction opposite to process 1 until the temperature drops to that of the low-temperature reservoir, T_L.
4. The working substance is maintained in contact with the reservoir at T_L, and a reversible isothermal process is performed in a direction opposite to process 2 until the working substance and the surroundings are in their initial states. During this process, heat $|Q_L|$ is rejected to the low-temperature reservoir.

An engine operating in a Carnot cycle is called a *Carnot engine*. A Carnot engine operates between two reservoirs in a particularly simple way. All the absorbed heat enters the system at a *constant* high temperature, namely, that of the hotter reservoir. Also, all the rejected heat leaves the system at a *constant* low temperature, that of the cooler reservoir. Notice that the exchange of heat in the Carnot cycle is unlike the situation for idealized real engines, which need a series of reservoirs to exchange heat during the constant-volume or constant-pressure processes in order to achieve reversibility. In the Carnot cycle, a *single* reservoir exchanges heat during a constant-temperature process. Since all four processes are reversible, *the Carnot engine is a reversible engine.*

7.2
EXAMPLES OF CARNOT CYCLES

The simplest example of a Carnot cycle is that of a gas (not necessarily an ideal gas) depicted on a PV diagram in Fig. 7-1. The dashed lines marked T_H and T_L are isothermal curves. The gas is initially in the state represented by the point 1. The four processes are then:

1. Process 1 → 2, reversible adiabatic compression until the temperature rises to T_H.
2. Process 2 → 3, reversible isothermal expansion until any desired point, such as 3, is reached.
3. Process 3 → 4, reversible adiabatic expansion until the temperature drops to T_L.
4. Process 4 → 1, reversible isothermal compression until the original state is reached.

During the isothermal expansion 2 → 3, heat $|Q_H|$ is absorbed from the hotter reservoir at T_H. During the isothermal compression 4 → 1, heat $|Q_L|$ is rejected to the cooler reservoir at T_L.

For a two-phase system, such as steam and water, the Carnot cycle has a shape quite different from a gaseous system. This is shown on a PV diagram in Fig. 7-2. The dashed line $L_A V_A$ denotes the isothermal and isobaric vaporization of the liquid at the higher temperature T_H; the (dashed) line $L_B V_B$ denotes the isothermal and isobaric condensation of the vapor at the lower temperature T_L. Any point between the dashed lines L and V represents a

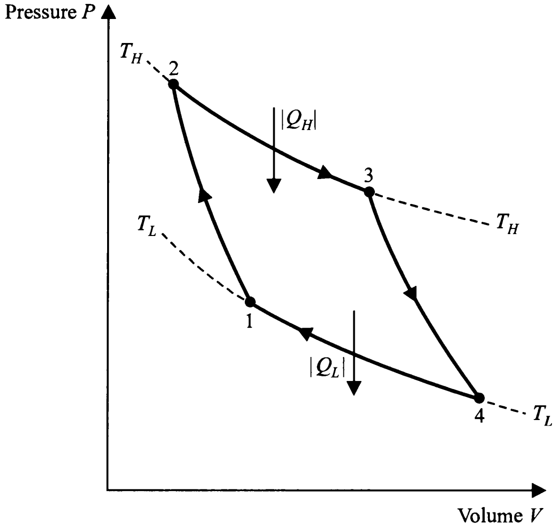

FIGURE 7-1
Carnot cycle of a real gas.

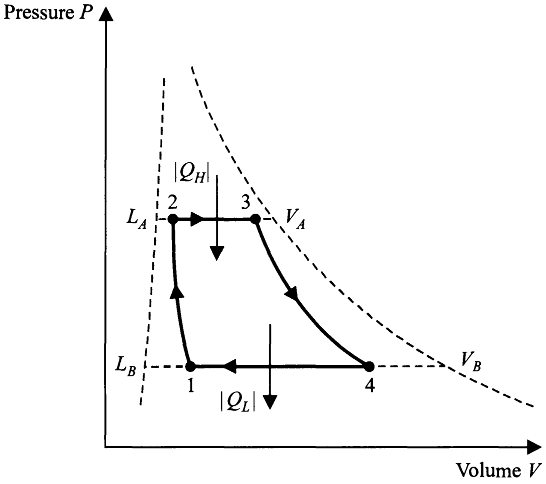

FIGURE 7-2
Carnot cycle of a mixture of liquid and vapor, such as water, plotted with pressure as a function of volume. To the left of the dashed line marked $L_A L_B$, the substance is completely liquefied; to the right of the dashed line marked $V_A V_B$, the substance is completely vaporized.

mixture of liquid and vapor. Starting at the point 1, the four processes in the Carnot cycle are as follows:

1. Process 1 → 2, reversible adiabatic compression until the temperature rises to T_H.
2. Process 2 → 3, reversible isothermal isobaric vaporization until any arbitrary point, such as 3, is reached.
3. Process 3 → 4, reversible adiabatic expansion until the temperature drops to T_L.
4. Process 4 → 1, reversible isothermal isobaric condensation until the initial state is reached.

During the isothermal vaporization 2 → 3, heat $|Q_H|$ is absorbed from the hotter reservoir at T_H. During the isothermal condensation 4 → 1, heat $|Q_L|$ is rejected to the cooler reservoir at T_L.

A Carnot cycle using an electrochemical cell (acid battery) is depicted on an $\mathcal{E}Z$ diagram in Fig. 7-3. The (dashed) lines marked T_H and T_L represent isothermal and constant emf curves at the two temperatures of the reservoirs. The point 1 indicates that the cell is well charged. The four processes are:

1. Process 1 → 2, reversible adiabatic flow of charge from − to + in the external circuit until the temperature rises to T_H.
2. Process 2 → 3, reversible isothermal flow of charge from + to − in the external circuit until an arbitrary point 3 is reached.
3. Process 3 → 4, reversible adiabatic flow of charge until the temperature drops to T_L.
4. Process 4 → 1, reversible isothermal flow of charge until the initial state is restored.

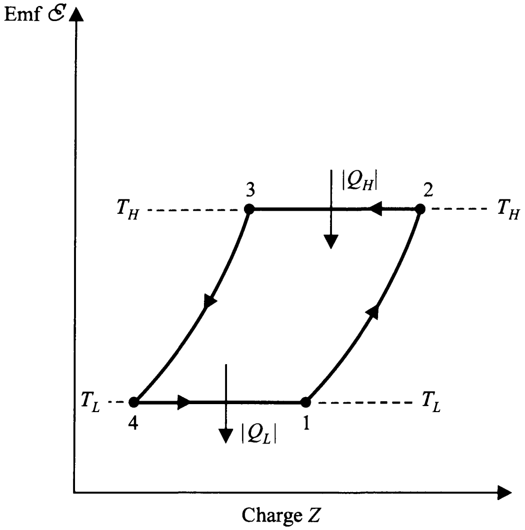

FIGURE 7-3
Carnot cycle of an electrochemical cell.

During the isothermal process 2 → 3, heat $|Q_H|$ is absorbed from the hotter reservoir at T_H. During the isothermal process 4 → 1, heat $|Q_L|$ is rejected to the cooler reservoir at T_L.

As a last example of a Carnot cycle, that of a paramagnetic substance which obeys Curie's law is shown on an $\mathscr{HM}$ diagram in Fig. 7-4. The (dashed) lines $0T_H$ and $0T_L$ represent isothermal lines at the temperatures T_H and T_L, respectively. Starting at point 1, the four processes are:

1. Process 1 → 2, reversible adiabatic magnetization until the temperature rises to T_H.
2. Process 2 → 3, reversible isothermal demagnetization until an arbitrary point 3 is reached.
3. Process 3 → 4, reversible adiabatic demagnetization until the temperature drops to T_L.
4. Process 4 → 1, reversible isothermal magnetization until the initial state is reached.

During the isothermal demagnetization 2 → 3, heat $|Q_H|$ is absorbed from the hotter reservoir at T_H. During the isothermal magnetization 4 → 1, heat $|Q_L|$ is rejected to the cooler reservoir at T_L.

The net work done in one cycle by any Carnot engine can be adjusted to any arbitrary amount by choosing the position of the point 3, that is, by adjusting the extent of the isothermal process 2 → 3, which controls the amount of heat $|Q_H|$ from the high-temperature reservoir. The nature of the working substance determines the thermodynamic coordinates used to plot a Carnot cycle, as well as the shape of the cycle. It will be shown, however, in the next chapter that it is possible to find two thermodynamic coordinates that

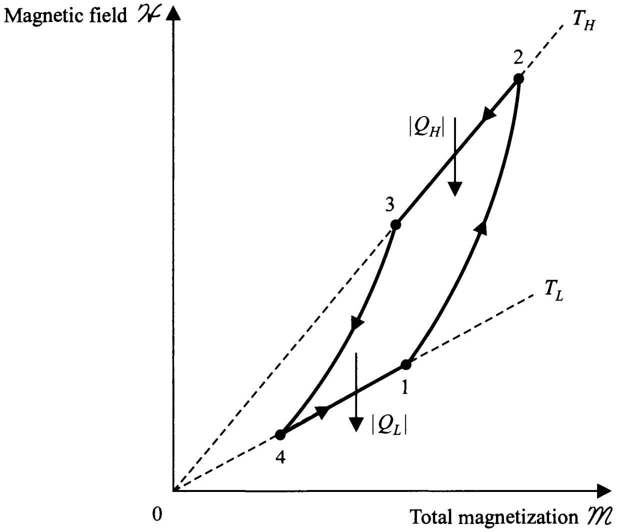

FIGURE 7-4
Carnot cycle of a paramagnetic substance.

form a rectangle for the graph of a Carnot cycle with *any* working substance. Consequently, we shall represent a Carnot engine symbolically with the aid of a rectangle, as shown in Fig. 7-5(*a*). The letter *R* inside the rectangle indicates that the Carnot cycle is a reversible cycle.

If an engine is to operate between only two reservoirs and still operate in a *reversible* cycle, then it must be a Carnot engine. For example, if an Otto cycle were performed between only two reservoirs, the heat transfers in the two isochoric processes would involve finite temperature differences and, therefore, could not be reversible. Conversely, if the Otto cycle were performed reversibly, it would require a series of reservoirs, not merely two reservoirs at different temperatures. The expression "Carnot engine," therefore, means "an ideal engine operating reversibly between only two reservoirs without the need for work to be done on the system."

7.3
CARNOT REFRIGERATOR

Since a Carnot cycle consists of reversible processes, it may be performed in either direction. When it is performed in a direction opposite to that shown in the examples, it is a refrigeration cycle. A Carnot refrigerator is represented symbolically in Fig. 7-5(*b*). *The important feature of a Carnot refrigeration*

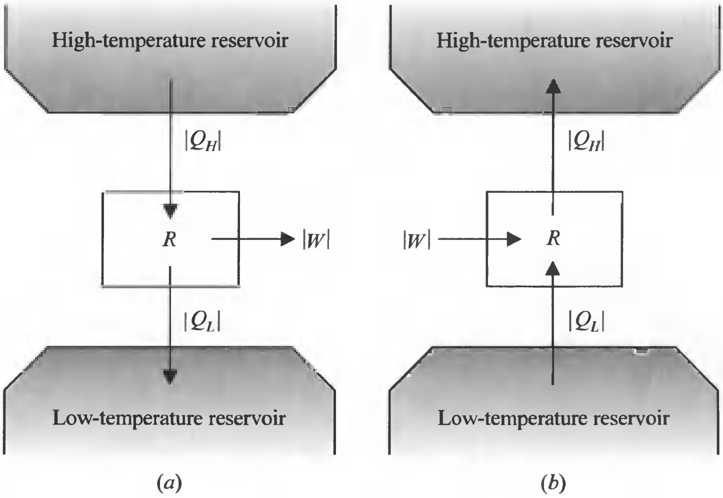

FIGURE 7-5
Schematic representation of (*a*) the Carnot engine, and (*b*) the Carnot refrigerator.

cycle, which distinguishes it from any general reversed engine cycle, is that the quantities $|Q_H|$, $|Q_L|$, and $|W|$ are numerically equal to those quantities when the cycle is performed in the opposite direction. For example, exactly the same amount of heat that is absorbed by the Carnot engine from the high-temperature reservoir is rejected to the high-temperature reservoir when the cycle is reversed. This would not be the case if the cycle were irreversible, because of dissipative effects.

7.4
CARNOT'S THEOREM AND COROLLARY

We are now ready to prove Carnot's theorem, which is stated as follows: *No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.* Imagine a Carnot engine R, which is reversible, and any other engine I, which is irreversible, working between the same two reservoirs and adjusted so that they both deliver the same amount of work $|W|$. Thus:

Carnot engine R	Irreversible engine I
1. Absorbs heat $|Q_H|$ from the high-temperature reservoir.	1. Absorbs heat $|Q'_H|$ from the high-temperature reservoir.
2. Performs work $|W|$.	2. Performs work $|W|$.
3. Rejects heat $Q_H| - |W|$ to the low-temperature reservoir.	3. Rejects heat $|Q'_H| - |W|$ to the low-temperature reservoir.
4. Efficiency $\eta_R = |W|/|Q_H|$.	4. Efficiency $\eta_I = |W|/|Q'_H|$.

Let us assume that the efficiency of the engine I is greater than that of R. Thus,

$$\eta_I > \eta_R,$$

or

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|},$$

so,

$$|Q_H| > |Q'_H|.$$

Now let the engine I drive the Carnot engine R backward as a Carnot refrigerator. This is shown symbolically in Fig. 7-6. The engine and the refrigerator coupled together in this way constitute a self-contained machine, since all the work needed to operate the refrigerator is supplied by the engine. The net heat extracted from the low-temperature reservoir is

$$(|Q_H| - |W|) - (|Q'_H| - |W|) = |Q_H| - |Q'_H|,$$

which is positive. The net heat delivered to the high-temperature reservoir is also $|Q_H| - |Q'_H|$. Therefore, the effect of this self-contained machine is to transfer $|Q_H| - |Q'_H|$ units of heat from a low-temperature reservoir to a high-temperature reservoir without work being done by the surroundings. Since this device violates the second law of thermodynamics (Clausius statement), our original assumption that $\eta_I > \eta_R$ is false and Carnot's theorem is proved. We may express this result in symbols, thus:

$$\eta_I \leq \eta_R. \tag{7.1}$$

The following corollary to Carnot's theorem may be easily proved: *All Carnot engines operating between the same two reservoirs have the same efficiency*. Consider two Carnot engines R_1 and R_2, operating between the same

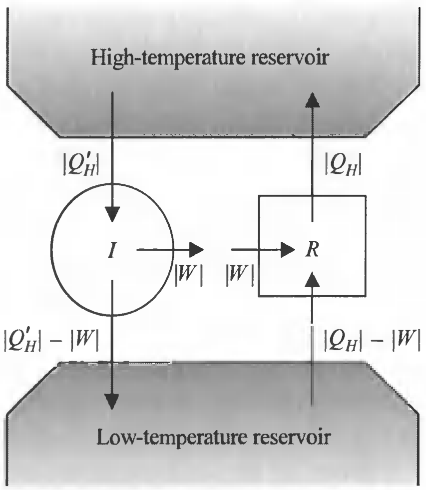

FIGURE 7-6
Irreversible engine I operating a Carnot refrigerator R.

two reservoirs. If we imagine R_1 driving R_2 backward, then Carnot's theorem states that

$$\eta_{R_1} \leq \eta_{R_2}.$$

If R_2 drives R_1 backward, then

$$\eta_{R_2} \leq \eta_{R_1}.$$

But, the efficiency of the first reversible engine cannot be both less than or equal to the efficiency of the second reversible engine, as well as greater than or equal to the efficiency of the second reversible engine. Therefore, it follows that the efficiencies can only be equal:

$$\eta_{R_1} = \eta_{R_2}. \tag{7.2}$$

It is clear from the above result that the nature of the working substance which is undergoing the Carnot cycle has no influence on the efficiency of the Carnot engine.

To summarize, the maximum thermal efficiency that can be achieved by a heat engine operating between two heat reservoirs at different temperatures is the efficiency of a Carnot engine operating between the same two reservoirs. The essential characteristic of a Carnot engine is that it is reversible and operates between two reservoirs, rather than two series of reservoirs. The superior efficiency of the Carnot cycle is due to its absorbing all heat at the highest temperature and rejecting all heat at the lowest temperature. Furthermore, a Carnot engine is independent of the working substance of the system.

7.5

THE THERMODYNAMIC TEMPERATURE SCALE

In Chap. 1, it was pointed out that the zeroth law of thermodynamics establishes the basis for the measurement of temperature, but an empirical temperature scale must be defined in terms of the thermometric property of a specific substance and thermometer, such as the ideal-gas temperature scale using the constant-volume gas thermometer. A temperature scale that is independent of the nature of the working substance, which is called an *absolute* or *thermodynamic* temperature scale, would be most desirable. In Sec. 7.4, it was proven that the efficiency of a Carnot cycle is independent of the working substance and depends only on temperature. The Carnot engine provides the basis for the thermodynamic temperature scale.

A Carnot engine absorbing $|Q_H|$ units of heat from a reservoir at a higher temperature T_H and rejecting $|Q_L|$ units of heat to a reservoir at a lower temperature T_L has an efficiency η_R that is independent of the nature of the working substance. The thermal efficiency is given by Eq. (6.2), namely,

$$\eta_R = 1 - \frac{|Q_L|}{|Q_H|}.$$

The efficiency depends only on the two temperatures of the reservoirs,

$$\eta_R = \phi(T_H, T_L),$$

where $\phi(T_H, T_L)$ is an unknown function of the two temperatures. Rearranging the above two equations, we get

$$\frac{|Q_H|}{|Q_L|} = \frac{1}{1 - \phi(T_H, T_L)} = f(T_H, T_L), \tag{7.3}$$

where $f(T_H, T_L)$ is also an unknown function of the two temperatures.

Let us apply Eq. (7.3) to the three Carnot engines operating between the three reservoirs shown in Fig. 7-7, where $T_1 > T_3 > T_2$. For engine R_A,

$$\frac{|Q_1|}{|Q_2|} = f(T_1, T_2).$$

Now consider the second Carnot engine R_B and third Carnot engine R_C. Since the heat $|Q_3|$ rejected by the second Carnot engine R_B is absorbed by the third Carnot engine R_C, both engines working together are equivalent to the first Carnot engine R_A. Thus, engine R_B absorbs the same heat $|Q_1|$ from the reservoir at T_1 that engine R_A absorbs. So, for engine R_B,

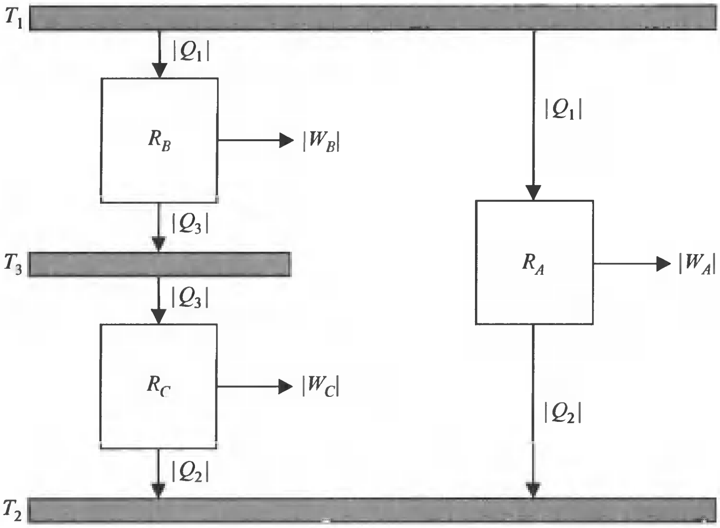

FIGURE 7-7
Schematic diagram of Carnot engines used to demonstrate the thermodynamic temperature scale.

$$\frac{|Q_1|}{|Q_3|} = f(T_1, T_3).$$

Engine R_A rejects heat $|Q_2|$ to the low-temperature reservoir, so engine R_C must also reject heat $|Q_2|$ to the low-temperature reservoir. Thus, for engine R_C,

$$\frac{|Q_3|}{|Q_2|} = f(T_3, T_2).$$

Since

$$\frac{|Q_1|}{|Q_2|} = \frac{|Q_1|/|Q_3|}{|Q_2|/|Q_3|},$$

we have the result that

$$f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)}. \tag{7.4}$$

Now, the temperature T_3 is arbitrarily chosen; and since it does not appear in the left-hand member of Eq. (7.4), T_3 must, therefore, drop out of the ratio on the right. After it has been canceled, the numerator can be written $\psi(T_1)$ and the denominator $\psi(T_2)$, where ψ is another unknown function of one temperature. Thus,

$$\frac{|Q_1|}{|Q_2|} = \frac{\psi(T_1)}{\psi(T_2)}. \tag{7.5}$$

The ratio on the right is defined as the ratio of *two thermodynamic temperatures* and is denoted by T_1/T_2. We have, therefore, finally,

$$\boxed{\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2}.} \tag{7.6}$$

Thus, *two temperatures on the thermodynamic scale are to each other as the absolute values of the heats absorbed and rejected, respectively, by a Carnot engine operating between reservoirs at these temperatures.* It is seen that the thermodynamic temperature scale is independent of the specific characteristics of any particular substance. Thus, the Carnot engine supplies the universality that is lacking in the ideal-gas temperature scale. Finally, the thermodynamic temperatures are called "absolute" temperatures, because they are independent of any material.

Equation (7.5) is the fundamental relationship based on the second law of thermodynamics and the Carnot cycle. All that is necessary of the *arbitrary* function ψ is that ψ be a function of the thermodynamic temperature. Any function will do. In 1848, Kelvin was forced to choose a linear function of temperature in Eq. (7.6), because all the scientific and engineering data had been obtained from the mercury-in-glass thermometer, which is essentially linear over its useful range. As a result, on the thermodynamic scales now in use (Kelvin or Rankine), the temperatures vary from 0 to $+\infty$ for ordinary systems. Kelvin recognized the asymmetry of the end-points of the linear scale and proposed, *as his first choice*, that ψ be a logarithmic function of the thermodynamic temperature. On the logarithmic scale, temperatures vary from $-\infty$ to $+\infty$. The advantage of the logarithmic scale is that absolute zero is far removed from the normal freezing point of water, whereas, on the linear scale, absolute zero is "only" a few hundred degrees below the ice point.

At first thought, it might seem that the ratio of two Kelvin temperatures would be impossible to measure, since a Carnot engine is an ideal engine, quite impossible to construct. The situation, however, is not as bad as it seems. The ratio of two Kelvin temperatures is the ratio of two heats that are transferred during two isothermal processes bounded by the same two adiabatic curves. The two adiabatic boundaries may be located experimentally, and the heats transferred during two isothermal "nearly reversible" processes can be measured with considerable precision. As a matter of fact, this is one of the methods used in measuring temperatures below 1 K.

To complete the definition of the thermodynamic scale, we proceed to assign the arbitrary value of 273.16 K to the temperature of the triple point of water T_{TP}, as in Chap. 1. Thus,

$$\boxed{T_{TP} = 273.16\,\mathrm{K}.}$$

For a Carnot engine operating between reservoirs at the temperatures T and T_{TP}, we have

$$\frac{|Q|}{|Q_{TP}|} = \frac{T}{T_{TP}},$$

or

$$T = 273.16\,\mathrm{K}\,\frac{|Q|}{|Q_{TP}|}. \tag{7.7}$$

Comparing Eq. (7.7) with the corresponding equation for the ideal-gas temperature, namely, Eq. (1.7),

$$T = 273.16\,\mathrm{K}\lim_{P_{TP}\to 0}\left(\frac{P}{P_{TP}}\right),$$

it is seen that, in the thermodynamic scale, $|Q|$ plays the role of a "thermometric property" for a Carnot cycle, just as pressure is the thermometric property for a constant-volume gas thermometer. Heat does not, however, have the objection attached to the thermodynamic coordinate pressure of the arbitrarily chosen gas-thermometer, inasmuch as the behavior of a Carnot engine is independent of the nature of the working substance.

7.6
ABSOLUTE ZERO AND CARNOT EFFICIENCY

It follows from Eq. (7.7),

$$T = 273.16\,\mathrm{K}\,\frac{|Q|}{|Q_{TP}|},$$

that the smaller the value of $|Q|$, the lower the corresponding T. The smallest possible value of $|Q|$ is zero, and the corresponding T is absolute zero. *Thus, if a system undergoes a reversible isothermal process without transfer of heat, the temperature at which this process takes place is called absolute zero.* In other words, at absolute zero, an isotherm and an adiabatic are identical.

It should be noticed that the definition of absolute zero holds for all substances and is, therefore, independent of the specific properties of any arbitrarily chosen substance. Furthermore, the definition is in terms of purely macroscopic concepts. No reference is made to atoms or molecules. Whether absolute zero may be achieved is a question that is left to experiment.

A Carnot engine absorbing heat $|Q_H|$ from a hotter reservoir at T_H and rejecting heat $|Q_L|$ to a cooler reservoir at T_L has an efficiency

$$\eta_R = 1 - \frac{|Q_L|}{|Q_H|}.$$

Since

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H},$$

we have the result that the efficiency of a Carnot engine can be expressed in terms of the absolute temperatures of its two heat reservoirs, namely,

$$\boxed{\eta_R = 1 - \frac{T_L}{T_H}.} \tag{7.8}$$

For a Carnot engine to have an efficiency of 100 percent, it is clear that T_L must be zero. Only when the lower reservoir is at absolute zero will all the heat be converted into work. Since nature does not provide us with a reservoir at absolute zero, a heat engine with 100 percent efficiency is a practical impossibility.

7.7
EQUALITY OF IDEAL-GAS AND THERMODYNAMIC TEMPERATURES

In Chap. 1, the ideal-gas temperature was defined in terms of the ratio of the pressure P to the pressure of the system at the triple point of water P_{TP} in the limit as P_{TP} approaches zero. In anticipation of this section, the ideal-gas temperature was given the symbol T for thermodynamic temperature, but let us return to the earlier symbol θ and proceed to prove their equality.

A Carnot cycle of an ideal gas is depicted on a PV diagram in Fig. 7-8.[†] The two isothermal processes $2 \rightarrow 3$ at temperature θ_1 and $4 \rightarrow 1$ at temperature θ_2 are represented by equilateral hyperbolas whose equations are, respectively,

$$PV = nR\theta_1$$

and

$$PV = nR\theta_2.$$

For any infinitesimal reversible process of an ideal gas, the first law may be written

$$\text{đ}Q = C_V\,d\theta + P\,dV.$$

Applying this equation to the isothermal process $2 \rightarrow 3$, the heat absorbed is found to be

$$\begin{aligned} |Q_1| &= \int_{V_2}^{V_3} P\,dV \\ &= nR\theta_1 \ln \frac{V_3}{V_2}. \end{aligned}$$

Similarly, for the isothermal process $4 \rightarrow 1$, the heat rejected is

$$|Q_2| = nR\theta_2 \ln \frac{V_4}{V_1},$$

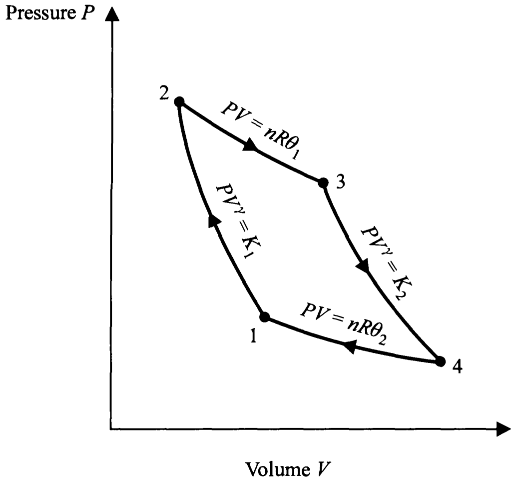

FIGURE 7-8
Carnot cycle of an ideal gas. (*Note*: The processes are shown with exaggerated line segments in order to separate clearly the adiabatic curves from the isothermal curves.)

[†] It is customary, in most thermodynamics books, to emphasize the difference between the adiabatic and isothermal processes by distorting the processes, as shown in Fig. 7-8. Accurately drawn figures for the Carnot cycle of the ideal gas are shown in the problems at the end of this chapter.

where the rejection of heat interchanged the limits of integration. Therefore,

$$\frac{|Q_1|}{|Q_2|} = \frac{\theta_1 \ln(V_3/V_2)}{\theta_2 \ln(V_4/V_1)}. \tag{7.9}$$

Since the process 1 → 2 is adiabatic, we may write, for any infinitesimal portion,

$$-C_V\, d\theta = P\, dV,$$

or

$$-C_V\, d\theta = \frac{nR\theta}{V}\, dV.$$

Integrating from 1 → 2, we get

$$\frac{1}{nR}\int_{\theta_1}^{\theta_2} C_V \frac{d\theta}{\theta} = \ln \frac{V_2}{V_1}.$$

Similarly, for the adiabatic process 3 → 4,

$$\frac{1}{nR}\int_{\theta_2}^{\theta_1} C_V \frac{d\theta}{\theta} = \ln \frac{V_4}{V_3}.$$

Therefore,

$$\ln \frac{V_2}{V_1} = \ln \frac{V_3}{V_4},$$

or

$$\ln \frac{V_3}{V_2} = \ln \frac{V_4}{V_1}. \tag{7.10}$$

Combining Eqs. (7.9) and (7.10), we obtain

$$\frac{|Q_1|}{|Q_2|} = \frac{\theta_1}{\theta_2}. \tag{7.11}$$

The thermodynamic temperature scale, defined by Eq. (7.6), allows us to replace the ratio of heats by the ratio of the thermodynamic temperatures to yield

$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2}.$$

If θ_1 and T_1 refer to any temperature, and θ_2 and T_2 refer to the triple point of water, then the preceding equation becomes

$$\frac{\theta}{\theta_{TP}} = \frac{T}{T_{TP}}.$$

Since $\theta_{TP} = T_{TP} = 273.16\,\mathrm{K}$, it follows that

$$\boxed{\theta = T.}$$

The thermodynamic temperature is, therefore, numerically equal to the ideal-gas temperature and, in the proper range, may be measured with a gas thermometer.

PROBLEMS

7.1. Take an ideal monatomic gas ($\gamma = \frac{5}{3}$) around the Carnot cycle, where $T_H = 600\,\text{K}$ and $T_L = 300\,\text{K}$. Point 1 at the beginning of the adiabatic compression has pressure $P_1 = P_0$ (atmospheric pressure) and volume $V_1 = 50$ liters. Point 3 has a volume $V_3 = 75$ liters. The resulting Carnot cycle is shown in Fig. P7-1. Calculate the values of volume and pressure at all four points, which have the same meaning as those in Fig. 7-8.

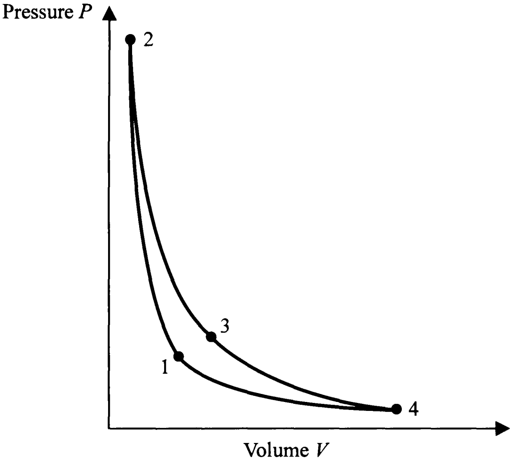

FIGURE P7-1
An accurately drawn Carnot cycle for an ideal gas with the ratio $V_3/V_1 = \frac{3}{2}$.

7.2. Take an ideal monatomic gas ($\gamma = \frac{5}{3}$) around the Carnot cycle, where point 1 at the beginning of the adiabatic compression has pressure $P_1 = P_0$ (atmospheric pressure), volume $V_1 = 13$ liters, and temperature $T_1 = 300\,\text{K}$. Point 3 has pressure $P_3 = 2P_0$ and volume $V_3 = 26$ liters. The resulting Carnot cycle is shown in Fig. P7-2. Calculate the values of volume and pressure at all four points, which have the same meaning as those in Fig. 7-8.

7.3. An inventor claims to have developed an engine that takes in 100,000 Btu at a temperature of 400 K, rejects 40,000 Btu at a temperature of 200 K, and delivers 15 kW · h of work. Would you advise investing money to put this engine on the market?

7.4. A Carnot engine absorbs 100 J of heat from a reservoir at the temperature of the normal boiling point of water and rejects heat to a reservoir at the temperature of the triple point of water. Find the heat rejected, the work done by the engine, and the thermal efficiency.

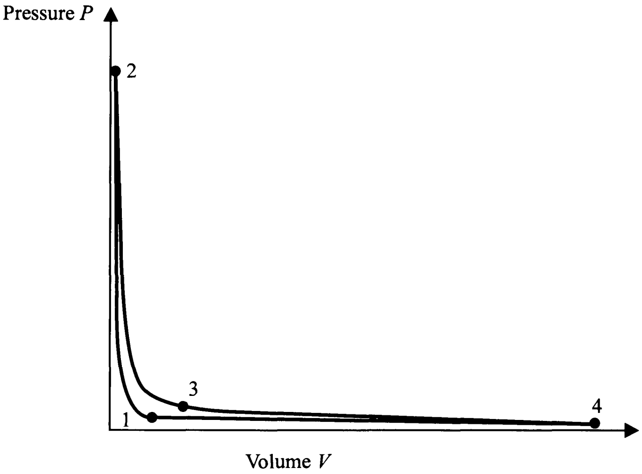

FIGURE P7-2
An accurately drawn Carnot cycle for an ideal gas with the ratio $V_3/V_1 = 2$.

7.5. Which is the more effective way to increase the thermal efficiency of a Carnot engine: to increase T_H, keeping T_L constant; or to decrease T_L, keeping T_H constant?

7.6. Imagine an irreversible engine I and a Carnot engine R operating between the same two reservoirs. Suppose that they absorb different amounts of heat from the high-temperature reservoir, perform different amounts of work, but reject the *same* amounts of heat to the low-temperature reservoir. Prove Carnot's theorem with the aid of the Kelvin-Planck statement of the second law.

7.7. In Sec. 7.4, suppose that engine I executes an irreversible cycle, and assume that $\eta_I = \eta_R$. Show that this assumption leads to a result that is inconsistent with the irreversibility of I, and, therefore, that $\eta_I < \eta_R$.

7.8. Draw a symbolic diagram of a set of Carnot engines with the following characteristics: Each engine absorbs the heat rejected by the preceding one at the temperature at which it was rejected, and each engine delivers the same amount of work. Show that the temperature intervals between which these engines operate are all equal.

7.9. Take a gas whose equation of state is $P(v - b) = R\theta$ and whose heat capacity C_V is a function of θ only through a Carnot cycle, and prove that $\theta = T$.

7.10. The initial state of 0.1 mol of an ideal monatomic gas is $P_0 = 32\,\text{Pa}$ and $V_0 = 8\,\text{m}^3$. The final state is $P_1 = 1\,\text{Pa}$ and $V_1 = 64\,\text{m}^3$. Suppose that the gas undergoes a process along a *straight line* joining these two states with an equation $P = aV + b$, where $a = -31/56$ and $b = 255/7$. Plot this straight line to scale on a PV diagram. Calculate:

(*a*) Temperature T as a function of V along the straight line.
(*b*) The value of V at which T is a maximum.
(*c*) The values of T_0, $T_{\max}$, and T_1.

(*d*) The heat Q transferred from the volume V_0 to any other volume V along the straight line.
(*e*) The values of P and V at which Q is a maximum.
(*f*) The heat transferred along the line from V_0 to V when Q is a maximum.
(*g*) The heat transferred from V at maximum Q to V_1.

7.11. Show that the two states specified in Prob. 7.10 lie on an adiabatic curve. A cycle described by J. Willis and D. Kirwan, and called the "Sadly Cannot" cycle, is obtained by proceeding from the initial state to the final state along the straight line specified in Prob. 7.10 and back to the initial state along the adiabatic curve. Calculate:
(*a*) The work done on the gas during the adiabatic process.
(*b*) The net work done in the cycle.
(*c*) The net heat transferred *to* the gas.
(*d*) The thermal efficiency of the cycle.
(*e*) The thermal efficiency of a Carnot cycle operating between a reservoir at the maximum temperature in the cycle and a reservoir at the minimum temperature in the cycle.

7.12. A logarithmic thermodynamic temperature scale, which can be constructed to agree with the Celsius scale at NMP-H_2O and NBP-H_2O, is related to the Celsius scale by the formula

$$L = (99.974)\frac{\log T - \log 273.15}{\log 373.124 - \log 273.15},$$

where L is any temperature on the logarithmic temperature scale and T is the corresponding Kelvin temperature on the linear temperature scale. The formula reduces to

$$L = 738.08 \log T - 1798.26.$$

(*a*) Calculate logarithmic temperatures for several representative temperatures between 10^{-3} K and 15×10^6 K.
(*b*) Consider two different temperature ranges on the linear scale that yield the same thermal efficiency for a Carnot cycle. Calculate the temperature ranges on the logarithmic scale and draw a conclusion about efficiency on the logarithmic scale.

CHAPTER 8

Entropy

8.1
REVERSIBLE PART OF THE SECOND LAW

Work diagrams in which a generalized force such as P, $\mathcal{J}$, γ, $\mathcal{E}$, or $\mu_0\mathcal{H}$ is plotted against the corresponding generalized displacement V, L, A, Z, or $\mathcal{M}$ have been used to indicate processes of various systems. An isothermal process or an adiabatic process is represented by a different curve on each diagram. In this chapter, it is desired to formulate general principles that apply to all systems. If we let the symbol Y denote any generalized force and the symbol X its corresponding generalized displacement, a generalized work diagram in which Y is plotted against X may be used to depict processes common to all systems and will thus be suitable for general discussions.

Consider a reversible process represented by the smooth curve $i \rightarrow f$ on the generalized work diagram shown in Fig. 8-1. The nature of the system is not essential. The dashed curves through i and f, respectively, represent portions of adiabatic processes. Let us draw a curve $a \rightarrow b$, representing an isothermal process, in such a way that the area under the smooth curve *if* is equal to the area under the zigzag sequence of processes, path *iabf*. Then, the work done in traversing both paths is the same, or

$$W_{if} = W_{iabf}.$$

From the first law,

$$Q_{if} = U_f - U_i - W_{if},$$

and

$$Q_{iabf} = U_f - U_i - W_{iabf}.$$

Therefore,

$$Q_{if} = Q_{iabf}.$$

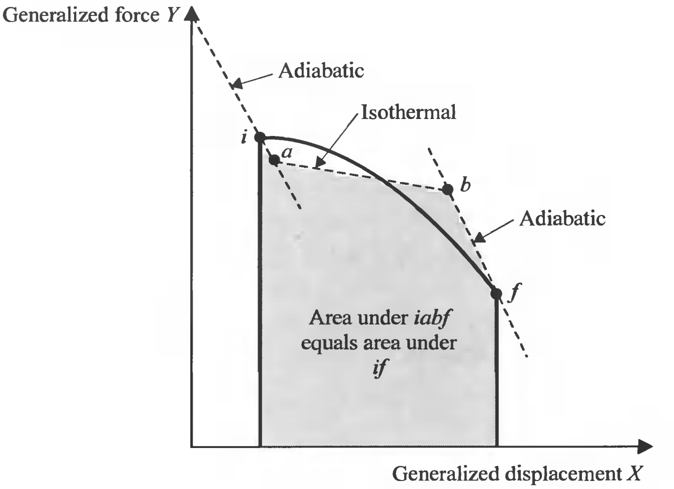

FIGURE 8-1
Generalized work diagram, where $i \rightarrow f$ is any reversible process; $i \rightarrow a$ is a reversible adiabatic process; $a \rightarrow b$ is a reversible isothermal process; and $b \rightarrow f$ is a reversible adiabatic process.

But, since no heat is transferred in the two adiabatic processes *ia* and *bf*, we have

$$Q_{if} = Q_{ab}. \tag{8.1}$$

If we are given, therefore, a reversible process in which the temperature may change in any manner, it is always possible to find a reversible zigzag path between the same two states, consisting of an adiabatic process followed by an isothermal process followed by an adiabatic process, such that the heat transferred during the isothermal segment is the same as that transferred during the original process.

Now, consider the smooth closed curve on the generalized work diagram shown in Fig. 8-2. Since no two adiabatic lines can intersect (see Prob. 6.13), a number of adiabatic lines may be drawn, dividing the cycle into a number of adjacent strips. A zigzag closed path may now be drawn, consisting of alternate adia-batic and isothermal portions, such that the heat transferred during all the isothermal portions is equal to the heat transferred in the original cycle. Consider the two isothermal processes *ab* at the temperature T_1, during which heat Q_1 is absorbed, and *cd* at the temperature T_2, during which heat Q_2 is rejected. Since *ab* and *cd* are bounded by the same adiabatic curves, *abcd* is a Carnot cycle, and we may write Eq. (7.6) as

$$\frac{|Q_1|}{T_1} = \frac{|Q_2|}{T_2}.$$

For the sake of clearness and simplicity, we have been considering only the absolute values of heat entering or leaving a system, thus ignoring the sign

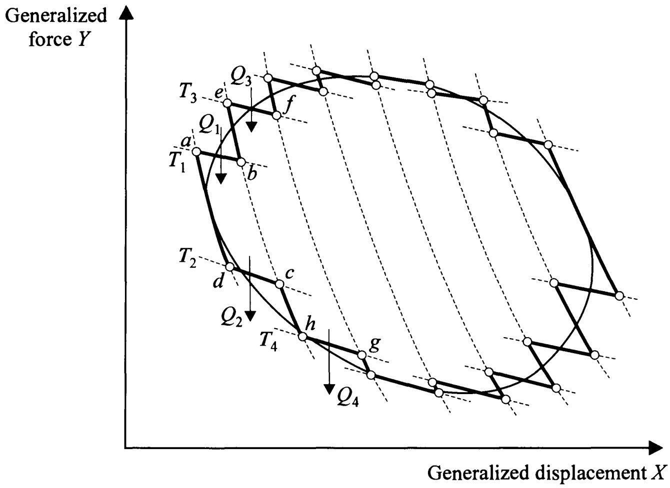

FIGURE 8-2
Generalized work diagram, where the smooth closed curve is a reversible cycle and the zigzag closed path is made up of alternating reversible isothermal and reversible adiabatic processes.

convention introduced in Chap. 4. Let us now return to the sign convention and regard any Q as an algebraic symbol, positive for heat absorbed by a system and negative for heat rejected from a system. We may then write the equation cited above as

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0,$$

where Q_1 is a positive number and Q_2 is a negative number. Since the isothermal curves *ef* and *gh* are bounded by the same two adiabatic curves, *efgh* is also a Carnot cycle, and

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0.$$

If a similar equation is written for each pair of isothermal curves bounded by the same two adiabatic curves and if all the equations are added, then the result obtained is that

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \cdots = 0.$$

Since no heat is transferred during the adiabatic portions of the zigzag cycle, we may write

$$\sum_j \frac{Q_j}{T_j} = 0, \tag{8.2}$$

where the summation is taken over the entire zigzag cycle consisting of Carnot cycles, j in number.

Now, imagine the cycle divided into a very large number of strips by drawing a large number of adiabatic curves close together. If we connect these adiabatic curves with small isothermal curves, in the manner already described, then a zigzag path may be traced that can be made to approximate the original cycle as closely as we please. When these isothermal processes become infinitesimal, the ratio $đQ/T$ for an infinitesimal isothermal between two adjacent adiabatic curves is equal to the ratio $đQ/T$ for the infinitesimal piece of the original cycle bounded by the same two adiabatic curves. In the limit, therefore, we may write for Eq. (8.2) any reversible cycle,

$$\boxed{\oint_R \frac{đQ}{T} = 0.} \tag{8.3}$$

The circle through the integral sign signifies that the integration takes place over the complete cycle, and the letter R emphasizes the fact that the equation is true only for a reversible cycle. This result, known as *Clausius' theorem*, is one part of Clausius' mathematical statement of the second law. The other part applicable to irreversible cycles will be presented in Sec. 8.8.

8.2
ENTROPY

Let an initial equilibrium state of any thermodynamic system be represented by the point i on any convenient diagram, such as the generalized work diagram of Fig. 8-3. Denote a final equilibrium state by the point f. It is possible to take the system from i to f along any number of different reversible paths, since i and f are equilibrium states. Suppose the system is taken from i to f along the reversible path R_1 and then back to i again along another reversible path R_2. The two paths form a reversible cycle, and from Clausius' theorem we may write

$$\oint_{R_1R_2} \frac{đQ}{T} = 0.$$

The above integral may be expressed as the sum of two integrals, one for the path R_1 and the other for the path R_2. Then, we have

$$\int_{R_1\, i}^{f} \frac{đQ}{T} + \int_{R_2\, f}^{i} \frac{đQ}{T} = 0,$$

or

$$\int_{R_1\, i}^{f} \frac{đQ}{T} = -\int_{R_2\, f}^{i} \frac{đQ}{T}.$$

Since R_2 is a reversible path,

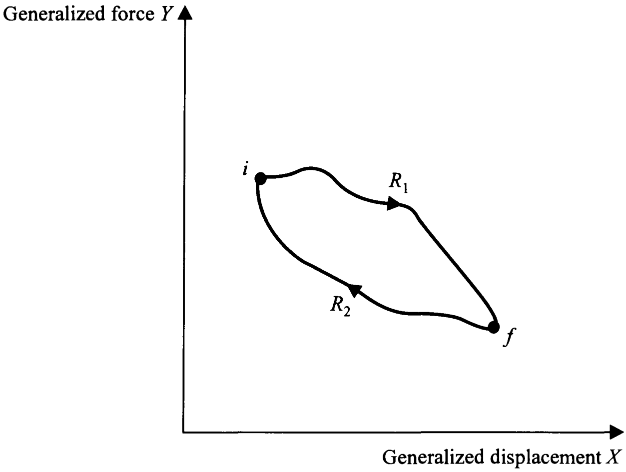

FIGURE 8-3
Two reversible paths joining two equilibrium states of a system.

$$-{}_{R_2}\int_f^i \frac{đQ}{T} = {}_{R_2}\int_i^f \frac{đQ}{T},$$

and, finally,

$$ {}_{R_1}\int_i^f \frac{đQ}{T} = {}_{R_2}\int_i^f \frac{đQ}{T}. \tag{8.4}$$

Since R_1 and R_2 were chosen at random and represent *any* two reversible paths, the above equation expresses the important fact that ${}_R\int_i^f đQ/T$ *is independent of the reversible path connecting* i *and* f. Therefore, it follows from Eq. (8.4) that *there exists a function of the thermodynamic coordinates of a system whose value at the final state minus its value at the initial state equals the integral* ${}_R\int_i^f đQ/T$. This state function was named the *entropy* by Rudolf Clausius in 1865 and is denoted by S. If S_i is the entropy at the initial state and S_f the entropy at the final state, then we have a finite *change of entropy* $S_f - S_i$ from state i to state f, given by

$$\boxed{S_f - S_i = {}_R\int_i^f \frac{đQ}{T},} \tag{8.5}$$

where the path from state i to state f is *any* reversible path R. Thus, the entropy change of the system between states i and f is independent of the path. This is a very remarkable result. Although the heat entering the system depends on the path between the states i and f, the entropy change does *not* depend on the path.

The existence of an entropy function S is deduced in the same way as that of the internal-energy function U, that is, by showing that a certain quantity is independent of choice of reversible processes connecting the initial equilibrium state with the final equilibrium state. Both U and S are state functions, which means that the difference of either function evaluated at the final and initial equilibrium states is independent of the path connecting the two states. In neither function, however, does the defining equation enable us to calculate a single value of the function, only the difference of two values.

If the two equilibrium states i and f are infinitesimally near, then the integral sign may be eliminated and $S_f - S_i$ becomes dS, an *infinitesimal* change of entropy of the system. Equation (8.5) then becomes

$$\boxed{dS = \frac{đQ_R}{T},} \tag{8.6}$$

where dS is an exact differential, since it is the differential of an actual function and not a small inexact quantity, such as $đQ$ or $đW$. The subscript R to $đQ$ indicates that the preceding equation is true *only* if a small amount of heat $đQ$ is transferred reversibly.

When Eq. (8.6) is written in the form $đQ_R = T\,dS$, it is seen that the difficulty of dealing with the inexact differential of heat is eliminated by substituting the product of the temperature and exact differential of the entropy. This is a major advancement in the formalism of thermodynamics, comparable to replacing $đW$ with $-P\,dV$ in a hydrostatic system. Entropy S joins P, V, and T as a thermodynamic variable to be used in the development of the formalism and mathematical methods of thermodynamics.

It is instructive to calculate a unit of entropy, a joule per kelvin, in order to gain a feeling for this new variable. Consider the Joule paddle wheel apparatus shown in Fig. 8-4. The system is a kilogram of water at room temperature T. The surroundings are the adiabatic cylindrical wall and top, the

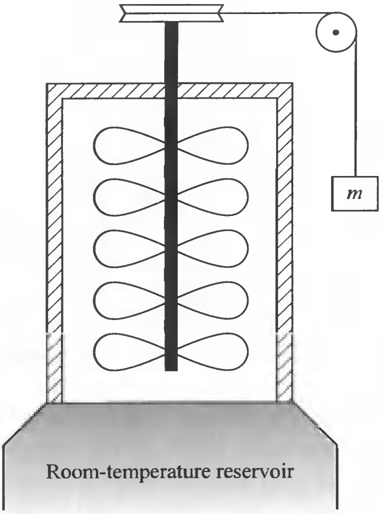

FIGURE 8-4
Joule paddle wheel apparatus, an "entropy generator."

diathermic bottom in contact with a heat reservoir, also at temperature T, and the paddle wheels. A slowly falling mass m causes the paddle wheels to turn, so the portion of the boundary formed by the paddle wheels moves. The falling mass does work on the system, which tends to experience an increase in the temperature of the water. However, the diathermic bottom prevents the temperature from rising by removing energy from the system in the form of heat.

The change of entropy of the reservoir ΔS is given by

$$\Delta S = \int \frac{đQ_R}{T} = \frac{Q}{T},$$

which is also the total change of entropy for the composite system of liquid plus reservoir, since the state of the water in the apparatus is unchanged at the end of the process. Furthermore, since the temperature of the water and the volume of the water are both unchanged, the internal energy is unchanged. Thus, the work done by the falling mass equals the heat that enters the reservoir. If the paddle wheel is driven by a mass of 29.9 kg (approximately 66 lb) that falls 1 m, then the change of entropy is given by

$$\begin{aligned}\Delta S &= \frac{W}{T} = \frac{(29.9\,\mathrm{kg})(9.8\,\mathrm{N/kg})(1\,\mathrm{m})}{293\,\mathrm{K}}\\ &= 1.00\,\mathrm{J/K}.\end{aligned}$$

The entropy of the mass turning the paddle wheels is not changed during the process, because no heat enters or leaves the mass. Rather, the entropy is generated by the conversion of work (done by the mass) into heat (entering the reservoir). Thus, the paddle wheel apparatus serves as an entropy generator.

8.3

PRINCIPLE OF CARATHÉODORY

We have arrived at the mathematical formulation of the second law by the historical method initiated by the engineer Carnot and elaborated by the physicists Kelvin and Clausius. They thought in terms of practical engines, ideal engines, and physical models. Starting with a statement expressing the impossibility of converting heat completely into work, or the impossibility of spontaneous heat flow from a low-temperature body to a high-temperature body, they conceived of the ideal Carnot engine having maximum thermal efficiency. With the aid of this ideal engine, an absolute thermodynamic temperature scale was defined, and the Clausius theorem was proved. On the basis of Clausius' theorem, the existence of an entropy function was deduced. From a mathematical point of view, this procedure is somewhat unsatisfactory. Mathematicians often prefer an "axiomatic treatment," that is, a statement of the minimum number of fundamental axioms and then a purely formal mathematical deduction from these axioms.

In 1909, the mathematician Carathéodory sought to find a statement of the second law which, without the aid of Carnot engines and refrigerators but only by mathematical deduction, would lead to the existence of an entropy function satisfying the equation $đQ_R = T\,dS$. He was led to his formulation of the second law by a mathematical theorem that he proved and which may be stated in simple form[†] as follows.

Imagine a space of three dimensions with rectangular coordinates x, y, z. Carathéodory's theorem states that, *in the neighborhood of any arbitrary point* P_0, *there are points that are not accessible from* P_0 *along solution curves of the equation*

$$A(x,y,z)\,dx + B(x,y,z)\,dy + C(x,y,z)\,dz = 0,$$

if, and only if, the equation is integrable. The equation is said to be integrable if there exist functions $\lambda(x,y,z)$ and $F(x,y,z)$ such that

$$A\,dx + B\,dy + C\,dz = \lambda\,dF.$$

The proof of this purely mathematical theorem is somewhat involved and it will not be given here. It holds for any number of variables.

Let us now consider how this theorem has a bearing on thermodynamics. Consider a system whose states are determined, for the sake of argument, by three thermodynamic coordinates x, y, and z. Then, the first law in differential form may be written

$$đQ = A\,dx + B\,dy + C\,dz,$$

where A, B, and C are functions of x, y, and z. The adiabatic, reversible transitions of this system are subject to the condition

$$đQ = A\,dx + B\,dy + C\,dz = 0.$$

Let us now take as Carathéodory's statement of the second law the following:

> *In the neighborhood of any arbitrary initial state* P_0 *of a physical system, there exist neighboring states that are not accessible from* P_0 *along quasi-static adiabatic paths.*

It follows from Carathéodory's theorem that his statement of the second law is possible if, and only if, there exist functions T and S such that

$$đQ = A\,dx + B\,dy + C\,dz = T\,dS.$$

Thus, by stating the second law in terms of the inaccessibility of certain states by adiabatic paths, and by using a mathematical theorem, Carathéodory deduced the existence of an entropy function and an integrating factor connected with Kelvin temperature, which reassures us of the validity of Clausius'

[†] For a complete discussion, see H. A. Buchdahl: *Twenty Lectures on Thermodynamics*, Pergamon, Elmsford, NY, 1975.

theorem. The difficulty with Carathéodory's statement of the second law is that no physical intuition is developed, as is in the study of the characteristics of heat engines.

8.4
ENTROPY OF THE IDEAL GAS

If a system absorbs an infinitesimal amount of heat $đQ_R$ during a reversible process, the entropy change of the system is given by Eq. (8.6),

$$dS = \frac{đQ_R}{T}.$$

It is interesting to notice that, although $đQ_R$ is an inexact differential, the ratio $đQ_R/T$ is exact. The reciprocal of the absolute thermodynamic temperature is, therefore, the integrating factor of $đQ_R$. If $đQ_R$ is expressed as a sum of differentials involving thermodynamic coordinates, then, upon dividing by T, the expression may be integrated and the entropy of the system obtained. As an example of this procedure, consider one of the expressions for $đQ_R$ of the ideal gas, namely, Eq. (5.10),

$$đQ_R = C_P\, dT - V\, dP.$$

Dividing by T, we get

$$\frac{đQ_R}{T} = C_P \frac{dT}{T} - \frac{V}{T}\, dP,$$

or

$$dS = C_P \frac{dT}{T} - nR \frac{dP}{P}. \tag{8.7}$$

Let us now calculate the entropy change ΔS of the ideal gas between an arbitrarily chosen *reference state r* with coordinates T_r, P_r, and any other state with coordinates T, P. Integrating between these two states, we get

$$\Delta S = \int_{T_r}^{T} C_P \frac{dT}{T} - nR \ln \frac{P}{P_r}.$$

Suppose we assign to the reference state an entropy S_r and choose *any arbitrary numerical value* for this quantity. Then, an entropy S may be associated with the other state where $S - S_r = \Delta S$. To make the discussion simpler, let C_P be constant. Then,

$$S - S_r = C_P \ln \frac{T}{T_r} - nR \ln \frac{P}{P_r},$$

and this may be rewritten

$$S = C_P \ln T - nR \ln P + (S_r - C_P \ln T_r + nR \ln P_r).$$

Denoting the quantity in parentheses by the *constant* S_0, we get, finally,

$$S = C_P \ln T - nR \ln P + S_0. \tag{8.8}$$

Substituting for T and P thousands of different values, we may calculate thousands of corresponding values of S, which form an *entropy table*. Any one value from this table, taken alone, will have no meaning. The difference between two values, however, will be an actual change of entropy.

Let us investigate the meaning of the standard state entropy S_0 by returning to Eq. (8.7),

$$dS = C_P \frac{dT}{T} - nR \frac{dP}{P}.$$

Again, for simplicity, assuming C_P to be constant, we may take the indefinite integral and obtain

$$S = C_P \ln T - nR \ln P + S_0,$$

where S_0 is the constant of integration. This result is precisely Eq. (8.8) obtained previously by taking into account the reference state. We see that, in taking the indefinite integral of dS, we do not obtain an "absolute entropy," but merely an entropy referred to an unspecified reference state whose coordinates are contained within the constant of integration. The reference state is arbitrarily chosen, usually for convenience and practicality. Thus, chemists use 0.1 MPa and 25°C (298 K) as the reference state for chemical reactions; engineers use the triple point of water for steam processes; and physicists use 0.1 MPa and absolute zero for low-temperature calculations. Once the reference state is chosen, the constant of integration S_0 can be evaluated and entropy tables constructed.

Let us calculate the *change of* entropy of the ideal gas as a function of T and V by using the expression for $đQ_R$ of the ideal gas, namely, Eq. (5.8). Thus,

$$\frac{đQ_R}{T} = C_V \frac{dT}{T} + \frac{P}{T}\, dV,$$

and

$$dS = C_V \frac{dT}{T} + nR \frac{dV}{V},$$

where C_V is the heat capacity at constant volume. Integrating dS, we obtain

$$S = \int C_V \frac{dT}{T} + nR \ln V + S_0. \tag{8.9}$$

In terms of the molar specific heat at constant volume c_V, the change of entropy of the ideal gas between an initial state and final state is given by

$$\boxed{\Delta S = n \int_i^f c_V \frac{dT}{T} + nR \ln \frac{V_f}{V_i}.} \tag{8.10}$$

Similarly, for the change of entropy of an ideal gas as a function of T and P, we use Eq. (8.7) to obtain

$$\boxed{\Delta S = n \int_i^f c_P \frac{dT}{T} + nR \ln \frac{P_f}{P_i},} \tag{8.11}$$

where c_P is the molar specific heat at constant pressure.

8.5
TS DIAGRAM

For every infinitesimal amount of heat that enters a system during an infinitesimal portion of a reversible process, there is an equation

$$đQ_R = T\,dS.$$

It follows, therefore, that the total amount of heat transferred in a reversible process is given by

$$Q_R = \int_i^f T\,dS.$$

This integral can be interpreted graphically as the area under a curve on a diagram in which T is plotted along the y-axis and S along the x-axis, a so-called "*TS* diagram." The shape of the curve on the *TS* diagram is determined by the kind of reversible process that the system undergoes. Obviously, an isothermal process is a horizontal line, but in the case of a reversible adiabatic process, we have

$$dS = \frac{đQ_R}{T}.$$

Also, for an adiabatic process,

$$đQ = 0.$$

So, if T is not zero, then

$$dS = 0,$$

and S is constant. Therefore, during a reversible adiabatic process, the entropy of a system remains constant, or, in other words, the system undergoes an *isentropic process*. An isentropic process on a *TS* diagram is obviously a vertical line, called an "isentrope." Also obvious is that an isothermal process on a *TS* diagram is a horizontal line, called an "isotherm."

It is clear that the two isothermal and the two adiabatic processes that make up *any* Carnot cycle form a rectangle on a *TS* diagram, regardless of the nature of the working substance, unlike the many shapes found in work diagrams for the heat engines in Chaps. 6 and 7. It was with this knowledge that we represented a Carnot engine symbolically as a rectangle in Figs. 7-5 and 7-7. Only reversible processes may be plotted on a *TS* diagram, because of the definition of entropy in Eq. (8.6). The *TS* diagram is particularly convenient for representing all the idealized reversible cycles for various heat engines. The closed curve shown in Fig. 8-5 consisting of an upper portion R_1 and a lower portion R_2 represents any reversible engine cycle that is not a Carnot cycle. The area under R_1 (positive area) is equal to the positive heat Q_1 absorbed by the system, and the area under R_2 (negative area) is equal to the negative heat Q_2 rejected by the system. The area inside the closed curve is, therefore, $Q_1 - Q_2$, or W. The thermal efficiency of the engine is W/Q_1, which may be measured directly from the diagram.

Other processes are also plotted on a *TS* diagram. For a reversible *isobaric* process, the curve has a slope that follows from Eq. (8.7) by imposing constant pressure; thus,

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}. \tag{8.12}$$

Similarly, by imposing the condition of constant volume on the equation preceding Eq. (8.9), the slope of a reversible *isochoric* process is given by

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}. \tag{8.13}$$

The slopes given by Eqs. (8.12) and (8.13) are independent of the nature of the hydrostatic system, because the requirement of constant pressure and constant volume eliminated the equation of state of the ideal gas used in Eqs. (8.7) and

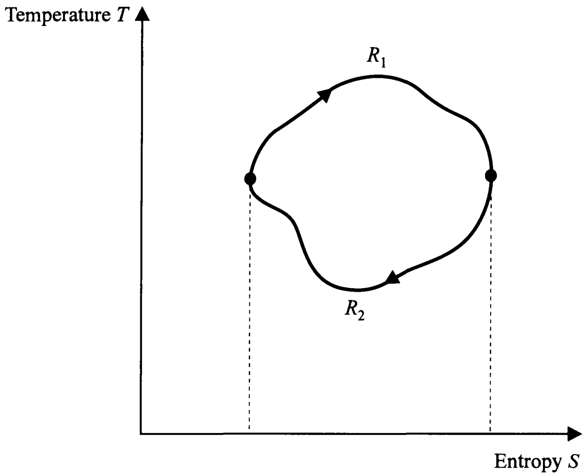

FIGURE 8-5
An arbitrary reversible cycle on a *TS* diagram. The area under upper portion R_1 equals the positive heat Q_1 absorbed by the system; the area under lower portion R_2 equals the negative heat Q_2 rejected by the system. The Carnot cycle for the same system would be represented by a rectangle enclosing the closed curve.

(8.10). Curves representing various types of processes of a hydrostatic system are shown on a *TS* diagram in Fig. 8-6.

8.6
ENTROPY AND REVERSIBILITY

In order to understand the physical meaning of entropy and its significance, it is necessary to study *all* the entropy changes that take place when a system undergoes a reversible process. If we calculate the entropy change of the system and add the calculated entropy change of the surroundings, then we obtain the sum of the entropy changes brought about by this particular process. We may call this sum the *entropy change of the universe* due to the process in question.

When a finite amount of heat is absorbed or rejected by a reservoir, extremely small changes in the coordinates occur in every unit of mass of the reservoir. The entropy change of a unit of mass is, therefore, very small. However, since the total mass of a reservoir is large, the total entropy change of the reservoir is finite. Suppose that a reservoir is in contact with a system and that heat Q is absorbed irreversibly by the reservoir at the temperature T. The reservoir undergoes nondissipative changes determined entirely by the quantity of heat absorbed. Exactly the same changes *in the reservoir* would occur if the same amount of heat Q were transferred reversibly. Hence, the entropy change of the reservoir is Q/T. Therefore, *whenever a reservoir absorbs heat Q at the temperature T from any system during any kind of process, the entropy change of the* **reservoir** *is Q/T.*

Consider now the entropy change of the universe that is brought about by the performance of any reversible process. The process will, in general, be accompanied by a flow of heat between a system and a set of reservoirs

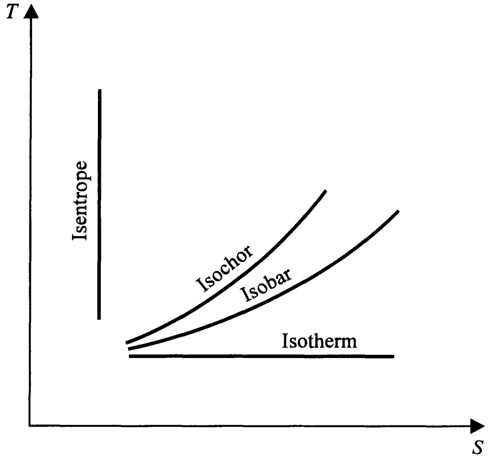

FIGURE 8-6
Curves representing reversible processes of a hydrostatic system on a *TS* diagram.

ranging in temperature from T_i to T_f. During *any* infinitesimal portion of the process, an amount of heat $đQ_R$ is transferred between the system and one of the reservoirs at the temperature T. If $đQ_R$ is absorbed by the system, then

$$dS \text{ of the system } = +\frac{đQ_R}{T},$$

$$dS \text{ of the reservoir } = -\frac{đQ_R}{T},$$

and the entropy change of the universe, which is the sum of these two changes, is zero. If $đQ_R$ is rejected by the system, then, obviously,

$$dS \text{ of the system } = -\frac{đQ_R}{T},$$

$$dS \text{ of the reservoir } = +\frac{đQ_R}{T},$$

and the entropy change of the universe is again zero. If no heat is transferred, then $đQ_R$ is zero. Neither the system nor the reservoir will have an entropy change, and the entropy change of the universe is still zero. Since there is no infinitesimal entropy change of the universe for any infinitesimal portion of the reversible process, then there is no entropy change for all such portions. In general, *the change of entropy of the universe is zero for a reversible process.* In other words, when a reversible process is performed, the entropy of the universe remains unchanged. However, all natural processes are irreversible and only ideal processes are reversible.

8.7
ENTROPY AND IRREVERSIBILITY

During an *irreversible* process, there is a different situation for the entropy change of the universe. When a system undergoes an irreversible process between an initial equilibrium state and a final equilibrium state, the irreversible process is replaced by a reversible one. This replacement is permitted when the initial and the final state of the system are equilibrium states. No integration is performed over the original irreversible path, because the path is not known. The entropy change of the system is equal to

$$S_f - S_i = {}_R\int_i^f \frac{đQ}{T},$$

where R indicates *any arbitrarily chosen* reversible process by which the system is brought from the given initial state to the given final state of the irreversible process. When either the initial or the final state is a nonequilibrium state, special methods must be used, which will discussed in Sec. 8.10. For the present, we shall limit ourselves to irreversible processes, all of which involve initial and final states of equilibrium.

Processes exhibiting external mechanical irreversibility

(*a*) Examples are those processes involving the isothermal dissipation of work through a system (which remains unchanged) into internal energy of a reservoir, such as:

1. Friction from two solids in contact with a reservoir.
2. Irregular stirring of a viscous liquid in contact with a reservoir (e.g., Joule paddle wheel apparatus).
3. Inelastic deformation of a solid in contact with a reservoir.
4. Transfer of charge through a resistor in contact with a reservoir.
5. Magnetic hysteresis of a material in contact with a reservoir.

In the case of any process involving the *isothermal* transformation of work W done by a system into internal energy of a reservoir, there is no entropy change of the system because the thermodynamic coordinates of the system do not change, as stated in Sec. 6.10. Heat Q is absorbed by the reservoir, where $Q = W$ from the work done on the reservoir. Since the reservoir absorbs $+Q$ units of heat at the temperature T, the entropy change of the reservoir is $+Q/T$ or $+W/T$. The entropy change of the universe is, therefore, also $+W/T$, which is a positive quantity.

(*b*) Further examples are those processes involving the adiabatic dissipation of work into internal energy of a system open to the atmosphere, such as:

1. Friction from rubbing thermally insulated liquids.
2. Irregular stirring of a viscous thermally insulated liquid.
3. Inelastic deformation of a thermally insulated solid.
4. Transfer of charge through a thermally insulated resistor.
5. Magnetic hysteresis of a thermally insulated material.

In the case of any process involving the *adiabatic* transformation of work W into internal energy of a system whose temperature *rises* from T_i to T_f at constant atmospheric pressure, there is no flow of heat to or from the surroundings, and, therefore, the entropy change of the local surroundings is zero. To calculate the entropy change of the system, the original irreversible process must be replaced by a reversible one that will take the system from the given initial state (temperature T_i, pressure P) to the final state (temperature T_f, pressure P). Let us replace the irreversible performance of work by a reversible isobaric flow of heat from a series of reservoirs ranging in temperature from T_i to T_f. The entropy change of the system will then be

$$S_f - S_i\,(\text{system}) = {}_R\!\int_{T_i}^{T_f} \frac{đQ}{T}.$$

For an isobaric process,

$$đQ = C_P\,dT,$$

and, so,
$$S_f - S_i\,(\text{system}) = \int_{T_i}^{T_f} C_P \frac{dT}{T}.$$

Finally, if C_P is assumed not to be a function of temperature, then the entropy change of the system is

$$S_f - S_i\,(\text{system}) = C_P \ln \frac{T_f}{T_i}. \tag{8.14}$$

Thus, the entropy change of the universe is also $C_P \ln\,(T_f/T_i)$, which is a positive quantity.

Processes exhibiting internal mechanical irreversibility. Examples are those processes involving the transformation of internal energy of a system enclosed by adiabatic walls into mechanical energy and then back into internal energy again, such as:

1. Ideal gas rushing into a vacuum (free expansion, i.e., Joule expansion).
2. Gas flowing through a porous plug (throttling process, i.e., Joule-Thomson expansion).
3. Snapping of a stretched wire after it is cut.
4. Collapse of a soap film after it is punctured.

In the case of a free expansion of the ideal gas, the entropy change of the local surroundings is zero, because there is no heat transfer through the adiabatic walls. In order to calculate the entropy change of the system, the free expansion must be replaced by a reversible process that will take the gas from its original state (volume V_i, temperature T) to the final state (volume V_f, temperature T), where temperature does not change for the ideal gas during expansion. Evidently, the most convenient reversible process to replace the irreversible process, for the purpose of calculation, is a reversible isothermal expansion at the temperature T from a volume V_i to the volume V_f. The entropy change of the system is then

$$S_f - S_i\,(\text{system}) = {}_R\!\int_{V_i}^{V_f} \frac{đQ}{T}.$$

For an isothermal process of the ideal gas,

$$đQ_R = P\,dV,$$

and
$$\frac{đQ_R}{T} = nR\,\frac{dV}{V},$$

which yields, for the entropy change of the system,

$$S_f - S_i\,(\text{system}) = nR\ln\frac{V_f}{V_i}. \tag{8.15}$$

The entropy change of the universe is, therefore, $nR\ln(V_f/V_i)$, which is a positive number.

Once again, we see that the entropy of the universe, which is the system, has increased, even though no heat entered or left the system. This result may seem puzzling, because entropy is defined in terms of the heat entering or leaving a system. The puzzle is resolved by recognizing that the free expansion of the ideal gas within an adiabatic container is not a *reversible* process. During an irreversible process, the entropy change of the universe, even if the process is adiabatic, is always positive.

Processes exhibiting external thermal irreversibility. Examples are those processes involving a transfer of heat by virtue of a *finite* temperature difference, such as:

1. Conduction or radiation of heat from a system to its cooler surroundings.
2. Conduction or radiation of heat through a system (which remains unchanged) from a hot reservoir to a cooler one.

In the case of the conduction of Q units of heat from one end to the other end of a system (which remains unchanged) from a hotter reservoir at T_1 to a cooler reservoir at T_2, the following steps are obvious:

$$S_f - S_i\,(\text{system}) = 0.$$

$$S_f - S_i\ (\text{hotter reservoir}) = -\frac{Q}{T_1}.$$

$$S_f - S_i\ (\text{cooler reservoir}) = +\frac{Q}{T_2}.$$

$$S_f - S_i\ (\text{universe}) = \frac{Q}{T_2} - \frac{Q}{T_1}. \tag{8.16}$$

The entropy change of the universe is positive, because T_2 is less than T_1.

Processes exhibiting chemical irreversibility. Examples are those processes involving a spontaneous change of internal structure, density, chemical composition, etc., such as:

1. Diffusion of two dissimilar inert ideal gases.
2. Mixing of alcohol and water.
3. Osmosis.
4. Freezing of supercooled liquid.
5. Condensation of a supersaturated vapor.
6. Dissolution of a solid in water.
7. A chemical reaction.

Assume that the diffusion of two dissimilar inert ideal gases is equivalent to two separate free expansions in an adiabatic enclosure with chambers of equal volume. For one of the gases, the change of entropy is given by Eq. (8.15),

$$S_f - S_i \text{ (system)} = nR \ln \frac{V_f}{V_i},$$

namely,

$$S_f - S_i \text{ (one gas)} = nR \ln \frac{V_f}{V_i},$$

which is a positive number, because $V_f/V_i > 1$. The other half of the system experiences the same entropy change. Since there is no entropy change of the reservoir, the entropy change of the universe is

$$S_f - S_i \text{ (universe)} = 2nR \ln \frac{V_f}{V_i}, \tag{8.17}$$

which is a positive number. In general, *the change of entropy is positive for any irreversible process.* All the results of this section are summarized in Table 8.1.

TABLE 8.1
Entropy change of the universe due to natural processes

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal energy of a reservoir	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system	$C_P \ln \frac{T_f}{T_i}$	0	$C_P \ln \frac{T_f}{T_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas	$nR \ln \frac{V_f}{V_i}$	0	$nR \ln \frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hotter to a cooler reservoir	0	$\frac{Q}{T_2} - \frac{Q}{T_1}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases	$2nR \ln \frac{V_f}{V_i}$	0	$2nR \ln \frac{V_f}{V_i}$

8.8
IRREVERSIBLE PART OF THE SECOND LAW

The first part of the second law considered only reversible processes. The second part deals with irreversible processes. Recall that for a reversible cycle, Eq. (8.3) states that

$$\oint_R \frac{đQ}{T} = 0 \qquad \text{(reversible)}. \tag{8.3}$$

Let us consider an *irreversible* cycle and calculate its closed integral. Figure 8-7 shows a high-temperature reservoir at T_1 supplying a small quantity of heat $đQ_1$ to an auxiliary reversible engine R. The purpose of R is to provide reversible heat for the irreversible engine I. Engine R rejects a small amount of heat $đQ$ at temperature T that is supplied to the irreversible engine I. Engine I does a small amount of work $đW$ during an irreversible cycle, so the combined system of engine R and engine I also performs an irreversible cycle. The net work of the combined system, according to the first law, equals $\oint đQ_1$. But the net work cannot be positive, according to the Kelvin-Planck statement of the second law, since the combined system exchanges heat with a single reservoir. So, $\oint đQ_1$ cannot be positive. Moreover, if $\oint đQ_1$ equals zero, then, at the end of the cycle, engine I and its surroundings have returned to their original state. This result, however, is contrary to the irreversibility of engine I. So, we conclude,

$$\oint_R đQ_1 < 0; \tag{8.18}$$

that is, engine I generates heat that flows out of the system. From the definition of the thermodynamic temperature scale, Eq. (7.6), we have, in differential form for reversible engine R,

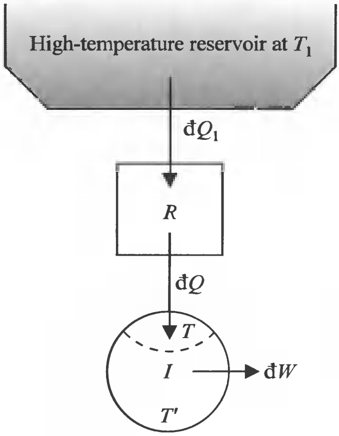

FIGURE 8-7
A high-temperature reservoir at temperature T_1 supplies heat $đQ_1$ to an auxiliary reversible engine R. Irreversible engine I receives heat $đQ$ at temperature T, even though the system was initially at temperature T'.

$$\frac{đQ_1}{T_1} = -\frac{đQ}{T}.$$

Integrating around a cycle,

$$\oint_R \frac{-đQ}{T} = \oint_R \frac{đQ_1}{T_1}.$$

However, T_1 is the constant temperature of the reservoir, so

$$-\oint_R \frac{đQ}{T} = \frac{1}{T_1} \oint_R .đQ_1. \tag{8.19}$$

The heat $đQ$ rejected from R is absorbed by I, so, $-đQ_R = đQ_I$. Substituting this expression in Eq. (8.19) and recognizing that the closed integral on the left now applies to the irreversible system, we obtain

$$\oint_I \frac{đQ}{T} = \frac{1}{T_1} \oint_R đQ_1,$$

or

$$T_1 \oint_I \frac{đQ}{T} = \oint_R đQ_1 < 0$$

from Eq. (8.18). Since $T_1 > 0$, the result is

$$\boxed{\oint_I \frac{đQ}{T} < 0} \quad \text{(irreversible).} \tag{8.20}$$

Equation (8.20) provides the second part of the second law and is known as the *inequality of Clausius*. It states that *for an internally irreversible cycle, the closed integral* $_I\oint đQ/T$ *of the ratio of the heat absorbed by a system to the temperature* **at which the heat is received** *is always less than zero.* Compare Eq. (8.20) with Eq. (8.3) and notice that the closed integral is less than zero for an irreversible cycle and equal to zero for a reversible cycle. Combining the two equations yields Clausius' mathematical statement of the second law:

$$\boxed{\oint \frac{đQ}{T} \leq 0.} \tag{8.21}$$

In order to avoid misunderstandings as to the meaning of Eq. (8.3), the equality for reversible cycles, and Eq. (8.20), the inequality for irreversible cycles, we must point out that T represents the temperature of the reservoir or auxiliary reversible engine that provides the small quantity of heat $đQ$, and is *not* necessarily equal to the temperature T' of the system (or part of the system) that receives the heat $đQ$. Indeed, if the cycle is irreversible, then $T' \leq T$ when $đQ$ is positive, because heat cannot flow spontaneously from a cooler to a hotter body. Similarly, $T' \geq T$ when $đQ$ is negative. On the other hand, if the cycle is reversible, then we must always have $T' = T$, because an exchange of heat between two bodies at different temperatures is not reversible. In Eq. (8.3), we may take T to be the temperature of the reservoir or auxiliary surroundings and also the temperature of the part of the system that absorbs the heat $đQ$. In Eq. (8.3), all quantities refer to the system itself, and the integral is evaluated for a closed path taken by the reversible system. In Eq. (8.20), everything refers to the auxiliary reservoirs, and the integral is evaluated for a closed range of reservoir temperatures through which, incidentally, the irreversible system is brought back to its initial state.

8.9
HEAT AND ENTROPY IN IRREVERSIBLE PROCESSES

In order to relate change of entropy to heat in irreversible processes, consider a cycle in which a system begins in an initial equilibrium state i, passes during an irreversible process I to a final equilibrium state f, and then returns by a reversible process R to the initial state i, as shown in Fig. 8-8. Since entropy is a state function, its closed integral is always zero:

$$\oint dS = {}_{I}\!\int_i^f dS + {}_{R}\!\int_f^i dS = 0. \tag{8.22}$$

From Eq. (8.20) we obtain

$$_{I}\!\oint \frac{đQ}{T} = {}_{I}\!\int_i^f \frac{đQ}{T} + {}_{R}\!\int_f^i \frac{đQ}{T} < 0. \tag{8.23}$$

From Eq. (8.6), the definition of entropy, we can write

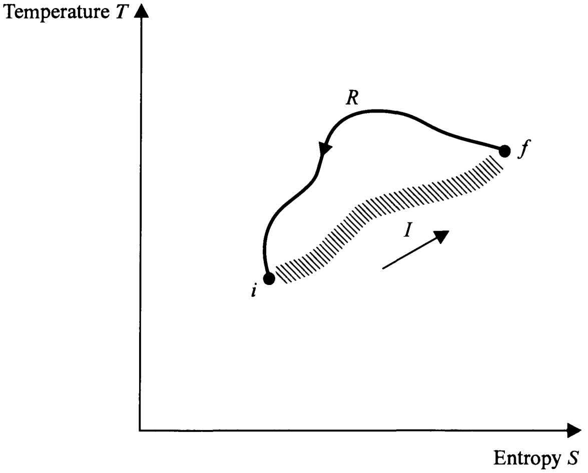

FIGURE 8-8
An irreversible process followed by a reversible process to complete an irreversible cycle.

$$\int_{R\,i}^{f} \frac{đQ}{T} = \int_{R\,i}^{f} dS.$$

Subtract Eq. (8.23) from Eq. (8.22) and substitute the equation cited above; then,

$$\int_{I\,i}^{f} dS - \int_{I\,i}^{f} \frac{đQ}{T} > 0,$$

or

$$\int_{I\,i}^{f} dS > \int_{I\,i}^{f} \frac{đQ}{T}, \tag{8.24}$$

which means that the change of entropy during an irreversible process is greater than the integral of the heat divided by the temperature of the auxiliary reservoirs.

For small changes in state, Eq. (8.24) can be written

$$dS_I > \left(\frac{đQ}{T}\right)_I. \tag{8.25}$$

In general, we have

$$dS \geq \frac{đQ}{T}, \tag{8.26}$$

where the equality applies to reversible processes and the inequality applies to irreversible processes.

Various expressions for conditions involving entropy require careful consideration. According to the definition of entropy in Eq. (8.6),

$$dS = \frac{đQ_R}{T},$$

the change in entropy in a reversible and adiabatic process ($đQ_R = 0$) is zero. Thus, the term *reversible adiabatic* implies the term *isentropic*. *Isentropic*, however, does not necessarily imply *reversible adiabatic*. For an isentropic process, in general, we have

$$dS = 0.$$

Substituting Eq. (8.26) into this expression, we have

$$\frac{đQ}{T} \leq 0.$$

It follows that for an isentropic process, *either*

$$đQ = 0 \qquad \text{(reversible)},$$

or

$$đQ < 0 \qquad \text{(irreversible)}.$$

Thus, *reversible isentropic* implies *adiabatic*, and *isentropic adiabatic* implies *reversible*. But, *irreversible isentropic* is *not* adiabatic ($đQ < 0$) and implies that heat flows out of the system. Of course, if the process is *irreversible adiabatic*, then it is *not* isentropic (T not constant) and implies that the temperature increases. Finally, if the process is *isentropic adiabatic*, then it is *not* irreversible ($đQ_R = 0$) and implies that the process is reversible.

8.10
ENTROPY AND NONEQUILIBRIUM STATES

The calculation of the entropy changes associated with the irreversible processes discussed in Sec. 8.7 presented no special difficulties because, in all cases, the system either did not change at all (in which case, only the entropy changes of reservoirs had to be calculated) or *both* the initial and final states of a system were equilibrium states that could be connected by a suitable reversible process. Consider, however, the following process involving internal thermal irreversibility with equilibrium only in the final state. A thermally conducting bar has a nonuniform temperature distribution by connecting one end to a high-temperature reservoir and the other end to a low-temperature reservoir. The bar is removed from the reservoirs and is then thermally insulated with adiabatic walls at constant pressure. An internal flow of heat will finally bring the bar to a uniform temperature, so the irreversible process will be from an initial nonequilibrium state to a final equilibrium state. It is obviously impossible to replace the irreversible process with a reversible process, because the initial state is a nonequilibrium state. What meaning, therefore, may be attached to the entropy change associated with this irreversible process?

Let us consider a bar to be composed of an infinite number of infinitesimally thin slices (volume elements), each of which has a different initial temperature but all of which have the same final temperature. Suppose we imagine that all the slices are insulated from one another and all are kept at the same pressure, and then each slice is put in contact successively with a series of reservoirs ranging in temperature from the initial temperature of the particular section to the common final temperature. This model defines an infinite number of reversible isobaric processes for each slice, which may be used to take each slice of the system from its initial nonequilibrium state to its final equilibrium state. We shall now define the entropy change as the result of integrating $đQ/T$ over all of these reversible processes. In other words, in the absence of one reversible process to take the system from i to f, we conceive of an infinite number of reversible processes for each volume element.

Consider a uniform bar of length L as depicted in Fig. 8-9. A typical volume element at x has a mass

$$dm = \rho A\, dx,$$

where ρ is the density and A is the cross-sectional area of the bar. The heat capacity of the *volume element* is

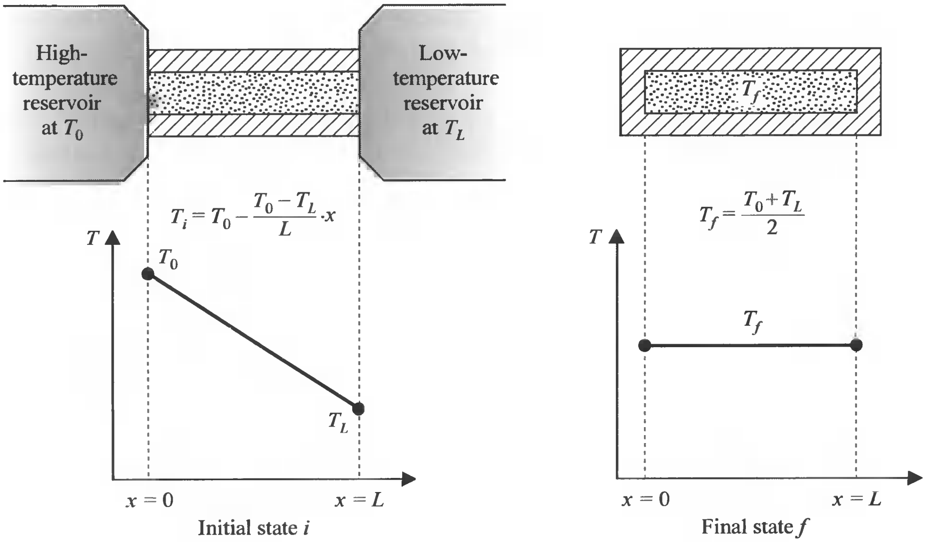

FIGURE 8-9
Process exhibiting internal thermal irreversibility.

$$c_P \, dm = c_P \rho A \, dx.$$

Let us suppose that the initial temperature distribution is linear along the length of the bar, so that the volume element at x has an initial temperature

$$T_i = T_0 - \frac{T_0 - T_L}{L} x,$$

where the temperature is T_0 at $x = 0$, and T_L at $x = L$. If no heat is lost and if we assume for the sake of simplicity that the thermal conductivity, density, and heat capacity of all volume elements remain constant, then the final temperature of the entire length of the bar will be

$$T_f = \frac{T_0 + T_L}{2}.$$

Integrating $\text{đ}Q/T$ over a reversible isobaric transfer of heat between a particular volume element and a series of reservoirs ranging in temperature from T_i to T_f, we get, for the entropy change of *this one volume element*,

$$\begin{aligned}
S_f - S_i \text{ (volume element)} &= c_P \rho A\, dx \int_{T_i}^{T_f} \frac{dT}{T} \\
&= c_P \rho A\, dx \ln \frac{T_f}{T_i} \\
&= c_P \rho A\, dx \ln \frac{T_f}{T_0 - \dfrac{T_0 - T_L}{L} x} \\
&= -c_P \rho A\, dx \ln \left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{L T_f} x \right).
\end{aligned}$$

Upon integrating over the whole bar, the total entropy change of the system is

$$S_f - S_i \text{ (system)} = -c_P \rho A \int_0^L \ln \left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{L T_f} x \right) dx,$$

which, after integration[†] and simplification, becomes

$$S_f - S_i \text{ (system)} = C_P \left[1 - \ln \left(\frac{T_L}{T_f} \right) + \frac{T_0}{T_0 - T_L} \ln \left(\frac{T_L}{T_0} \right) \right]. \tag{8.27}$$

Since the bar is enclosed by an adiabatic enclosure, there is no entropy change of the surroundings. Hence, the entropy change of the universe is also given by Eq. (8.27). In order to show that the entropy change is positive, let us take a convenient numerical case, such as $T_0 = 400\,\text{K}$, $T_L = 200\,\text{K}$; hence, $T_f = 300\,\text{K}$. Then,

$$\begin{aligned}
S_f - S_i \text{ (universe)} &= C_P(1 - \ln \tfrac{2}{3} + 2 \ln \tfrac{1}{2}) = C_P(1 + \ln 3 - 3 \ln 2) \\
&= 0.018\, C_P,
\end{aligned}$$

where it is seen that entropy and heat capacity have the same units: joule per kelvin.

The same method may be used to compute the entropy change of a system during a process from an initial nonequilibrium state, characterized by a nonuniform pressure distribution, to a final equilibrium state where the pressure is uniform. Examples of such processes are given in the problems at the end of the chapter.

8.11
PRINCIPLE OF INCREASE OF ENTROPY

The entropy change of the universe was found to be positive for each of the irreversible processes treated so far. We are led to believe, therefore, that

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[†] $\int \ln (a + bx)\, dx = \frac{1}{b}(a + bx)[\ln (a + bx) - 1]$.

whenever an irreversible process occurs, the entropy of the universe increases. To establish this proposition, known as the *entropy principle*, in a general manner, it is sufficient to confine our attention to adiabatic processes only, since we have already seen that the entropy principle is true for all processes involving the irreversible transfer of heat. We start by considering the special case of an adiabatic irreversible process between two equilibrium states of a system.

1. Let the initial state of the system be represented by the point i on the generalized work diagram of Fig. 8-10, and suppose that the system undergoes an *irreversible adiabatic process* to the state f. Then the entropy change is

$$\Delta S = S_f - S_i. \tag{8.28}$$

A temperature change may or may not have occurred in the system. Whether or not, let us cause the system to undergo a *reversible adiabatic process* $f \rightarrow k$ in a sequence of steps that brings the temperature of the system to the temperature of any arbitrarily chosen reservoir, say, at T'. Then, since $S_f = S_k$, Eq. (8.28) becomes

$$\Delta S = S_k - S_i. \tag{8.29}$$

Now, suppose that the system is brought into contact with the reservoir at T' and the system undergoes a *reversible isothermal process* $k \rightarrow j$ until its entropy is the same in state j as in the initial state i. A final *reversible adiabatic process* $j \rightarrow i$ will now bring the system back to its initial state with no change of entropy; and, since $S_j = S_i$, Eq. (8.29) becomes

$$\Delta S = S_k - S_j. \tag{8.30}$$

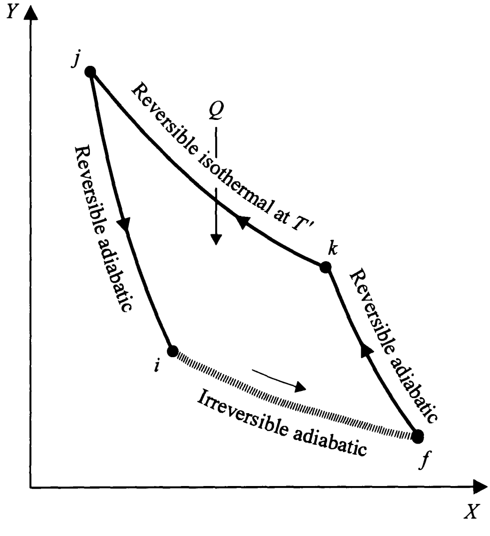

FIGURE 8-10
A cycle that contradicts the second law unless $S_f > S_i$.

The only heat transfer Q_R occurred in the cycle during the reversible isothermal process $k \rightarrow j$, where

$$Q_R = T'(S_j - S_k).$$

A net amount of work W has been done in the cycle, where

$$W = Q_R.$$

It is clear from the second law of thermodynamics that the heat Q_R cannot have entered the system, that is, Q_R cannot be positive, for then we would have a cyclic process where the only effect would be the absorption of heat from a single reservoir and the performance of an equivalent amount of work. Therefore, $Q_R \leq 0$, and

$$T'(S_j - S_k) \leq 0,$$

and, finally, since the process went from state k to state j,

$$T'(S_k - S_j) \geq 0.$$

However, $T' \geq 0$, so

$$S_k - S_j = \Delta S \geq 0. \tag{8.31}$$

2. If we assume that the original irreversible adiabatic process occurred without any change in entropy, then it would be possible to bring the system back to i by means of one reversible adiabatic process. Moreover, since the net heat transferred in this cycle is zero, the net work would also be zero. Therefore, under these circumstances, the system and its surroundings would have been restored to their initial states without producing changes elsewhere, which implies that the original process was reversible. Since this is contrary to our original assertion that the process was irreversible, the entropy of the system cannot remain unchanged. Therefore,

$$\Delta S > 0, \tag{8.32}$$

because the entropy change could not have decreased.

3. Let us now suppose that the system is not homogeneous and not at uniform temperature and pressure and that it undergoes an irreversible adiabatic process in which mixing and chemical reaction may take place. First, we assume that the system may be subdivided into parts (each one infinitesimal, if necessary) and that it is possible to assign a definite temperature, pressure, composition, etc., to each part, so that each part shall have a definite entropy depending on its coordinates, so we may define the entropy changes of the whole system as the sum of the entropy changes of its parts. Second, if we assume that it is possible to take *each part* back to its initial state by means of the reversible processes described in 1 above, using the same reservoir for each part, then it follows that ΔS of the whole system is positive.

It should be emphasized that we have had to make two assumptions, namely: (1) that the entropy change of a system may be defined by subdividing the system into parts and summing the entropy changes of these parts; and (2) that reversible processes may be found or imagined by which mixtures may be unmixed and reactions may be caused to proceed in the opposite direction. The justification for these assumptions rests, to a small extent, on experimental grounds. Thus, in a later chapter, there will be described a device involving semipermeable membranes whereby a mixture of two different inert ideal gases may be separated reversibly. A similar device through which a chemical reaction may be caused to proceed reversibly through any set of equilibrium states may also be conceived. Nevertheless, the main justification for these assumptions is that experiment completely agrees with the *entropy principle*, which states that the change of entropy of the universe increases in an irreversible process.

The behavior of the entropy of the universe as a result of *any* kind of process may now be represented simply:

$$\boxed{\Delta S\,(\text{universe}) \geq 0,} \tag{8.33}$$

where the equality sign refers to reversible processes and the inequality sign to irreversible processes. Equation (8.33) is a succinct statement of the second law of thermodynamics.

8.12
APPLICATION OF THE ENTROPY PRINCIPLE

We have seen that whenever irreversible processes occur, the entropy of the universe increases. In the actual operation of a machine, such as an engine or a refrigerator, it is often possible to calculate the sum of all the entropy changes. The fact that this sum is positive enables us to draw useful conclusions concerning the behavior of the machine. An important example from the field of low-temperature physics will illustrate the power and simplicity of the entropy principle. Suppose one wants to cool an object with a refrigerator to a desired low temperature, that is, to lower the temperature of a body of finite mass from the temperature T_1 of its surroundings to any desired low temperature T_2. A refrigerator operating in a cycle between a reservoir at T_1 and the body itself is utilized, and, after several complete cycles have been completed, a quantity of heat Q has been removed from the body, a quantity of work W has been supplied to the refrigerator, and a quantity of heat $Q + W$ has been rejected to the reservoir, as shown in Fig. 8-11. Listing the entropy changes, we have

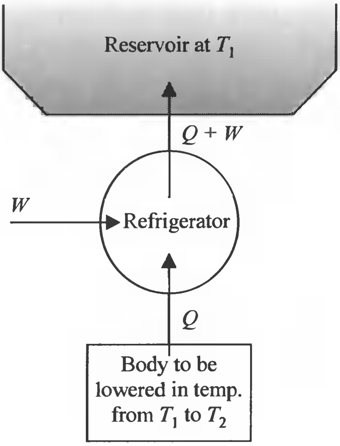

FIGURE 8-11
Operation of a refrigerator in lowering the temperature of a body from that of its surroundings T_1 to any desired temperature T_2.

$$\Delta S \text{ of the body} = S_2 - S_1,$$

$$\Delta S \text{ of the refrigerant} = 0,$$

and

$$\Delta S \text{ of the reservoir} = \frac{Q + W}{T_1}.$$

Applying the entropy principle, we obtain

$$S_2 - S_1 + \frac{Q + W}{T_1} \geq 0.$$

Multiplying by T_1 and transposing, we get

$$W \geq T_1(S_1 - S_2) - Q.$$

It follows that the smallest possible value for W is

$$W(\text{min}) = T_1(S_1 - S_2) - Q.$$

If tables of the thermodynamic properties of the material are available, then a knowledge of the initial and final states is all that is needed to read from the tables the values of $S_1 - S_2$ and, if the body undergoes an isobaric process, the values of Q. The calculated value of W (min) is used to provide an estimate of the minimum cost of operation of the refrigerator.

8.13
ENTROPY AND DISORDER

When applied to an irreversible process, Eq. (8.33) is very unusual in being an inequality. Unlike most quantities in physics and chemistry, the change of entropy of the system and its surroundings is not conserved, rather, it increases. In order to appreciate the concept of entropy, let us consider various natural processes and look for insights that are consistent with calculations.

First-order phase changes are irreversible,† isothermal processes that lend themselves to a descriptive discussion of entropy. For example, consider the phase change of sublimation, the transition of a solid to a vapor that occurs in dry ice. The change of entropy, which is the amount of heat absorbed during the sublimation divided by the sublimation temperature, increases as expected. But what can be said about the microscopic changes that occur when carbon dioxide molecules of dry ice escape from the solid into the vapor?

A solid is capable of supporting itself, whether in a crystalline state or amorphous state. Moreover, the material in the solid phase retains its size and shape, which means that the microscopic components (particles) of the system form a rigid structure. Simply stated, each particle retains its location in an organized strucure; that is, the solid is in a state of *order*.

As latent heat is supplied to a solid, the process of sublimation changes the solid into a vapor with no change of temperature. A vapor has no fixed size and shape; in fact, a vapor must be placed in a closed container or it is lost. The particles in the vapor are not individually restrained into any organized structure; rather, the vapor particles are free to move independently throughout the volume of the container. In other words, the vapor is in a state of *disorder*, relative to its solid phase. *An increase in entropy of a system can be described as an increase in the disorder of the system.* Notice that the concept of disorder is relative to a reference state, just as entropy is.

The use of disorder as a synonym for entropy can be extended beyond phase transitions as the following examples show.

1. The temperature of an ideal gas does not change and heat is not added to the system during a free expansion, yet the entropy increases, as seen in Eq. (8.15). The only difference between the initial state and the final state of the ideal gas is an increase of volume, which provides the gas particles with more space for their motion. Disorder, in this case, is not linked to a structural change that provides freedom of movement, as in the case of sublimation, but, rather, *more* freedom of movement is provided in a larger volume.
2. When the temperature of a ferromagnetic material is raised above its Curie point, the material suddenly loses its ferromagnetism and becomes paramagnetic. In the microscopic picture, the magnetic moments of the ferromagnetic material are mostly aligned in one direction (ordered). At temperatures above the Curie point, the magnetic moments are randomly

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† Ordinarily, there is a finite difference in temperature between the reservoir and a system experiencing a phase transition; hence, Eq. (8.16) applies and the process is irreversible. If the difference in temperature is made increasingly smaller, then the process becomes more nearly reversible, but at the expense of slowing the rate of heat-flow between the reservoir and the system, which slows the rate of the transition from one phase to the other phase.

oriented (disordered) to produce paramagnetic behavior. From a thermodynamic point of view, the entropy increases in the transition from ferromagnetism to paramagnetism.

3. In the case of conduction of heat through a metal bar from a high-temperature reservoir to a low-temperature reservoir, there is no change of phase, volume, or temperature of the conductor, but the entropy of the universe increases, as seen in Eq. (8.16). The internal energy becomes disordered in its passage between reservoirs, because the internal energy has been dissipated in the low-temperature reservoir and cannot be used to run a heat engine.
4. The entropy increases in an isothermal conversion of work into internal energy, which then flows into a heat reservoir, such as occurs with the Joule paddle wheel shown in Fig. 8.4. It has been emphasized that work is a macroscopic concept. Changes must be describable by macroscopic coordinates external to the system, although the internal situation may be discussed, at least in the equilibrium state. Haphazard motions of individual particles do not constitute work. Thus, during the isothermal dissipation of work into heat, the disorderly motion of the particles in the reservoir is increased. The process increases the entropy of the reservoir, since the system is unchanged.

All these examples, involving irreversible processes, show that the entropy of the universe increases. It is possible to regard all natural processes from the point of view of orderliness, and, in all cases, the result obtained is that *isolated systems or systems plus surroundings experiencing irreversible processes proceed toward a state of greater disorder.* The increase of entropy of the universe during natural processes is an expression of this tendency. Living processes, such as growth or decay, are natural processes that increase disorder, when both the system and surroundings are considered, but the calculation of the increase of entropy is not simple, even in idealized cases.

The concept of entropy has importance in the discussion of time, a topic usually avoided in thermodynamics. The increase of entropy (disorder) of a system and its surroundings occurs in all aging processes, whether in a living organism or in an inanimate system. There is no doubt which condition is prior in time: youth or maturity, green apple or overripe apple, structure or erosion. One condition always precedes the other; order precedes disorder. Entropy always increases during an aging process. So, in a metaphorical sense, *entropy is the arrow of time.* Furthermore, the arrow has only one direction: it points forward into the future. True, special relativity provides that the forward progress of time slows down when masses approach the speed of light. But, so far, there is no consensus that time can be reversed to move backward into the past.

8.14
EXACT DIFFERENTIALS

Experiment shows that internal energy is related to heat and work in the following equation,

$$dU = đW + đQ,$$

which is, of course, the first law of thermodynamics. Apart from the obvious observation that energy is conserved in all its forms, there are two other insights important for thermodynamics. First, the small quantities of heat and work are *not* differentials of a mathematical function; that is, they are inexact differentials. But, more importantly, the sum of two inexact differentials yields an exact differential! The mathematical problem is to convert the inexact differentials into exact differentials.

The situation for $đW$ is solved in mechanics, where the generalized work is the product of the generalized force and the generalized displacement, as shown in Table 3.1 (p. 66). The situation for $đQ$ is more complicated.

In order to clarify the notion of heat, the concept of temperature had first to be refined. That required a detailed discussion of thermometers, experimental temperature, and the second law of thermodynamics applied to the Carnot cycle. As a result, the concept of temperature was detached from experiment to become the theoretical absolute thermodynamic temperature. Furthermore, Clausius introduced a totally new concept based on his analysis of a reversible cycle composed of many infinitesimal Carnot cycles, namely, the concept of entropy. The union of the concepts of temperature and entropy produced a way to express the inexact differential of heat in terms of exact differentials,

$$đQ = T\,dS.$$

Now, the first law can be rewritten in usable mathematical form, as, for example, in a hydrostatic system,

$$dU = -P\,dV + T\,dS.$$

In some ways, the thermodynamics is complete now that the inexact differentials for work and heat have been replaced with exact differentials. The only other fundamental law in thermodynamics is the third law, which sets entropy to zero at absolute zero, rather than setting it to zero at an arbitrary state. The remainder of this book is devoted to developing more mathematical functions and methods to aid in the calculation of the thermodynamic quantities, and bringing in quantum mechanics in the calculation of statistical mechanical quantities.

PROBLEMS

8.1. (*a*) Derive the expression for the efficiency of a Carnot engine directly from a *TS* diagram.
(*b*) Compare the efficiencies of cycles *A* and *B* of Fig. P8-1.

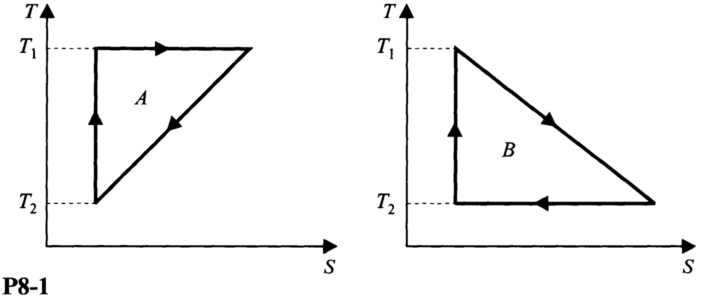

FIGURE P8-1

8.2. Prove that the slope on a *TS* diagram of:
(*a*) An isochoric curve is T/C_V.
(*b*) An isobaric curve is T/C_P.

8.3. Show that the partial derivatives given in Eqs. (8.12) and (8.13) are independent of the equation of state for the hydrostatic system.

8.4. Why does an isochoric curve plotted on a *TS* diagram have a greater slope than an isobaric curve at the same temperature?

8.5. Sketch *TS* diagrams for the following four ideal gas cycles: Otto; Diesel; a rectangle on a *PV* diagram; and a "right triangle" on a *PV* diagram in which the base is an isobaric, the altitude is an isochoric, and the "hypotenuse" is an adiabatic.

8.6. A current of 10 A is maintained for 1 s in a resistor of 25 Ω while the temperature of the resistor is kept constant at 27°C.
(*a*) What is the entropy change of the resistor?
(*b*) What is the entropy change of the universe?
The same current is maintained for the same time in the same resistor, but now thermally insulated, with the same initial temperature. If the resistor has a mass of 10 g and a specific heat of 836 J/kg · K:
(*c*) What is the entropy change of the resistor?
(*d*) What is the entropy change of the universe?

8.7. (*a*) One kilogram of water at 273 K is brought into contact with a heat reservoir at 373 K. When the water has reached 373 K, what is the entropy change of the water, of the heat reservoir, and of the universe?
(*b*) If the water had been heated from 273 to 373 K by first bringing it into contact with a reservoir at 323 K and then with a reservoir at 373 K, what would have been the entropy change of the universe?

(*c*) Explain how the water might be heated from 273 to 373 K with almost no change of entropy of the universe.

8.8. A body of constant heat capacity C_P and at a temperature T_i is put in contact with a reservoir at a higher temperature T_f. The pressure remains constant while the body comes to equilibrium with the reservoir. Show that the entropy change of the universe is equal to

$$\Delta S = C_P[x - \ln(1 + x)],$$

where $x = -(T_f - T_i)/T_f$. Prove that the entropy change is positive.

8.9. The molar heat capacity at constant magnetic field of a paramagnetic solid at low temperatures varies with the temperature and field according to the relation

$$c_{\mathcal{H}} = \frac{B + C\mathcal{H}^2}{T^2} + DT^2,$$

where B, C, and D are constants. What is the entropy change of n moles of material when the temperature changes from T_i to T_f while $\mathcal{H}$ remains constant at the value $\mathcal{H}_0$?

8.10. According to Debye's law, the molar heat capacity at constant volume of a diamond varies with the temperature as follows:

$$c_V = 3R\frac{4\pi^4}{5}\left(\frac{T}{\Theta}\right)^3.$$

What is the entropy change in units of R of a diamond of 1.2 g mass when it is heated at constant volume from 10 to 350 K? The molar mass of diamond is 12 g, and Θ is 2230 K.

8.11. A thermally insulated cylinder, closed at both ends, is fitted with a frictionless heat-conducting piston that divides the cylinder into two parts. Initially, the piston is clamped in the center with 1 liter of air at 300 K and 2 atm pressure on one side and 1 liter of air at 300 K at 1 atm pressure on the other side. The piston is released and reaches equilibrium in pressure and temperature at a new position. Compute the final pressure and temperature and increase of entropy if air is assumed to be the ideal gas. What irreversible process has taken place?

8.12. An adiabatic cylinder, closed at both ends, is fitted with a frictionless *adiabatic* piston that divides the cylinder into two parts. Initially the pressure, volume, and temperature are the same on both sides of the piston (P_0, V_0, and T_0). The gas is ideal with C_V independent of temperature and $\gamma = 1.5$. By means of a heating coil in the gas on the left side, heat is slowly supplied to the gas on the left until the pressure reaches $27P_0/8$. In terms of nR, V_0, and T_0:

(*a*) What is the final volume on the right side?
(*b*) What is the final temperature on the right side?
(*c*) What is the final temperature on the left side?
(*d*) How much heat must be supplied to the *gas* on the left side? (*Note*: Ignore the coil!)
(*e*) How much work is done on the gas on the right side?

(*f*) What is the entropy change of the gas on the right side?
(*g*) What is the entropy change of the gas on the left side?
(*h*) What is the entropy change of the universe?

8.13. Solve the problem of the uniform bar shown in Fig. 8-9 if only the hot reservoir is removed by showing that the entropy change of the universe is

$$\Delta S = C_P\left(1 + \frac{T_0 - T_L}{2T_L} - \frac{T_0}{T_0 - T_L}\ln\frac{T_o}{T_L}\right).$$

8.14. Calculate the entropy change of the universe as a result of the following processes:

(*a*) A copper block of 0.4 kg mass and with heat capacity at constant pressure of 150 J/K at 100°C is placed in a lake at 10°C.
(*b*) The same block at 10°C is dropped from a height of 100 m into the lake.
(*c*) Two such blocks at 100°C and 0°C are joined together.

8.15. What is the entropy change of the universe as a result of each of the following processes?

(*a*) A 1-μF capacitor is connected to a 100-V electrochemical cell at 0°C?
(*b*) The same capacitor, after being charged to 100 V, is discharged through a resistor kept at 0°C.

8.16. An ideal-gas cycle suggested by A. S. Arrott of British Columbia, Canada, is shown in Fig. P8-2, where there are shown on a PV two isothermal curves intersected by an adiabatic curve, referring to 1 mol of an ideal monatomic gas. A process takes the gas from the upper intersection point A and expands it isothermally at 600 K to a very special state B. The gas is then put in contact with a low-temperature reservoir at

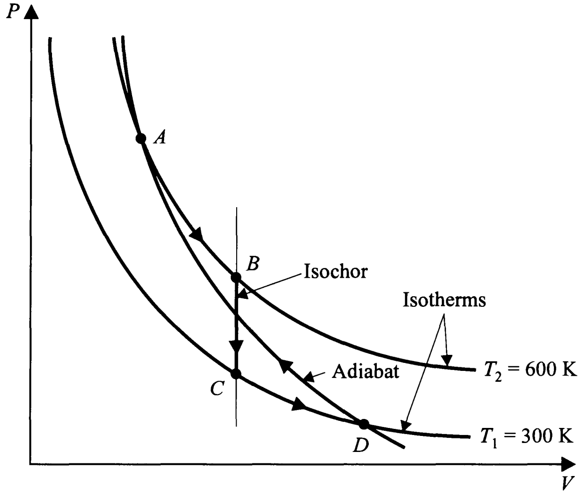

FIGURE P8-2
The zilch cycle for 1 mol of an ideal monatomic gas. (A. S. Arrott: *American Journal of Physics*, vol. 45, pp. 672–673, 1977. See also R. H. Dickerson and J. Mottmann: *American Journal of Physics*, vol. 62, pp. 558–562, 1994.)

300 K so that it cools isochorically to state C. Then, there is a further isothermal expansion from C to the lower intersection point D. The remainder of the zilch cycle is accomplished by an adiabatic compression from D back to A. The isochoric process BC is chosen to satisfy the condition that the net work in the cycle is zero.

(*a*) Calculate the work W_{DA}.

(*b*) Calculate the heat Q_{BC}.

(*c*) Calculate the net entropy change of the gas (*not the reservoirs*) and obtain the relationship

$$\frac{Q_{AB}}{600\,\mathrm{K}} + \frac{Q_{CD}}{300\,\mathrm{K}} = 8.64\,\frac{\mathrm{J}}{\mathrm{K}}.$$

(*d*) Calculate the work W_{AB}.

(*e*) Calculate the work W_{CD}.

(*f*) Calculate the net entropy change of the reservoirs.

(*g*) Draw the TS diagram.

8.17. (*a*) Prove that two isentropic curves do not intersect for systems of two independent variables.

(*b*) Show that isentropic curves *do* generally intersect for systems with more than two independent variables.

CHAPTER 9

Pure Substances

9.1
PV DIAGRAM FOR A PURE SUBSTANCE

Since the triple point of water is the basis of the thermodynamic temperature scale, let us investigate pure water as an example of a pure substance. The experiment consists of measurements of P and V in states of equilibrium for H_2O either as a single phase or coexisting as multiple phases. The sample is placed in a cylinder, closed at one end, and contained by a piston. No mass is allowed to escape. Ovens and refrigerators control the temperature of the system. Movement of the piston provides independent control of the volume of the system. The pressure is measured by means of a manometer. A small window permits observation of the state of the sample.

If 1 g of water at about 94°C is introduced into the cylinder 2 liters in volume, from which all the air has been removed, the water will evaporate completely and the system will be in the condition known as *unsaturated vapor*, the pressure of the vapor being less than standard atmospheric pressure. On the *PV* diagram shown in Fig. 9-1, this state is represented by the point A. If the vapor is then compressed slowly and isothermally, obviously the volume is decreasing, but more importantly the pressure will rise until the system reaches a state of *saturated vapor*, represented by the point B on the isotherm. If the compression is continued, *condensation* occurs to form droplets of water. During compression, the pressure remains constant (*isobaric* process) as long as the temperature remains constant. The horizontal straight-line segment BC represents the isothermal isobaric condensation of water vapor as the volume decreases, the constant pressure being called the *vapor pressure*. Alternately, as the volume increases, the vaporization line BC represents the isothermal isobaric *evaporation* of water vapor. At any point

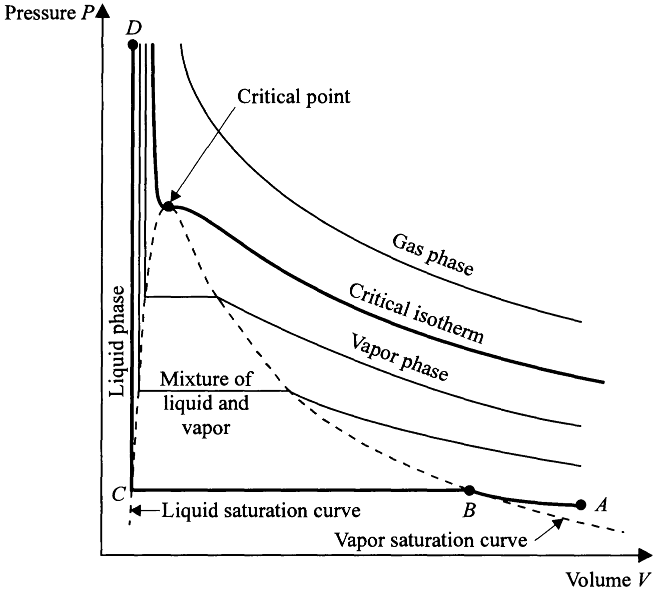

FIGURE 9-1
Isotherms of a pure substance such as H_2O. The solid phase, which would be at the bottom of the figure, is not shown.

between *B* and *C*, water and vapor coexist in equilibrium. At the point *C*, the sample is only liquid water, or *saturated liquid.*

In order to compress liquid water slightly, a very large increase of pressure is needed; hence, the line *CD* is almost vertical. At any point on the line *CD*, the water is said to be in the *liquid phase*; at any point on *AB* in the *vapor phase*; and at any point on line *BC*, between the two saturation curves, there is equilibrium between the liquid and the vapor phases. The curve *ABCD*, which is discontinuous at points *B* and *C*, is a typical isotherm of a pure substance on a *PV* diagram.

At other temperatures, the isotherms in the liquid–vapor region have a similar character, as shown in Fig. 9-1. It is seen that the vaporization lines representing equilibrium between coexisting liquid and vapor phases become shorter as the temperature rises and vanish at a certain temperature called the *critical temperature.* The isotherm at the critical temperature is called the *critical isotherm*, and the point that represents the limit of the vaporization lines is called the *critical point.* It is seen that the critical point is a point of inflection on the critical isotherm. The pressure and volume at the critical point are known as the *critical pressure* and the *critical volume*, respectively. All points at which the liquid is saturated lie on the *liquid saturation curve*, and all points representing saturated vapor lie on the *vapor saturation curve.* The two saturation curves denoted by dashed lines meet at the critical point.

Above the critical point, the isotherms are continuous curves, which at large volumes and low pressures lose their inflection points and approach equilateral hyperbolas, namely, the isotherms of an ideal gas. At temperatures above the critical temperature, there is no longer any distinction between a liquid and a vapor, that is, the meniscus between the liquid and the vapor disappears. For H_2O, the critical temperature is 647.067 K, the critical pressure is 22.046 MPa, the critical volume for 1 kg is 0.00309 m^3, and the critical density is 322.778 kg/m^3.

It is clear that the critical point is a limiting point at which the specific volume of a liquid is equal to that of an equal mass of vapor, or, in other words, at which the density of the liquid equals the density of the vapor. If the densities of both liquid and vapor of H_2O are measured as functions of the temperature and the results are plotted, as in Fig. 9-2, the critical temperature can be determined from the point where the two curves meet. At temperatures below the critical point, the liquid and vapor densities vary only slightly with the temperature and are significantly different from each other. It is interest-

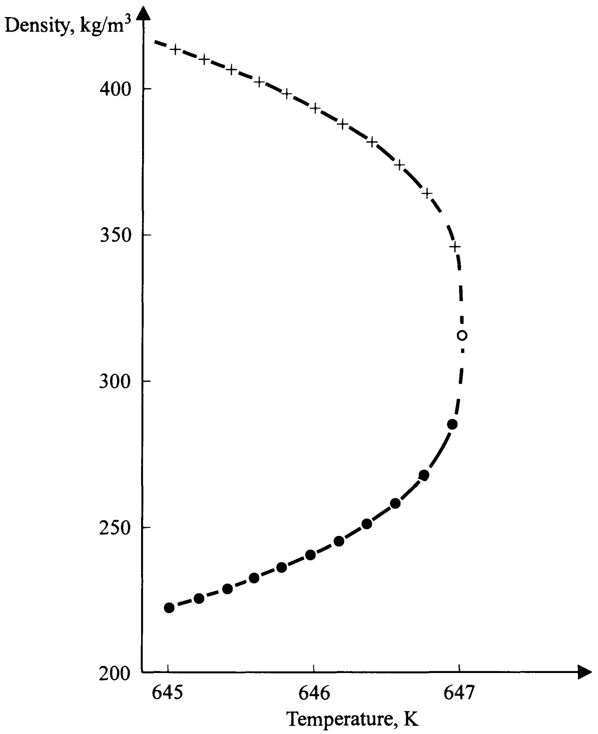

FIGURE 9-2
Density curves of liquid and vapor H_2O meet at the critical point (+, liquid; •, vapor; o, critical point).

ing that at no temperature near the critical temperature is the meniscus visible between liquid and vapor. It was once thought that the disappearance of the meniscus was the criterion for the attainment of the critical point. At temperatures just below the critical point, there are two distinct phases with different densities, but they cannot be distinguished visually. Critical temperatures, pressures, and densities are given for various substances in Table 9.1. Although the critical point represents a unique temperature, it is not easily achieved or maintained; therefore, it is not used in thermometry as a reference temperature. Instead, the low-pressure triple point of water is the experimental basis of the Kelvin temperature scale.

In the *PV* diagram shown in Fig. 9-1, the low-temperature region representing the solid phase at the bottom of the diagram had been omitted for the sake of clarity, but will be discussed further in the next section. Suffice it to say that there is a solid–vapor region below the liquid–vapor region in Fig. 9-1. In the solid–vapor region of the *PV* diagram, the isotherms have the same general character as the vaporization lines in the liquid–vapor region. These horizontal line segments represent the isobaric transition from solid to vapor, or *sublimation*. There is one such line that separates the solid–vapor region below from the liquid–vapor region above. This *line* is associated with the coexistence of all three phases together, namely, the *triple point*. In the case of ordinary water, the triple point is at a unique temperature of 273.16 K and a unique pressure of 611.73 Pa. The line representing the isobaric isothermal triple-point states, however, extends over a wide range of specific volumes for 1 kg, from $1.00 \times 10^{-3}\,\text{m}^3$ (saturated liquid) to $2.06 \times 10^{2}\,\text{m}^3$ (saturated vapor). The triple-phase line of water will be discussed in more detail in Sec. 9.3.

When a liquid or solid equilibrates with its vapor at a given temperature, the vapor exerts a pressure that depends only on the temperature. In general, the higher the temperature, the greater the vapor pressure. As the temperature of a liquid is lowered, a state is reached at which some of the liquid starts to

TABLE 9.1
Critical data

Substance	Temperature, K	Pressure, MPa	Density, kg/m^3
Helium-3	3.324	0.115	41.3
Helium-4	5.195	0.2275	69.64
Hydrogen (normal)	32.98	1.293	31.1
Nitrogen	126.20	3.390	313
Oxygen	154.58	5.043	436
Ammonia	405.5	11.35	236.4
Carbon dioxide	304.14	7.375	467.3
Water	647.067	22.0460	322.778

solidify, namely, at the triple point. The temperature and the vapor pressure correspond to the state in which solid, liquid, and vapor exist together in equilibrium. At lower temperatures, only solid and vapor are present. The vapor pressure of most solids is very small.

9.2

PT DIAGRAM FOR A PURE SUBSTANCE; PHASE DIAGRAM

Consider a solid at a very low temperature. If the vapor pressure of a solid is measured at various temperatures until the triple point is reached, and, if the vapor pressure of the liquid is measured as the temperature of the sample is raised to the critical temperature, then the results can be plotted on a *PT* diagram, such as Fig. 9-3, which is commonly called a *phase diagram.* If a substance at its triple point is compressed until there is no vapor left and the pressure on the resulting mixture of liquid and solid is increased, the temperature must change for equilibrium to exist between the solid and the liquid. Measurements of the pressures and temperatures of the solid coexisting with the liquid produce a third curve on the phase diagram, starting at the triple point and rising indefinitely. The data, representing the coexistence of: (1) solid and vapor, lie on the *sublimation curve*, which is bounded by absolute zero and the triple point; (2) solid and liquid, lie on the *fusion curve*, which starts at the triple point and is unbounded; (3) liquid and vapor, lie on the *vaporization curve*, which is bounded by the triple point and the critical point. In the particular case of water, the sublimation curve is called the *frost line*, the

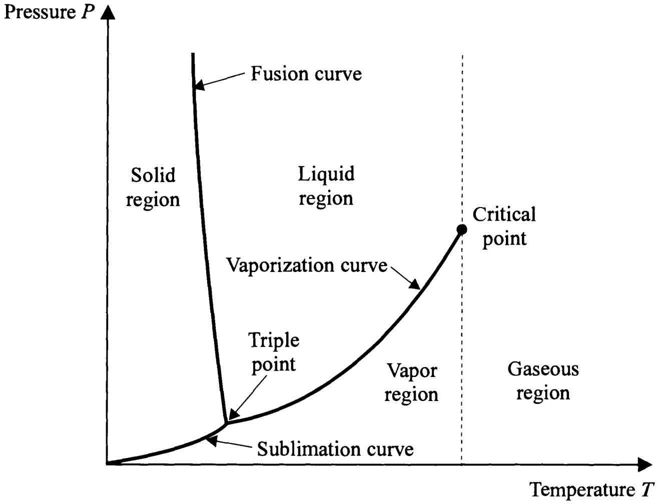

FIGURE 9-3
Phase diagram for H_2O.

fusion curve is called the *ice line*, and the vaporization curve is called the *steam line*. The temperatures along the vaporization curve are the boiling points as a function of pressure. At the *normal* boiling point, the vapor pressure is standard atmospheric pressure, or 101,325 Pa. For water, the temperature of the normal boiling point is 373.124 K, as discussed in Sec. 1.11.

On Fig. 9-3, no two-phase regions are shown, such as those found in the *PV* diagram in Fig. 9-1. Rather, all the two-phase states collapse onto one of the three curves on the *PT* diagram. Away from the curves, there are only single-phase equilibrium states. A substance with no free surface (meniscus) and with a volume determined by that of the container is called a *gas* when its temperature is *above* the critical temperature. Otherwise, it is called a *vapor*. The term "vapor" is usually applied to a gas in equilibrium with its liquid (a *saturated* vapor) or to a gas at a temperature *below* its critical temperature. The properties of a vapor are the same as those of a gas, except that a vapor can be liquefied by an isothermal increase of pressure due to compression, but a gas cannot be liquefied, no matter how high the pressure. Helium, however, is unique in that its gas can be *solidified* under high pressure.

The slopes of the sublimation and the vaporization curves for all substances are positive. The slope of the fusion curve, however, may be positive or negative. The fusion curve of most substances has a positive slope. Water is one of the important exceptions. When an equation known as the Clausius-Clapeyron equation is derived in Chap. 11, it will be seen that any substance, such as water, which expands upon freezing, has a fusion curve with a negative slope, whereas for a substance that contracts upon freezing, such as carbon dioxide, has a fusion curve with a positive slope.

The triple point is merely the point of intersection of the sublimation, fusion, and vaporization curves. It must be understood that *only* on a phase diagram is the triple point represented by a point. On a *PV* diagram, the triple-phase state is a line. Triple-point data for common substances are given in Table 9.2.

TABLE 9.2
Triple points of various substances

Substance	Temperature, K	Pressure, MPa	Liquid density, kg/m^3
Hydrogen (normal)	13.80	7.042	77
Neon	24.56	50	1251
Oxygen	54.3[illegible]	0.146	1306
Nitrogen	63.15	12.46	870
Carbon dioxide	216.6	518	1179
Water (H_2O)	273.16	0.612	999.78
Heavy water (D_2O)	276.97	0.661	1105.5

The essential feature of a triple point is that three phases coexist in equilibrium. Most commonly, the three phases are solid, liquid, and vapor. However, a triple point could be defined as the state in which two different solid phases coexist with a liquid, or three different solid phases coexist. For example, an investigation of the ice line of water at low temperatures or very high pressures reveals various modifications (known as *polymorphs* in geophysics) in the solid phase. The polymorphs of H_2O vary in crystal structure, density, or entropy of the protons of hydrogen. Ordinary ice is denoted ice I, and polymorphs up to ice IX have been found in experiments that ranged in temperature from −200 to 440°C and pressures from vacuum up to 170,000 atm (17 GPa). Equilibrium conditions among these polymorphs of ice and liquid give rise to eight stable triple points, which, including the thermometric low-pressure triple point at 273.16 K, are listed in Table 9.3. Both ice IV and ice IX are unstable and, therefore, are not listed. Interestingly, water has the largest number of triple points for any known substance.

9.3
PVT SURFACE

All the data that are represented on both the *PV* and the *PT* diagrams can be shown on one diagram if the three coordinates *P*, *V*, and *T* are plotted along orthogonal axes. The result is called the *PVT* surface. Two such surfaces are shown in Figs. 9-4 and 9-5, the first for a kilogram of an unusual substance like water that contracts upon melting, and the second for a kilogram of a typical substance like carbon dioxide that expands upon melting. The critical point is denoted by the letter *C* and the triple point by *TP*. The critical isotherm is marked T_C. These diagrams are not drawn to scale, the volume axis being considerably foreshortened. Every point on the *PVT* surface represents a state of equilibrium for the substance. If the *PVT* surface is projected on the *PV* plane, then the usual *PV* diagram is seen. Upon projecting the

TABLE 9.3
Equilibrium triple points of H_2O

Phases in equilibrium	Temperature, K	Pressure, MPa	Temperature, °C
Ice I, liquid, vapor	273.16	0.000612	+0.01
Ice I, liquid, ice III	251.15	207.4	−22.0
Ice I, ice II, ice III	238.45	212.8	−34.7
Ice II, ice III, ice V	248.85	344.2	−24.3
Ice III, liquid, ice V	256.15	346.2	−17.0
Ice V, liquid, ice VI	273.31	625.7	+0.16
Ice VI, liquid, ice VII	354.75	2199	+81.6
Ice VI, ice VII, ice VIII	274	2077	+1

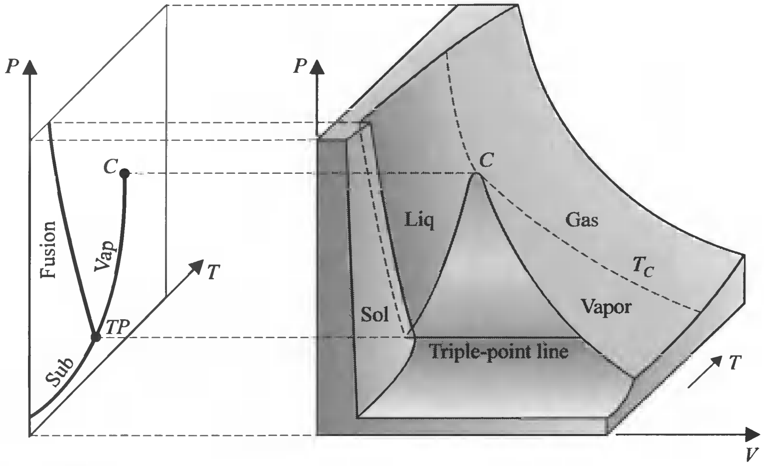

FIGURE 9-4
PVT surface for H_2O, which contracts while melting.

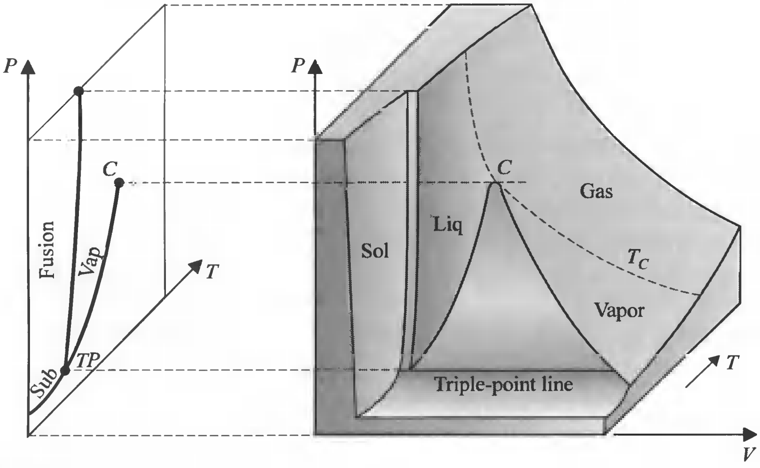

FIGURE 9-5
PVT surface for CO_2, which expands while melting.

PVT surface onto the *PT* plane, the entire solid–vapor region projects into the sublimation curve, the entire liquid–vapor region projects into the vaporization curve, the entire solid–liquid region projects into the fusion curve, and, finally, the *triple-point line* projects into the triple point on the phase diagram.

All the equilibrium triple points for a kilogram of water, as listed in Table 9.3, are shown on the *PVT* surface in Fig. 9-6. Not shown are the two unstable polymorphs: ice IV, discovered by P. W. Bridgman in 1935, and ice IX, discovered by E. Whalley, J. B. R. Heath, and D. W. Davidson (*Journal of Chemical Physics*, vol. 48, pp. 2362–2370) in 1968. In 1963, Kurt Vonnegut

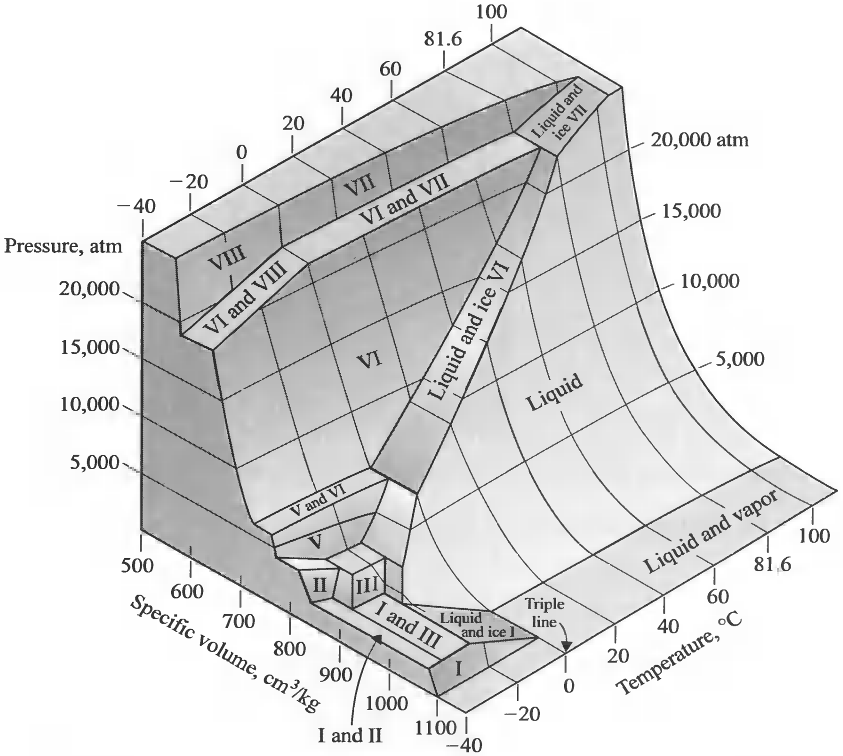

FIGURE 9-6
PVT surface for H_2O, showing all the equilibrium states. A triple line is a line parallel to the axis of specific volume.

described in his novel *Cat's Cradle* the properties of a fictional form of ice, which he called ice IX, that supposedly was capable of crystallizing all the water in the world. The reported properties of the real ice IX are less spectacular.

Another interesting substance with unusual stable triple points is the isotope ^{4}He. The *PVT* surface for a kilogram of ^{4}He and the accompanying *PT* projection are shown in Fig. 9-7, which reveals that ^{4}He has a number of remarkable properties. If we start at the critical point ($T_C = 5.2014\,\text{K}$, $P_C = 2.2746 \times 10^5\,\text{Pa}$) and lower the temperature, the liquid remaining in equilibrium with its vapor, a triple point is reached (known as the lower λ-point) at which three different phases are in equilibrium. At the lower λ-point, there is no solid. Instead of solid helium, another modification of liquid helium, known as helium II, is found. The coordinates of the lower λ-point for the coexistence of helium I, helium II, and helium vapor are $T = 2.1720\,\text{K}$ and $P = 0.050399 \times 10^5\,\text{Pa}$. Further reduction of the temperature (by rapid evaporation) still does not produce the solid phase. In order to produce solid

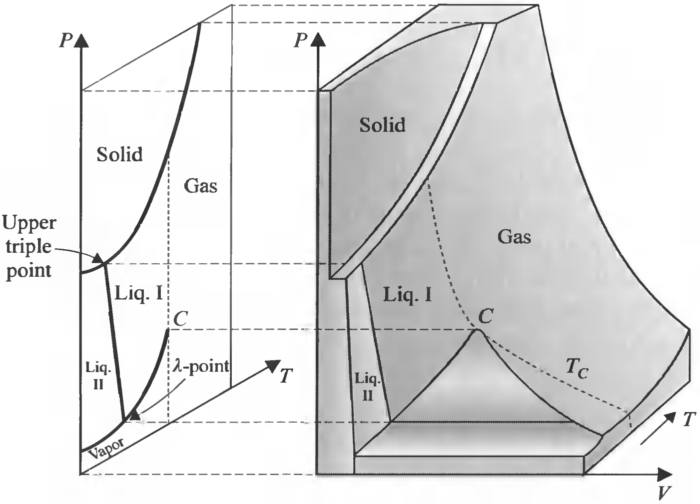

FIGURE 9-7
PVT surface and phase diagram for ^{4}He.

helium from either liquid I or liquid II, the pressure must be increased to over 29 atm, in which case another triple point (the upper λ-point at $T = 1.7633$ K, $P = 30.13 \times 10^5$ Pa) is reached at which both the liquids and the solid are in equilibrium. The *lambda line* connects the lower and upper λ-points and is the boundary between He I and He II. *There is no triple point for solid, liquid, and vapor in* ^{4}He.

The transition from liquid I to liquid II occurs at constant temperature and constant pressure with no "latent" heat and with no change of volume. Such a transition is known as a phase change of the second order and will be treated in detail in Chap. 14. When the two liquids of ^{4}He are in equilibrium, they both have the same density at a given temperature. Other properties, however, are remarkably different. For example, the thermal conductivity of liquid helium II is very much larger than that of liquid I; so much so, in fact, that a temperature gradient, which gives rise to bubbling in liquid I, does not exist in liquid II and, thus, one can tell when liquid II is formed by noting that the liquid suddenly becomes quiescent. Perhaps the most interesting property of liquid II is its remarkably low viscosity. It flows very rapidly through capillary tubes and goes through tightly packed porous materials as if through a sieve. Other interesting properties of liquid helium II are that it has a specific heat capacity at constant pressure larger than water, between the λ-point and approximately 1.9 K, and a negative volume expansivity between the λ-point and approximately 1.2 K.

9.4

EQUATIONS OF STATE

It is impossible to express the complete behavior of a substance over the whole range of measured values of P, V, and T by means of one simple equation. Several equations of state, such as the ideal gas law and those found in Prob. 5.6, can be used to study the vapor phase.

Since the critical point is the limiting position on a PV diagram as the two end-points (saturated liquid and saturated vapor) on the same isotherm approach each other, it follows that the slope of the isotherm passing through the critical point (the critical isotherm) is zero, or

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_C} = 0. \tag{9.1}$$

Also, the critical point is a point of inflection on the critical isotherm, because the isotherm is concave upward at volumes less than the critical volume and concave downward at specific volumes more than the critical volume; hence,

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_C} = 0. \tag{9.2}$$

Equations (9.1) and (9.2), along with the equation of state itself, enable one to calculate the critical P, V, and T, denoted by P_C, V_C, and T_C. Consider, for example, the van der Waals equation of state, which can be written

$$P = \frac{RT}{v-b} - \frac{a}{v^2},$$

where $v = V/n$ is the molar volume. This equation holds fairly well in the vapor region near and above the critical point. Equations (9.1) and (9.2) for molar volume yield, respectively,

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_C} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0, \tag{9.3}$$

and

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_C} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0. \tag{9.4}$$

Equations (9.3) and (9.4) can be rewritten as

$$\frac{2a}{v^3} = \frac{RT}{(v-b)^2},$$

and

$$\frac{3a}{v^4} = \frac{RT}{(v-b)^3}.$$

Divide the first equation by the second to obtain the critical molar volume,

$$v_C = 3b. \tag{9.5}$$

Substituting this value for v in the first of the two equations, we obtain the critical temperature,

$$T_C = \frac{8a}{27bR}, \tag{9.6}$$

and, finally, substitute these two values in the van der Waals equation to obtain the critical pressure,

$$P_C = \frac{a}{27b^2}. \tag{9.7}$$

It follows that for the van der Waals equation of state,

$$\begin{aligned} \frac{RT_C}{P_C v_C} &= \frac{R \cdot \dfrac{8a}{27bR}}{\dfrac{a}{27b^2} \cdot 3b} \\ &= 2.67. \end{aligned} \tag{9.8}$$

If a substance behaved like an ideal gas at the critical point, then $RT_C/P_C v_C$ would equal unity. If it obeys the van der Waals equation, then this ratio should equal 2.67, which would be a measure of the departure of the van der Waals gas from the ideal gas. In Table 9.4, the calculated values of $RT_C/P_C v_C$ are listed for a number of interesting gases, and in no case is this ratio equal to 2.67, or even close. Above the critical point, at higher pressure, the van der Waals equation is fairly satisfactory and is useful in many cases. Other equations of state give better values of $RT_C/P_C v_C$, but are no better in describing other properties of gases.

9.5
MOLAR HEAT CAPACITY AT CONSTANT PRESSURE

Except for temperature, heat capacity is the thermal property of pure substances that is the oldest and most thoroughly investigated in thermodynamics, dating back to the pioneering work of Joseph Black in the 1760s.

TABLE 9.4
Calculated values of $RT_C/P_C v_C$

Substance	$RT_C/P_C v_C$
Water	4.36
Ammonia	4.13
Carbon dioxide	3.64
Oxygen	3.49
Nitrogen	3.44
Helium	3.34
Hydrogen	3.26
Van der Waals gas	2.67
Ideal gas	1.00

The heat capacity was standardized to unit mass, that is, the specific heat was measured. Furthermore, the experiments were open to the atmosphere; hence, it was the specific heat capacity at constant pressure. Specific heat measurements at constant volume are much more difficult to perform, because the process of heating a sample causes thermal expansion, that is, a change of volume. For this reason, specific heat capacity at constant volume is usually not measured, but is calculated from other data, as we shall see later in this chapter.

The experimental measurement of heat capacity at constant pressure C_P has already been discussed in Sec. 4.7, and the general features of one type of calorimeter suitable for such measurements were described, as well as some details of technique. Data on the heat capacities of elements, alloys, compounds, plastics, etc., taken over as wide a temperature interval as possible, are of great importance in pure science and in engineering. Many interesting phenomena occur in the temperature range from absolute zero to about room temperature (300 K). In this temperature range, most materials are in the solid phase, which will be studied for the rest of this chapter. We shall limit ourselves to solids in the form of a cubic crystal, the simplest solid structure, either a single crystal, or a rod or powder consisting of a large number of small crystals. Furthermore, in order to facilitate comparison of different substances we shall investigate the *molar* heat capacity at constant pressure $c_P = C_P/n$, where C_P is the heat capacity of an arbitrary mass and n is the number of moles of the mass. In effect, the molar heat capacity measures the heat capacity of a substance having a fixed number of particles, namely, Avogadro's number.

The behavior of three different crystalline *nonmetals* is shown in Fig. 9-8. (Metals exhibit a special behavior because of the effect of free electrons; such behavior will be discussed in Chap. 13.) The molar heat capacity c_P of *all* materials approaches zero as T approaches zero. Between 25 and 100 K, c_P rises rapidly but then bends and begins to flatten out in the neighborhood of room temperature. In none of the three crystals, however, does the c_P curve actually become horizontal.

In the germanium (Ge) crystal, the crystal structure is such that each lattice site is occupied by a single Ge atom, and therefore 1 mol of germanium crystal consists of N_A vibrating particles, where N_A is Avogadro's number. The value of c_P at room temperature is very nearly equal to $3R$, but it is still increasing with temperature. For crystals of sodium chloride (NaCl), each lattice site is occupied alternately, either by a sodium ion or by a chlorine ion in a face-centered cubic lattice. Therefore, 1 mol of NaCl consists of N_A sodium ions in addition to N_A chlorine ions, so that altogether there are $2N_A$ vibrating particles. The value of c_P at room temperature is very nearly equal to $6R$. In nickel (IV selenide) ($NiSe_2$), the lattice sites are occupied by nickel atoms and by selenium atoms, with the center of the line joining the two selenium atoms and the nickel atom forming a face-centered cubic lattice similar to that of NaCl. In 1 mol of $NiSe_2$, there are $3N_A$ particles vibrating at their lattice sites, and the room-temperature value of c_P is very nearly equal

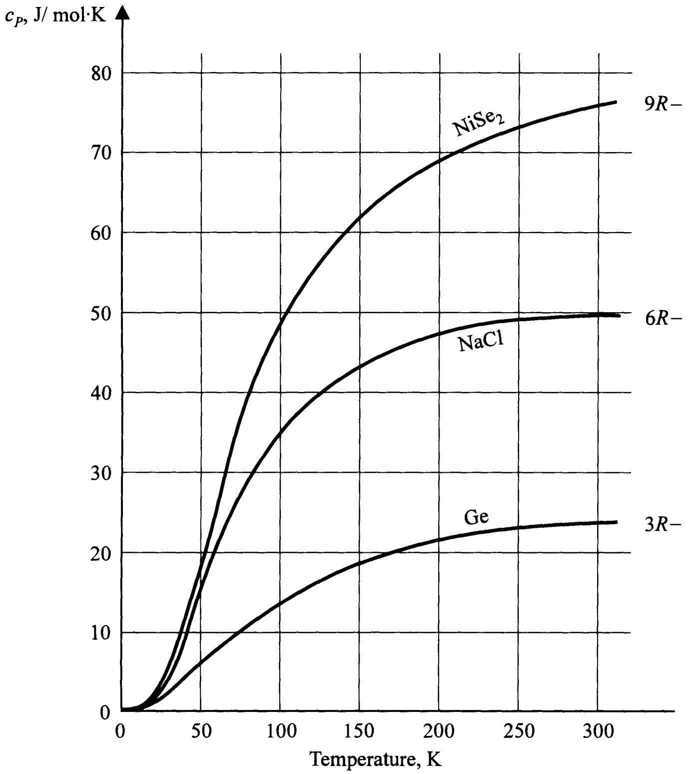

FIGURE 9-8

Molar heat capacity at constant pressure of three crystalline nonmetals. (Ge: P. H. Keesom and G. Seidel: *Physical Review*, vol. 113, pp. 33–39, 1959. NaCl: K. Clusius, J. Goldmann, and A. Perlick: *Zeitschrift für Naturforschung*, vol. 4a, pp. 424–432, 1949. NiSe$_2$: F. Grønvold and E. F. Westrum: *Inorganic Chemistry*, vol. 1, pp. 36–48, 1962.)

to $9R$. In all cases, the molar heat capacity c_P at room temperature of *exactly* N_A *atoms or ions* is approximately $3R$, about 25 J/mol · K.

The curves in Fig. 9-8 correspond to crystals that were deliberately chosen to illustrate a regularity at room temperature. There is nothing special about the temperature 300 K, however. Not all crystals have values of c_P whose rapid increase is tapering off at 300 K. The c_P of diamond, for example, rises so slowly that at 300 K it is still quite far from the value $3R$. A characteristic temperature, above which c_P is close to $3R$ and below which c_P increases rapidly with temperature, is known as the *Debye temperature*. The crystals in Fig. 9-8 have Debye temperatures below 300 K, while diamond has a large Debye temperature (2230 K), so its c_P is still much below $3R$ at room temperature. Furthermore, c_P never approaches any value asymptotically, but continues to rise at all temperatures. The laws governing the temperature variation of molar heat capacity cannot be stated simply in terms of c_P. To express experimental results in a neat form, and also to appreciate the relation between experiment and theory, it is necessary to study first the temperature variation of thermal expansivity and compressibility, and then mathematical methods (see Chap. 10).

9.6
VOLUME EXPANSIVITY; CUBIC EXPANSION COEFFICIENT

The volume expansivity $\beta = 1/V(\partial V/\partial T)_P$ for a gas or liquid is measured directly. But, in experiments on the expansion of solids, the *linear* expansion coefficient α, given in Chap. 2, is the quantity measured and usually reported in reference books under the heading of the elastic constants of a substance. Knowing the linear expansion coefficient α, one calculates the cubic expansion coefficient β, which we call simply volume expansivity. To see the relationship between the two expansion coefficients, consider a solid of three rectangular dimensions L_1, L_2, and L_3; then,

$$V = L_1 L_2 L_3,$$

$$\left(\frac{\partial V}{\partial T}\right)_P = L_2 L_3 \left(\frac{\partial L_1}{\partial T}\right)_P + L_1 L_3 \left(\frac{\partial L_2}{\partial T}\right)_P + L_1 L_2 \left(\frac{\partial L_3}{\partial T}\right)_P,$$

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{L_1}\left(\frac{\partial L_1}{\partial T}\right)_P + \frac{1}{L_2}\left(\frac{\partial L_2}{\partial T}\right)_P + \frac{1}{L_3}\left(\frac{\partial L_3}{\partial T}\right)_P,$$

and

$$\beta = \alpha_1 + \alpha_2 + \alpha_3, \tag{9.9}$$

where α_1, α_2, and α_3 are the linear expansion coefficients along the three axes, and β is the cubic expansion coefficient that we call the volume expansivity, or, simply, expansivity, as introduced in Chap. 2. In the case of quartz crystal, the two linear coefficients perpendicular to the z-axis are equal, so that $\beta = 2\alpha_\perp + \alpha_\parallel$. If the solid is isotropic, as in the case of a cubic crystal, then $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$, and

$$\beta = 3\alpha. \tag{9.10}$$

There are several absolute methods of measuring the linear expansion coefficients of solids, but the principal ones are based on the interference fringes of visible light and the variation of electric capacitance. The measurements in the 0 to 50 K range involve much auxiliary cryogenic equipment, but the physical principles for measuring the linear expansion coefficients in any temperature range are easily understood.

The optical method uses an interferometer, shown in Fig. 9-9 in a schematic diagram, which is a modification by Waterhouse and Yates of a Fizeau interferometer (straight fringes). Monochromatic light from a laser is reflected from mirror M_1 onto plates P_1 and P_2, which are separated by a ring or cylinder R made of the material whose linear expansion coefficient, hence, expansivity, is to be studied. The ring and plates are placed at the bottom of a cryostat, where liquid nitrogen or liquid helium is used to provide the low

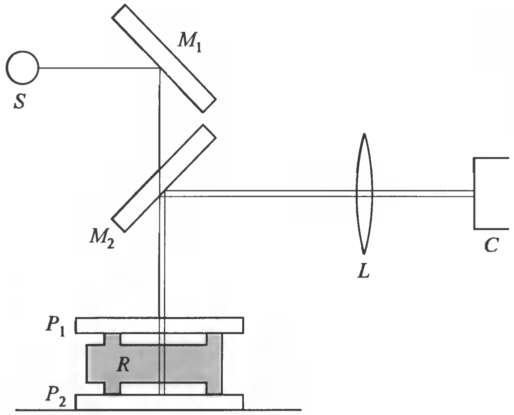

FIGURE 9-9
Modified version of an interferometer used to measure the linear coefficient of thermal expansion.

temperatures at which measurements are often made. In Fig. 9-9, all details of the cryostat, heater, thermometer, venting tubes, electric leads, etc., have been omitted. Interference takes place between the rays of light reflected from the bottom of P_1 and the top of P_2, and a camera C is used to photograph the interference fringes. The temperature is varied slowly from, let us say, 4 K up to room temperature, and the fringe system is photographed at regular intervals.

If N fringes travel across the field of view while the temperature changes from T_0 to T, then the optical path difference has changed by $N\lambda$ where λ is the wavelength of the light, and the thickness of the air space has changed by $N\lambda/2$. If L_0 is the length of the specimen at temperature T_0 and L is the length at T, then

$$\frac{L - L_0}{L_0} = \frac{N\lambda}{2L_0}.$$

If, therefore, $N\lambda/2L_0$ is plotted against T and the slope of the resulting curve is taken at various temperatures, the linear expansion coefficient is obtained. Thus,

$$\alpha = \frac{d}{dT}\left(\frac{N\lambda}{2L_0}\right).$$

In order to automate data acquisition, a photoelectric interferometer detects the movement of interference fringes by means of a photomultiplier tube. The number of fringes is automatically recorded as a function of the measured temperature of the specimen. Thus, the data are recorded in digital form suitable for calculation of linear and cubic expansion coefficients. The sensitivity $\Delta L/L_0$ of this experiment is 10^{-7}.

In the electric method, the expansion of the specimen is communicated to one of the plates of a capacitor, the other plate being held fixed. The change in capacitance due to expansion of the sample is measured by an extremely sensitive bridge; and, in the experiments done by Carr and colleagues, this method has proved capable of sensitivities of 2×10^{-10}. This method is the basis of most of the measurements of expansion coefficients at cryogenic temperatures.

The temperature dependence of the volume expansivity β of many substances is the same as that of NaCl, which is shown in Fig. 9-10; namely, β is zero at absolute zero, rises rapidly in the interval from 0 to 50 K, then bends and flattens out without actually becoming horizontal. Thus, the temperature variation of β is almost identical with that of c_P, also shown in Fig. 9-10. Another similarity between β and c_P is the insensitivity of both quantities to

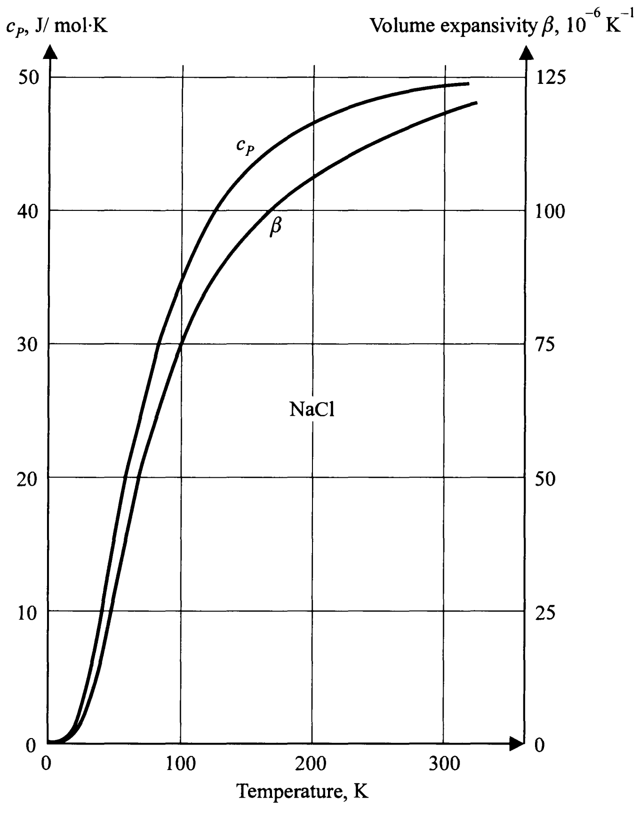

FIGURE 9-10
Temperature variation of molar heat capacity c_P and volume expansivity β for NaCl, which are almost identical in temperature dependence. (c_P: K. Clusius, J. Goldmann, and A. Perlick: *Zeitschrift für Naturforschung*, vol. 4a, pp. 424–432, 1949. β: P. P. M. Meincke and G. M. Graham: *Canadian Journal of Physics*, vol. 43, pp. 1853–1866, 1965.)

changes of pressure. For example, β varies only from $119 \times 10^{-6}\,\mathrm{K}^{-1}$ to $96 \times 10^{-6}\,\mathrm{K}^{-1}$ for NaCl between atmospheric pressure and 7000 times atmospheric pressure at room temperature. Grüneisen, in 1908, first noticed that the ratio $\beta/c_P|_T$ is approximately constant at all temperatures.

9.7
COMPRESSIBILITY

Compressibility measurements are made in two different ways in order to determine compressibility under two different conditions. Installations are capable of subjecting solids to enormous hydrostatic pressures at constant temperature and capable of providing numerical values of the *isothermal compressibility* κ, where, from Chap. 2,

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{9.11}$$

which is also the reciprocal of the isothermal bulk modulus. Isothermal compressibilities, which are measured at fixed pressures up to many tens of thousands of atmospheres, are used to study phase transitions, changes of crystal structure, and other internal changes of solids and liquids, such as those of the polymorphs of ice. These are *static measurements*. Measurements of the speed of longitudinal waves in liquids and both longitudinal and transverse waves in solids, at atmospheric or moderate pressures, are *dynamic measurements*, which provide numerical values of the *reversible adiabatic compressibility* κ_S, which is defined as

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \tag{9.12}$$

where the subscript S means isentropic, that is, adiabatic and reversible. It was shown in Chap. 5 that the speed of a longitudinal wave w in a fluid is given by

$$w = \sqrt{\frac{1}{\rho\kappa_S}}, \tag{9.13}$$

where ρ is the density of the fluid. Measurements of w and ρ are sufficient to provide κ_S of a fluid, but the measurement of κ_S of a crystalline *solid* is more difficult. For a cubic crystal, it is necessary to measure the speed of the shear wave in the [110] direction as well as that of the longitudinal wave in the [100] direction, and, from the two measurements, to calculate two different elastic constants. In the case of NaCl, these quantities are designated c_{11} and c_{12}, and it is known from the theory of elasticity that κ_S can be calculated from

$$\kappa_S = \frac{3}{c_{11} + 2c_{12}}. \tag{9.14}$$

Once the adiabatic compressibility κ_S is obtained, either from Eq. (9.13) for fluids or from Eq. (9.14) for cubic solids, the isothermal compressibility may be calculated by using two equations that will be derived in the next chapter, namely, the difference between the molar heat capacities at constant pressure and volume,

$$c_P - c_V = \frac{Tv\beta^2}{\kappa}, \tag{9.15}$$

and the ratio of molar heat capacities,

$$\gamma = \frac{c_P}{c_V} = \frac{\kappa}{\kappa_S}. \tag{9.16}$$

Eliminating the molar heat capacity at constant volume c_V from Eqs. (9.15) and (9.16), we get

$$c_P - \frac{c_P\kappa_S}{\kappa} = \frac{Tv\beta^2}{\kappa},$$

which reduces to

$$\kappa - \kappa_S = \frac{Tv\beta^2}{c_P}. \tag{9.17}$$

Equation (9.17) permits the isothermal compressibility κ to be calculated from measured values of κ_S, T, v, β, and c_P.

The method of measuring wave speeds that is most suitable for crystalline solids is one that incorporates the pulse-echo technique. Short ultrasonic pulses of about 1 μs duration are sent into the crystal from a transducer that emits sound waves. After reflection from an end of the crystal, the ultrasonic pulses are received by the same transducer. The pulse and the echo are observed on an oscilloscope, and the wave speed is calculated from the dimensions of the crystal and the time delay between pulse and echo. This method has a resolution of 10^{-5} in measurements of the wave speed and 10^{-7} in changes of the wave speed. Overton and Swim used this method to obtain the values of κ_S listed in Table 9.5.

The temperature variation of κ_S and κ of NaCl are shown in Fig. 9-11, where it may be seen that both κ_S and κ, unlike c_P and β, do *not* approach zero as T approaches zero. From 0 to 40 K, the adiabatic and isothermal compressibilities are nearly equal. At higher temperatures, the isothermal κ is larger than the adiabatic κ_S, as required by Eq. (9.17).

The speed of longitudinal waves *in a liquid or a gas* is usually measured with the aid of an acoustic interferometer, such as the one described in Sec. 5.7, which was used with argon gas to measure the molar gas constant R. Results of measurements of the isothermal and adiabatic compressibilities of water are listed in Table 9.6 and are shown in Fig. 9-12. The minimum in the curve of isothermal compressibility for water at about 50°C is quite anomalous. As a rule, the isothermal compressibility of most liquids increases as the temperature is raised and follows a simple exponential equation quite well:

TABLE 9.5
Thermal properties of NaCl
(Compiled by P. P. M. Meincke and G. M. Graham, *Canadian Journal of Physics*, vol. 43, pp. 1853–1866, 1965.)

T K	c_P, J/mol·K	β, $10^{-6}\,K^{-1}$	κ, $10^{-12}\,Pa^{-1}$	v, $kmol^{-1}$	c_V, J/mol·K	κ_S, $10^{-12}\,Pa^{-1}$
10	0.151	0.18	38.9	26.4	0.151	38.9
20	1.30	1.68	38.9	26.4	1.30	38.9
30	4.76	7.50	38.9	26.4	4.76	38.9
40	9.98	17.0	38.9	26.4	9.97	38.9
50	15.7	28.8	39.0	26.4	15.7	38.9
60	21.0	40.9	39.2	26.4	20.9	39.1
70	25.5	51.8	39.4	26.4	25.3	39.2
80	29.3	61.0	39.6	26.5	29.1	39.3
90	32.3	69.1	39.8	26.5	32.0	39.4
100	35.0	75.9	40.0	26.5	34.7	39.6
125	40.1	87.1	40.4	26.6	39.5	39.8
150	43.3	95.1	40.7	26.6	42.4	39.9
175	45.4	96.3	41.1	26.7	44.2	40.0
250	48.6	115	42.3	26.9	46.6	40.6
290	49.2	119	43.0	27.0	46.7	40.8

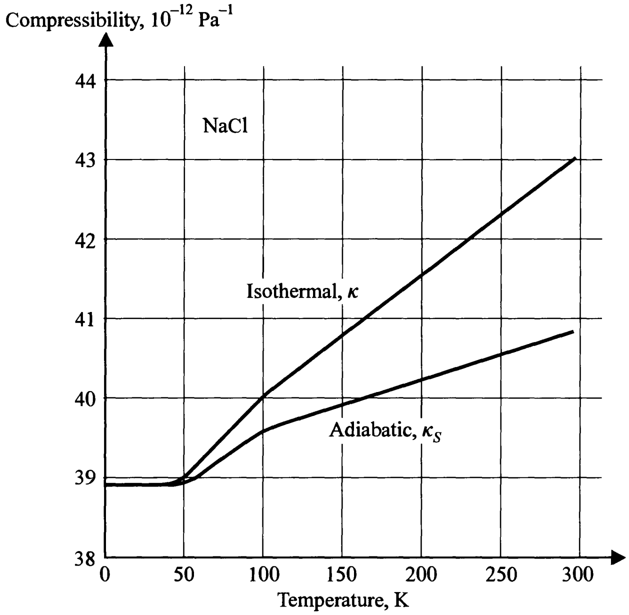

FIGURE 9-11
Temperature variation of isothermal and adiabatic compressibilities of NaCl. (W. C. Overton and R. T. Swim: *Physical Review*, vol. 84, pp. 758–762, 1951.)

TABLE 9.6
Thermal properties of water

T °C	w, m/s	ρ, kg/m^3	c_P, kJ/kg·K	β, 10^{-6} K^{-1}	κ, 10^{-10} Pa^{-1}	κ_S, 10^{-10} Pa^{-1}
0	1402.4	999.84	4.2176	−67.89	5.0885	5.0855
10	1447.2	999.70	4.1921	87.96	4.7810	4.7758
20	1482.3	998.21	4.1818	206.80	4.5891	4.5591
30	1509.1	995.65	4.1784	303.23	4.4770	4.4100
40	1528.8	992.22	4.1785	385.30	4.4240	4.3119
50	1542.5	998.03	4.1806	457.60	4.4174	4.2536
60	1550.9	983.20	4.1843	523.07	4.4496	4.2281
70	1554.7	977.78	4.1895	583.74	4.5161	4.2307
80	1554.4	971.82	4.1963	641.11	4.6143	4.2584
90	1550.4	965.35	4.2050	696.24	4.7430	4.3093
100	1543.2	958.40	4.2159	750.30	4.9018	4.3819

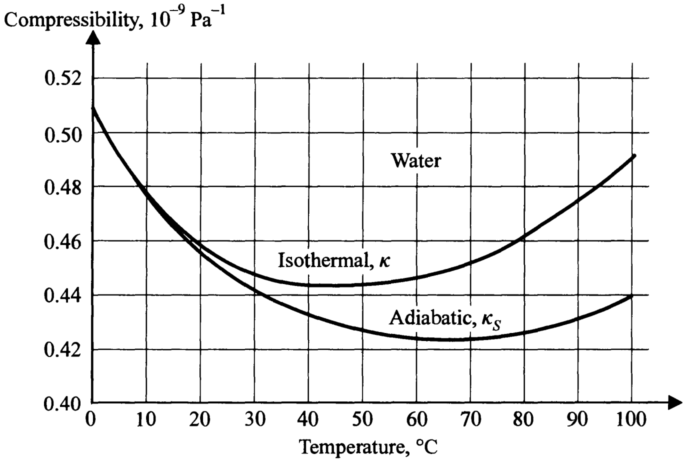

FIGURE 9-12
Isothermal and adiabatic compressibilities of water.

$$\kappa = \kappa_0 e^{aT}, \tag{9.18}$$

where κ_0 and a are constants. The constant a for mercury is 1.37×10^{-3} K^{-1}.

All liquids, including water, become less compressible the more they are compressed; the reciprocal of the isothermal compressibility increases linearly with respect to the pressure; that is,

$$\frac{1}{\kappa} - \frac{1}{\kappa_0} = bP, \tag{9.19}$$

where κ_0 is the isothermal compressibility at zero pressure, and the coefficient b is 6.7 for water and 8.2 for mercury.

9.8
MOLAR HEAT CAPACITY AT CONSTANT VOLUME

The measurement of c_P, β, and κ of crystalline solids, both metallic and nonmetallic, particularly at low temperatures, is important in the progress of solid-state theory. Our purpose, at present, is to use these measurements in conjunction with Eq. (9.15),

$$c_P - c_V = \frac{Tv\beta^2}{\kappa},$$

to find the complete temperature dependence of c_V. All the measurements for NaCl are listed in Table 9.5, along with the calculated values of c_V, and both c_P and c_V are plotted as a function of T up to 1000 K in Fig. 9-13. Since 1 mol of NaCl consists of $2N_A$ ions, the heat capacities refer to $\frac{1}{2}$mol, or N_A ions.

At low temperatures, below 100 K, c_P and c_V are practically the same. At all higher temperatures, while c_P continues to increase, c_V approaches a constant value $3R$, which is called the *Dulong and Petit value*, named after the two scientists who first observed that c_P came near this value at about room temperature. We see now that this value is actually approached by c_V and is exceeded only in special situations. The temperature dependence of $c_V/3R$ of five representative nonmetals is shown in Fig. 9-14, where it may be seen that RbI practically reaches the Dulong and Petit value even before room temperature, whereas diamond has reached only one-fifth this value at

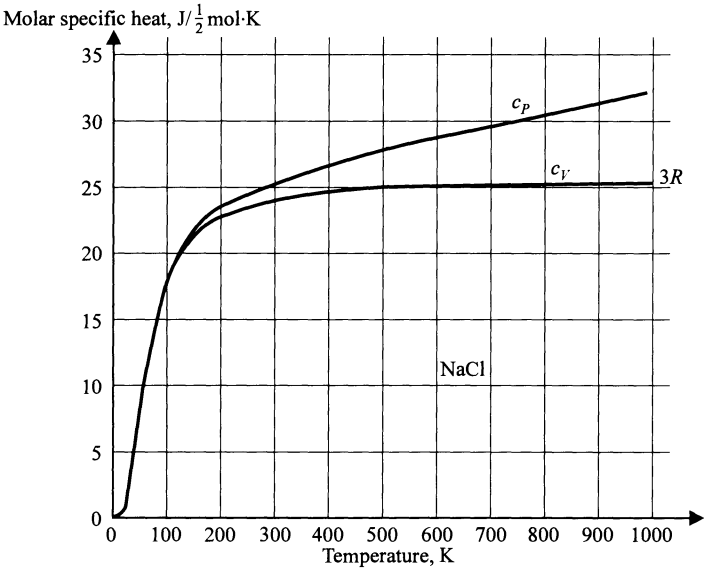

FIGURE 9-13
Temperature variation of c_P and c_V of $\frac{1}{2}$mol of NaCl. The value of c_V is close to $3R$ at high temperatures.

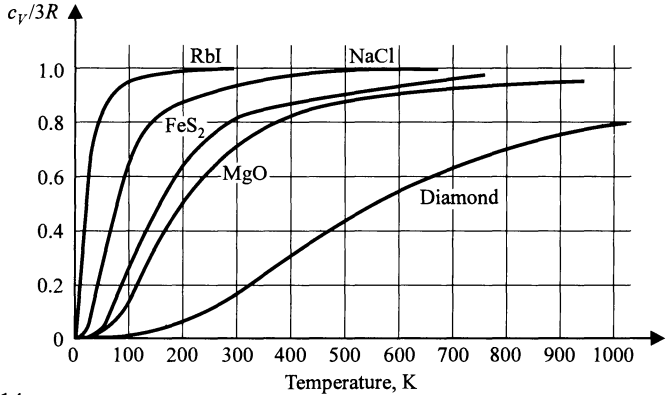

FIGURE 9-14
Temperature variation of $c_V/3R$ of nonmetals. (1 mol of diamond, $\frac{1}{2}$mol of RbI, NaCl, and MgO; and $\frac{1}{3}$mol of FeS_2.)

room temperature. As a matter of fact, it requires a temperature greater than 2000 K to bring the c_V of diamond near $3R$.

Although the five curves in Fig. 9.14 differ markedly in the temperature at which $c_V \to 3R$, the curves are still very similar in shape. An experienced experimenter would be led to suspect that there existed a parameter — the Debye temperature Θ — small for RbI and large for diamond, such that c_V is a *universal function* of the ratio T/Θ, as we shall see in Chap. 13.

9.9
TS DIAGRAM FOR A PURE SUBSTANCE

The entropy of a system is a function of the thermodynamic coordinates, whose change during a process in which the system goes from an equilibrium state i to another equilibrium state f is equal to

$$S_f - S_i = {}_R\int_i^f \frac{đQ}{T},$$

where the symbol R indicates that the integration is to be performed over any reversible path connecting i and f. If the two equilibrium states are infinitesimally near, then

$$đQ = T\,dS,$$

and

$$\frac{đQ}{dT} = T\frac{dS}{dT}.$$

At constant pressure,

$$\boxed{\left(\frac{đQ}{dT}\right)_P = C_P = T\left(\frac{\partial S}{\partial T}\right)_P,} \tag{9.20}$$

and, at constant volume,

$$\boxed{\left(\frac{đQ}{dT}\right)_V = C_V = T\left(\frac{\partial S}{\partial T}\right)_V.} \tag{9.21}$$

The boxed equations relate partial derivatives of the state function S, $(\partial S/\partial T)_P$ and $(\partial S/\partial T)_V$, which are also state functions, to quantities that can be measured experimentally, namely, C_P, C_V and T. For example, once the measurements of C_P are made at different temperatures, C_P/T can replace $(\partial S/\partial T)_P$ in any equation in which $(\partial S/\partial T)_P$ appears, even though, in general, the equation refers to a process in which the pressure is not constant, or to a process that is not reversible. Because $(\partial S/\partial T)_P$ is a state function of the system, C_P/T is also a state function and will change in value with changes in temperature and pressure.

If the temperature variation of C_V is known, the entropy change during an isobaric process may be calculated from the equation

$$S_f - S_i \text{ (isobaric)} = \int_i^f \frac{C_P}{T}\, dT.$$

Similarly, for an isochoric process,

$$S_f - S_i \text{ (isochoric)} = \int_i^f \frac{C_V}{T}\, dT.$$

The above equations provide a general method for calculating an entropy change but no way of calculating the absolute entropy of a system in a given state. If a set of tables is required that is to be used to obtain entropy differences and not absolute entropy, then it is a convenient procedure to choose an arbitrary standard state and to calculate the entropy change of the system from this standard state to all other states. Thus, in the case of water, the standard state is chosen to be water at its triple point at 273.16 K, and all entropies for water are referred to this state.

The *TS* diagram for a substance such as carbon dioxide is shown in Fig. 9-15. The segmented curve from *A* to *F* is a typical isobar representing a series of reversible isobaric processes in which solid is transformed finally into vapor. Thus,

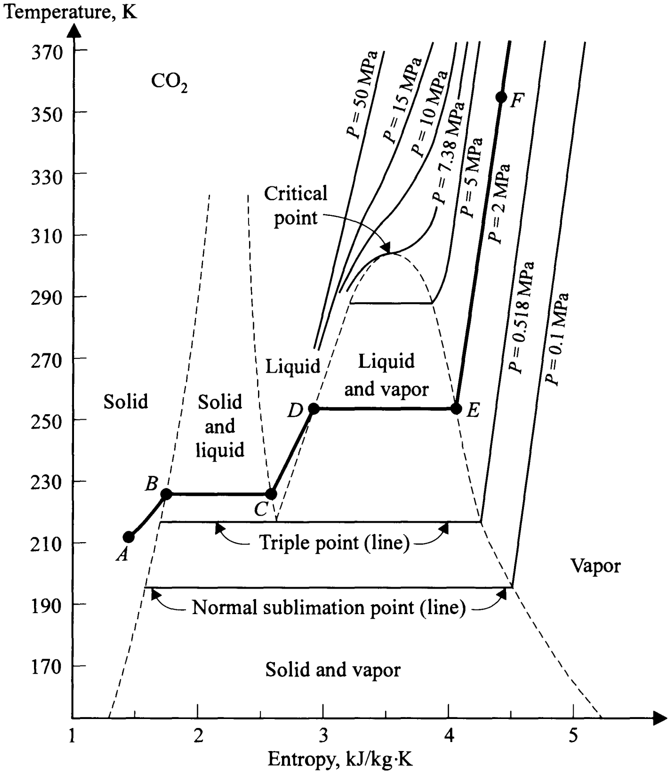

FIGURE 9-15
TS diagram for CO_2 showing isobaric process *ABCDEF*.

AB = isobaric heating of solid to its melting point,
BC = isobaric isothermal melting,
CD = isobaric heating of liquid to its boiling point,
DE = isobaric isothermal vaporization,
EF = isobaric heating of vapor (superheating).

The area under the line *BC* represents the latent heat of fusion at the particular temperature, and the area under the line *DE* represents the latent heat of vaporization. Similarly, the latent heat of sublimation is represented by the area under any sublimation line. It is obvious from the diagram that the latent heat of vaporization decreases as the temperature rises, and becomes zero at the critical point. At the triple point, but not in general, the latent heat of sublimation is equal to the sum of the latent heat of fusion and the latent heat of vaporization.

PROBLEMS

9.1. A capsule containing a liquid is broken while inside a small vacuum chamber. Describe the behavior of the meniscus when the temperature of the system is raised under the following conditions:

(*a*) The volume of the chamber is much greater than the critical volume.
(*b*) The volume of the chamber is much less than the critical volume.
(*c*) The volume of the chamber is only slightly different from the critical volume.

9.2. (*a*) What happens when helium gas is compressed isothermally above the critical temperature?
(*b*) If water vapor is compressed isothermally above the critical temperature, will ice I form? Is it possible that ice VII will form?

9.3. Using the Dieterici equation of state,

$$P = \frac{RT}{v-b} e^{-a/RTv},$$

show that

$$P_C = \frac{a}{4e^2b^2}, \qquad v_c = 2b, \qquad T_C = \frac{a}{4Rb},$$

and compare the value of RT_C/P_Cv_C with the values in Table 9.4.

9.4. Using the Berthelot equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{Tv^2},$$

show that

$$P_C = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}, \qquad v_C = 3b, \qquad T_C = \sqrt{\frac{8a}{27bR}},$$

and compare the value of RT_C/P_Cv_C with the values in Table 9.4.

9.5. If P, v, and T are the pressure, molar volume, and temperature of a gas and P_C, v_C, and T_C are the critical pressure, critical molar volume, and critical temperature, then the reduced pressure P_R, the reduced molar volume v_R, and the reduced temperature T_R are defined as

$$P_R = \frac{P}{P_C}, \qquad v_R = \frac{v}{v_C}, \qquad T_R = \frac{T}{T_C}.$$

(*a*) Show that, in terms of reduced quantities, the van der Waals equation becomes

$$\left(P_R + \frac{3}{v_R^2}\right)\left(v_R - \frac{1}{3}\right) = \frac{8}{3}T_R.$$

When the van der Waals equation is in this form, the material constants a and b do not appear explicitly. Thus, all gases that obey the van der Waals equation may be considered in the same state when the values of P_R, v_R, and T_R are the same (i.e., each gas is measured in units of its particular values of P_C, v_C, and T_C). This is the *principle of corresponding states*, which is a principle of universal similarity established first by van der Waals.

(*b*) Plot three curves for P_R as a function of v_R, one for $T = \frac{1}{2}T_C$, one for $T = T_C$, and one for $T = 2T_c$. What happens physically when the equation indicates three allowed values of v_R for a single P_R and T?

9.6. (*a*) The specific entropy of saturated water at 100°C is 1.307 kJ/kg · deg and that of saturated steam at the same temperature as 7.355 kJ/kg · deg. What is the specific enthalpy of vaporization at this temperature?

(*b*) The specific enthalpy of saturated steam at 100°C is 2676 kJ/kg. From part (*a*), calculate the specific enthalpy of saturated water at this temperature.

9.7. The specific heat capacity at constant pressure of steam at atmospheric pressure is given by

$$c_P = a + bT + cT^2,$$

where $a = 1.912\,\mathrm{kJ/kg\cdot deg}$

$b = 1.727 \times 10^{-3}\,\mathrm{kJ/kg\cdot deg^2}$,

$c = -4.667 \times 10^{-6}\,\mathrm{kJ/kg\cdot deg^3}$.

If the specific enthalpy of saturated steam at 100°C is 2676 kJ/kg, what is the specific enthalpy of superheated steam at the same pressure and a temperature of 300°C?

CHAPTER 10

Mathematical Methods

10.1
CHARACTERISTIC FUNCTIONS

Often, important laws are reformulated to change variables in order to simplify the analysis of a system. For example, Newton's laws of motion can be rewritten in completely equivalent Lagrange's equations for appropriate coordinate systems in classical mechanics. The Lagrange's equations, in turn, can undergo a change of variable to produce the related Hamilton's equations that are fundamentally important in quantum mechanics. Changes of variables, known as *Legendre differential transformations*, yield functions that are fundamentally important in thermodynamics.

If the state of a system is described by a function of two variables $f(x, y)$, which satisfies the equation

$$df = u\,dx + v\,dy, \tag{10.1}$$

and we wish to change the description to one involving a new function $g(u, y)$, satisfying a similar equation in terms of du and dy, then it is necessary to define the Legendre transform $g(u, y)$ as

$$g \equiv f - ux. \tag{10.2}$$

It is readily verified that g satisfies the equation

$$dg = -x\,du + v\,dy. \tag{10.3}$$

Let us use Eq. (10.2) to define new thermodynamic state functions.

Consider the first law of thermodynamics for a hydrostatic system with heat expressed in terms of temperature and entropy, namely,

$$dU = -P\,dV + T\,dS, \tag{10.4}$$

where U is a function characterized by V and S. Therefore, U is convenient for situations involving changes in volume and entropy. For other situations, it is easier to work with different variables involving different functions.

Define a new characteristic function H, called *enthalpy*, using Eq. (10.2) to obtain

$$H \equiv U + PV. \tag{10.5}$$

Since U, P, and V are all state functions, H is also a state function. In differential form,

$$dH = V\,dP + T\,dS, \tag{10.6}$$

where H is a function characterized by P and S. Enthalpy is a convenient function for problems involving heat quantities, such as heat capacities, latent heats, and heats of reaction, when pressure is the variable being controlled.

Equation (10.4) may be rewritten as

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

in order to generate a characteristic function other than enthalpy, namely, the *Helmholtz function A*, given by the Legendre transform

$$A \equiv U - TS, \tag{10.7}$$

which is also a state function. In differential form,

$$dA = -S\,dT - P\,dV, \tag{10.8}$$

where A is a function of T and V. This function is appropriate for problems in which temperature and volume are the convenient independent variables, such as the *partition function* in statistical mechanics.

The last characteristic function, known as the *Gibbs function G*, is generated by a Legendre transformation of

$$dH = T\,dS + V\,dP,$$

that is,

$$G \equiv H - TS, \tag{10.9}$$

which is also a state function. In differential form,

$$dG = V\,dP - S\,dT, \tag{10.10}$$

where G is a function characterized by P and T. The Gibbs function is designed for problems in which pressure and temperature are the convenient independent variables, namely, phase transitions and most chemical reactions.

It is important to realize that no information is lost in the transformation from one characteristic function to another. The gain is a new function expressed in thermodynamic coordinates amenable to the experimental situation at hand. This remarkable formalism and procedure was introduced into thermodynamics during the 1870s by J. Willard Gibbs, Professor of Mathematical Physics at Yale for his entire career, but the names of the functions and their symbols were chosen by other scientists.

In terms of the state functions so far defined, we have written four differential equations that are formulations of the first law, namely,

$$dU = -P\,dV + T\,dS,$$

$$dH = V\,dP + T\,dS,$$

$$dA = -P\,dV - S\,dT,$$

and

$$dG = V\,dP - S\,dT.$$

These differential equations expressing U in terms of V and S, H in terms of P and S, and so forth, form a complete set of functions, based on successive Legendre transformations of the four thermodynamic variables P, V, T, and S for a hydrostatic system. The characteristic functions $U(V, S)$, $H(P, S)$, $A(V, T)$, and $G(P, T)$ are known as *thermodynamic potential functions,* because they have the property that if the functions are expressed in terms of the appropriate thermodynamic variables, then *all the thermodynamic properties of a system can be calculated by differentiation only.* For instance, if the internal-energy function U is known as a function of V and S for a system, then we can calculate all the other thermodynamic properties of the system by differentiation, and no new constants or functions appear in the calculation. We may write

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS,$$

from which it follows, from comparison with Eq. (10.4), that

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S}\right)_V = T. \tag{10.11}$$

However, if the internal-energy function U were chosen to be a function of V and T, we could not obtain the rest of the thermodynamic properties of the system without performing integrations, which introduce unknown constants of integration. For U to be classified as a thermodynamic potential function, it must be given as a function characterized by V and S.

There can be characteristic functions calculated for hydrostatic systems other than the four functions just mentioned. Any of the four differential equations could be rearranged to produce another function. For example, $U(V, S)$ could be solved to give $S(V, U)$, and we could then say that S is the characteristic function for volume and internal energy, just as U is the characteristic function for volume and entropy. The choice of U, H, A, and G as the *fundamental* set of functions has the advantage that all four functions are energies, which, of course, are conserved.

For other simple systems, such as wires, surfaces, batteries, electrets, or paramagnets, the thermodynamic coordinates of pressure and volume are replaced by appropriate conjugate variables, as given in Table 3.1 (p. 66). But, notice that the extensive quantities simply replace volume, whereas intensive quantities replace *negative* pressure. For example, in Sec. 3.13, a composite system of an ideal paramagnetic gas was considered. Its four characteristic functions are:

$$
\begin{aligned}
dU &= -P\,dV + \mu_0 \mathscr{H}\,d\mathscr{M} + T\,dS,\\
dH &= V\,dP - \mathscr{M}\mu_0\,d\mathscr{H} + T\,dS,\\
dA &= -P\,dV + \mu_0 \mathscr{H}\,d\mathscr{M} - S\,dT,
\end{aligned}
\tag{10.12}
$$

and $$dG = V\,dP - \mathscr{M}\mu_0\,d\mathscr{H} - S\,dT.$$

Obviously, in a simple system of a paramagnetic solid, the terms involving the hydrostatic variables would not be present.

10.2
ENTHALPY

In discussing some of the properties of gases in Chap. 4, the sum of U and PV appeared several times (see Probs. 4.7 and 4.9). In order to investigate this sum, imagine a cylinder, thermally insulated and equipped with two adiabatic pistons on opposite sides of a *porous* wall that is also adiabatic, as shown in Fig. 10-1(*a*). The importance of the porous wall is to permit mass to flow from one chamber to another while controlling the pressure, unlike a free expansion. The wall, shown ruled in horizontal lines, can be a porous plug, a narrow constriction, or a series of small holes. Between the left-hand piston and the wall there is a gas at a pressure P_i and a volume V_i; since the right-hand piston against the wall prevents any gas from seeping through the porous plug, the initial state of the gas is an equilibrium state contained between the faces of the two pistons. Now, imagine that both pistons move simultaneously at different speeds to the right such that a *constant higher pressure* P_i is maintained on the left-hand side of the porous plug and a *constant lower pressure* P_f is maintained on the right-hand side. After all the gas has flowed through the porous plug, the final equilibrium state of the system is shown in Fig. 10-1(*b*). There is no knowledge of the temperature of the gas in either the initial state or the final state. A throttling process is also known as a *porous plug process* or a *Joule-Thomson expansion.*†

A throttling process exhibits internal mechanical irreversibility, due to friction between the gas and the walls of the pores in the plug. In other words, the gas passes through dissipative nonequilibrium states on its way from the initial equilibrium state to the final equilibrium state. These intermediate nonequilibrium states cannot be described by thermodynamic coordinates, but an interesting conclusion can be drawn about the initial and final

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† Also known as a *Joule-Kelvin expansion*: in the middle of the nineteenth century, James Prescott Joule collaborated on this experiment with William Thomson, who did not become known as Lord Kelvin until the end of the nineteenth century.

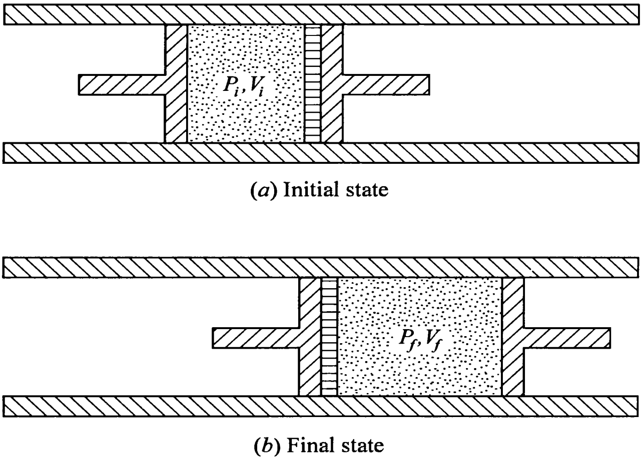

FIGURE 10-1
Throttling process (Joule-Thomson expansion).

equilibrium states, which are described by thermodynamic coordinates. From the first law,

$$(U_f - U_i) = W + Q. \tag{10.13}$$

The throttling process occurs in an adiabatic enclosure, so

$$Q = 0. \tag{10.14}$$

The net work done by the pistons on the gas causes the gas to flow across the boundary of the system enclosing the porous plug; that is,

$$W = -\int_{V_f}^{0} P_f\, dV - \int_{0}^{V_i} P_i\, dV.$$

Since both pressures remain constant on either side of the porous plug, the net work is

$$W = -(P_f V_f - P_i V_i). \tag{10.15}$$

Comparison of Eq. (10.15) with Eq. (10.13) shows that the internal energy U is different for the two equilibrium end-states of the Joule-Thomson expansion. A state function can be devised for which there is no difference in the end-states. If Eqs. (10.13), (10.14), and (10.15) are combined to obtain

$$(U_f - U_i) = -(P_f V_f - P_i V_i),$$

then

$$U_i + P_i V_i = U_f + P_f V_f. \tag{10.16}$$

Of course, the sums in Eq. (10.16) are simply the characteristic function enthalpy introduced in Eq. (10.5); that is,

$$H = U + PV. \tag{10.5}$$

So, Eq. (10.16) becomes

$$H_i = H_f \qquad \text{(throttling process)} \qquad \text{[property (1)]}, \tag{10.17}$$

which is the first of several experimental properties of enthalpy. Notice that in a throttling process the initial and final enthalpies are equal. One is not entitled to say that the enthalpy remains constant, since one cannot speak of the enthalpy of a system while it is passing through nonequilibrium states during this irreversible process. In plotting a throttling process on any diagram, the initial and final equilibrium states may be represented by points. The intermediate nonequilibrium states, however, cannot be plotted.

A continuous throttling process may be achieved by a pump that maintains a constant high pressure on one side of a porous wall or expansion valve, and a constant lower pressure on the other side, as shown in Fig. 10-2. For every kilogram of fluid that undergoes the throttling process, we may write

$$h_i = h_f,$$

where $h = H/m$ indicates *specific enthalpy*. The continuous Joule-Thomson expansion, which is essential in the production of liquid nitrogen and other cryogenic liquids, is also used in mechanical refrigerators for attaining low temperatures in situations where liquids are unavailable or undesirable.

In order to determine other properties of enthalpy, consider the change in enthalpy that occurs when an arbitrary system undergoes any infinitesimal quasi-static process from an initial equilibrium state to a final equilibrium state. We have, from Eq. (10.5),

$$dH = dU + P\,dV + V\,dP; \tag{10.18}$$

but,

$$đQ = dU + P\,dV.$$

Therefore,

$$dH = đQ + V\,dP. \tag{10.19}$$

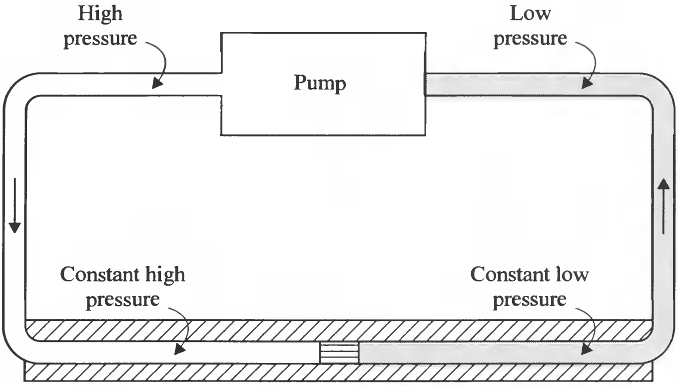

FIGURE 10-2
Apparatus for performing a continuous throttling process.

Dividing both sides by dT, we obtain

$$\frac{dH}{dT} = \frac{đQ}{dT} + V\frac{dP}{dT},$$

and, at constant P,

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{đQ}{dT}\right)_P = C_P \qquad \text{[property (2)].} \qquad (10.20)$$

Equation (10.20) shows that the state function enthalpy H is related to an experimental quantity, the isobaric heat capacity, which is also a state function. Notice that H must be a function of T and P in order to perform the partial differentiation in Eq. (10.20). If H were a function of other variables, then the partial derivative would be complicated with terms in addition to the isobaric heat capacity. Furthermore, Eq. (10.20) provides a means of calculating the enthalpy from isobaric heat capacity data, namely,

$$H_f - H_i = \int_i^f C_P\, dT \qquad \text{(all processes).} \qquad (10.21)$$

For an ideal gas, the isobaric heat capacity is constant and $H_f - H_i = C_P(T_f - T_i)$. Enthalpy values for real vapors and gases at low pressures, with empirical temperature dependence of C_P, are calculated using Eq. (10.21) and the results are expressed as specific enthalpy or molar enthalpy as a function of temperature. Such data are extremely useful in experimental or practical work, even though, in theory, the characteristic function enthalpy $H(P, S)$ is not expressly a function of temperature.

The enthalpy is related to heat, as shown in Eq. (10.19),

$$dH = đQ + V\, dP.$$

Thus, the change in enthalpy during an *isobaric* process is equal to the heat that is transferred between the system and the surroundings,

$$H_f - H_i = Q_P \qquad \text{(isobaric)} \qquad \text{[property (3)].} \qquad (10.22)$$

Equation (10.22) completes the explanation of the concept of heat begun in Sec. 4.4, where the mathematical formulation of the first law was introduced and heat was explained as heat in transit due to a difference in temperature between the system and surroundings. For an isochoric (constant volume) process in a hydrostatic system, heat is the flow of internal energy; whereas for an isobaric (constant pressure) process in a hydrostatic system, heat is the flow of enthalpy. The change of enthalpy of a system during an isobaric chemical process is commonly called the "heat of reaction," but the phrase *enthalpy of reaction* is more informative.

If heat is added to the system during a first-order phase transition (e.g., melting, boiling, or sublimation), then the change of enthalpy of the system is called "latent heat." The word "latent" acknowledges that there is no change in temperature *of the system* when heating the system during a phase transition, unlike heating without a phase transition. Again, it is more informative to use the phrase *latent enthalpy*.

The change in enthalpy of a system undergoing a reversible *adiabatic* process has an interesting graphical interpretation. From the expression

$$dH = đQ + V\,dP,$$

the change of enthalpy for an adiabatic process is

$$H_f - H_i = \int_i^f V\,dP \qquad \text{(adiabatic)} \qquad \text{[property (4)]}. \qquad (10.23)$$

The integral in Eq. (10.23) is represented by the area to the *left* of a curve for an isentropic process on a PV diagram, such as Fig. 10-3, whereas the integral $-\int P\,dV$ is represented by the area *under* an adiabatic curve on a PV diagram. There is a thermodynamic difference between the two integrals. The integral $-\int P\,dV$ is adiabatic work, which changes the configuration of a system with constant mass by changing the volume. The integral $\int V\,dP$, known as (negative) *flow-work* in engineering practice, is energy that is received by a flowing gas in a region of higher pressure, perhaps from a pump or piston, and then carried to a region of lower pressure, such as in the continuous Joule-Thomson expansion.

If a pure substance undergoes an infinitesimal reversible process, then Eq. (10.19) may be written

$$dH = T\,dS + V\,dP,$$

which, of course, is the same as Eq. (10.6). Partial differentiation yields

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \text{and} \qquad \left(\frac{\partial H}{\partial P}\right)_S = V. \qquad (10.24)$$

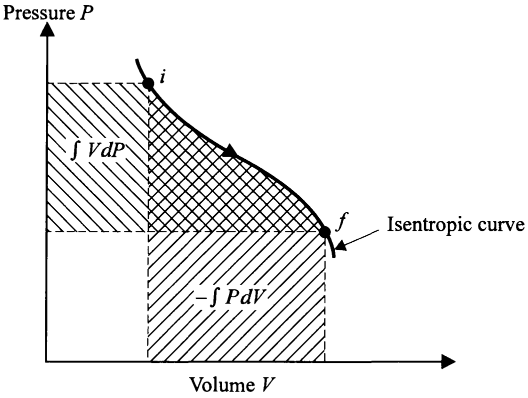

FIGURE 10-3
PV diagram illustrating the difference between work and flow-work.

The relations given in Eq. (10.24) are analogous to similar relations for internal energy given in Eq. (10.11). The properties of internal energy $U(V,S)$ and the enthalpy $H(P,S)$ are given in Table 10.1 for comparison of the two functions. The free expansion of a gas occurs in a rigid adiabatic container, which prevents work and heat from entering or leaving the system. Consequently, the internal energy U is unchanged; that is, $U_i = U_f$. Notice that the system is the entire interior volume, including the chamber that was initially empty of gas. Furthermore, the gas expands irreversibly, so no statement can be made about U during the process, only at the initial and final equilibrium states.

TABLE 10.1
Comparison of properties of *U* and *H* for a hydrostatic system

Internal energy $U(V,S)$	**Enthalpy $H(P,S)$**
Free expansion (irreversible) $U_i = U_f$	Throttling process (irreversible) $H_i = H_f$
In general $dU = đQ - P\,dV$ $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	In general $dH = đQ + V\,dP$ $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
Isochoric process $U_f - U_i = Q_V$	Isobaric process $H_f - H_i = Q_P$
For an ideal gas $U_f - U_i = \int_i^f C_V\,dT$	For an ideal gas $H_f - H_i = \int_i^f C_P\,dT$
Adiabatic process $U_f - U_i = -\int_i^f P\,dV$	Adiabatic process $H_f - H_i = \int_i^f V\,dP$
Nearby equilibrium states $dU = T\,dS - P\,dV$ $\left(\frac{\partial U}{\partial S}\right)_V = T$ $\left(\frac{\partial U}{\partial V}\right)_S = -P$	Nearby equilibrium states $dH = T\,dS + V\,dP$ $\left(\frac{\partial H}{\partial S}\right)_P = T$ $\left(\frac{\partial H}{\partial P}\right)_S = V$

10.3
HELMHOLTZ AND GIBBS FUNCTIONS

The Helmholtz function $A(V, T)$ was introduced in Eq. (10.7) as another Legendre transformation of the internal-energy function $U(V, S)$; that is,

$$A = U - TS.$$

For an infinitesimal reversible process, the Helmholtz function is given by Eq. (10.8),

$$dA = -P\,dV - S\,dT.$$

So, it follows:

1. For a *reversible isothermal process*,

$$dA = -P\,dV,$$

or

$$(A_f - A_i)_T = -\int_i^f (P\,dV)_T. \qquad (10.25)$$

Hence, the *increase* of the Helmholtz function during a reversible isothermal process equals the work done *on* the system. Alternatively, in a reversible isothermal process, the decrease in the Helmholtz function is the maximum amount of work done by the system; hence, A is sometimes called the Helmholtz *free* energy.

For any finite isothermal process, we may write, from Eq. (10.7),

$$\Delta A_T = \Delta U_T - T\,\Delta S_T,$$

or

$$\Delta A_T = \Delta U_T - \Delta Q_T = \Delta W_T.$$

The decrease of the Helmholtz energy ΔA_T of a system equals the maximum amount of isothermal work ΔW_T that is performed by the system. The internal energy U_T also decreases, but the decrease ΔU_T does not equal the work that the system can perform, as in the case of purely mechanical systems. In fact,

$$\Delta W_T \gtreqless \Delta U \qquad \text{depending on} \qquad \Delta Q_T \gtreqless 0.$$

Thermodynamic work is significantly different from mechanical work. Mechanical systems are usually considered to be reversible, whereas thermodynamic systems are only reversible in idealized cases needed for simple calculations, but are irreversible in any real, natural process.

2. For a *reversible isothermal and isochoric process*,

$$dA = 0,$$

and

$$A = \text{const.} \qquad (10.26)$$

In other words, the Helmholtz function has the same initial and final values when the initial and final temperatures and volumes are unchanged.

From the differential of the Helmholtz function,

$$dA = -P\,dV - S\,dT,$$

the pressure and the entropy may be calculated by performing the partial differentiations:

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S. \tag{10.27}$$

All the other thermodynamic variables can be calculated by differentiating the Helmholtz function, as shown in one of the problems at the end of the chapter.

The Gibbs function $G(P, T)$ was introduced in Eq. (10.9) as the last Legendre transformation, that is,

$$G = H - TS.$$

For an infinitesimal reversible process,

$$dG = V\,dP - S\,dT,$$

so the volume and the entropy may then be calculated by the partial differentiations:

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S. \tag{10.28}$$

In the case of a *reversible isothemal and isobaric process*,

$$dG = 0,$$

and

$$G = \text{const.}$$

This is a particularly important result in connection with processes involving a change of phase. Sublimation, fusion, and vaporization take place isothermally and isobarically. Hence, during such processes, the Gibbs function of the system remains constant. If we denote by the symbols g', g'', and g''', the molar Gibbs functions of a saturated solid, saturated liquid, and saturated vapor, respectively, then the equation of the fusion curve is

$$g' = g'',$$

the equation of the vaporization curve is

$$g'' = g''',$$

and the equation of the sublimation curve is

$$g' = g'''.$$

At the triple point, two equations hold simultaneously, namely,

$$g' = g'' = g'''. \tag{10.29}$$

All the g's can be regarded as functions of P and T only, and hence Eq. (10.29) serves to determine the P and T of the triple point uniquely.

The Gibbs function is extremely important in chemistry, since chemical reactions begin and end at the same equilibrium atmospheric pressure and ambient temperature.

10.4
TWO MATHEMATICAL THEOREMS

THEOREM 1. If a relation exists among x, y, and z, then we may imagine z expressed as a function of x and y; whence,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy.$$

If we let

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x,$$

then

$$dz = M\,dx + N\,dy,$$

where z, M, and N are all functions of x and y. Partially differentiating M with respect to y, and N with respect to x, we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x\,\partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y\,\partial x}.$$

Since the two second derivatives of the right-hand terms are equal, it follows that

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y.} \tag{10.30}$$

This is known as the *condition for an exact differential,* and it applies to all four characteristic functions.

THEOREM 2. If a quantity f is a function of x, y, and z, and a relation exists among x, y, and z, then f may be regarded as a function of *any two* of x, y, and z. Similarly, any one of x, y, and z may be considered to be a function of f and one other of x, y, and z. Thus, regarding x to be a function of f and y,

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy.$$

Considering y to be a function of f and z,

$$dy = \left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz.$$

Substituting this expression for dy in the preceding equation, we get

$$dx = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z\right] df + \left[\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f\right] dz.$$

But, $$dx = \left(\frac{\partial x}{\partial f}\right)_z df + \left(\frac{\partial x}{\partial z}\right)_f dz.$$

Equate the *dz* terms of the last two equations to obtain

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f = \left(\frac{\partial x}{\partial z}\right)_f,$$

that is, $$\boxed{\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1.} \qquad (10.31)$$

Notice that Eq. (10.31) is not the same as Eq. (2.6), which is an expression involving three variables instead of four variables.

Equating the *df* terms, we obtain

$$\boxed{\left(\frac{\partial x}{\partial f}\right)_z = \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z.} \qquad (10.32)$$

10.5
MAXWELL'S RELATIONS

We have seen that the hydrostatic properties of a pure substance are conveniently represented in terms of the differentials of any of these four functions:

$$dU = -P\,dV + T\,dS,$$

$$dH = V\,dP + T\,dS,$$

$$dA = -P\,dV - S\,dT,$$

and $$dG = V\,dP - S\,dT.$$

Since U, H, A, and G are actual functions, their differentials are exact differentials of the type

$$dz = M\,dx + N\,dy,$$

where z, M, and N are all functions of x and y. Apply Eq. (10.30), the condition for an exact differential, to the four exact differentials dU, dH, dA, and dG to obtain:

$$\begin{aligned}
&1.\quad dU = T\,dS - P\,dV;\ \text{hence,}\ \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.\\
&2.\quad dH = T\,dS + V\,dP;\ \text{hence,}\ \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.\\
&3.\quad dA = -S\,dT - P\,dV;\ \text{hence,}\ \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.\\
&4.\quad dG = -S\,dT + V\,dP;\ \text{hence,}\ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.
\end{aligned} \tag{10.33}$$

The four equations on the right are known as *Maxwell's relations*. These equations do not refer to a process but express relations that hold at any equilibrium state of a hydrostatic system. Of course, the reciprocals of Maxwell's relations are also valid equations.

Maxwell's relations are enormously useful, because they provide relationships between measurable quantities and those which either cannot be measured or are difficult to measure. In particular, it should be noted that pressure, volume, and temperature can be measured by experimental techniques, whereas entropy cannot be determined experimentally. By using the Maxwell relations, one can determine changes of entropy by quantities that can be measured, namely, P, V, and T in a hydrostatic system. For example, the fourth Maxwell relation,

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

may be combined with the volume expansivity β of a pure substance in order to provide information concerning the statistical interpretation of entropy in the following way. If a substance has a positive expansivity, then $(\partial V/\partial T)_P$ is positive and the derivative $(\partial S/\partial P)_T$ is negative. If the pressure on a substance is increased isothermally and if no unusual molecular rearrangements take place (such as association or dissociation), the molecules experience a decrease in entropy and are, therefore, in a more orderly state, according to microscopic theory. In other words, our knowledge about these molecules is increased.

The four characteristic functions and associated Maxwell relations need to be remembered. A useful mnemonic device for this purpose, which is shown in Fig. 10-4, is called a *König-Born diagram*, named after Max Born whose students popularized it and F. O. König who first published it. The square is also referred to as a *VAT-VUS* diagram because of the labels on the top and left side. A characteristic function is indicated at the midpoint of each side and its thermodynamic coordinates at the ends of the side. So, for example, the Helmholtz function A is a function of thermodynamic coordinates V and T, and the internal-energy function U is a function of thermodynamic coordinates V and S. The differential of the characteristic function for a simple system always equals the sum of two terms that include the differential of

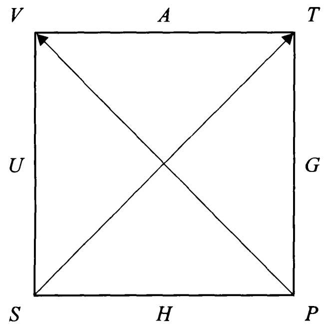

FIGURE 10-4
The *VAT-VUS* diagram; a mnemonic device for writing the differential forms of the four thermodynamic potentials.

the thermodynamic coordinates. The coefficient of the differential in each term is found by connecting the arrow from the thermodynamic coordinate of the differential to its conjugate coordinate across the *VAT-VUS* diagram. The Maxwell relations are obtained by applying Eq. (10.30) to each of the four thermodynamic potential functions.

Consider, for example, the internal-energy function $U(V, S)$. The differential dU equals the sum of terms including dV and dS. The coefficient of dV is found by the arrow that connects V to P. Notice that the connection goes against the arrow, so the coefficient of dV is not P, but $-P$. Similarly, the coefficient of dS is found by going in the direction of the arrow that connects S to T. The *VAT-VUS* diagram is modified for other simple systems by replacing P and V by the appropriate intensive and extensive variables in the new system, except that P is replaced by the *negative* of the intensive variable.

10.6
T dS EQUATIONS

The entropy of a pure substance can be considered as a function of any two variables, such as T and V; thus,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

and
$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV.$$

Since $T\,dS = đQ$ for a reversible isochoric process, it follows that

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

And, from Maxwell's third relation,

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

therefore,

$$\boxed{T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV.} \tag{10.34}$$

We shall call Eq. (10.34) the *first TdS equation.* It is useful in a variety of ways. For example, 1 mol of a van der Waals gas undergoes a reversible isothermal expansion from an initial molar volume v_i to a final molar volume v_f. How much heat has been transferred?

For 1 mol,

$$T\,ds = c_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dv,$$

where s, v, and c_V indicate molar quantities. Using the molar van der Waals equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{v^2},$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b};$$

hence,

$$T\,ds = c_V\,dT + RT\frac{dv}{v-b}.$$

Since T is constant, $c_V\,dT = 0$; and, since the process is reversible, $q = \int T\,ds$. Therefore,

$$q = RT\int_{v_i}^{v_f} \frac{dv}{v-b},$$

and, finally,

$$q = RT \ln\frac{v_f - b}{v_i - b}.$$

A second $T\,dS$ equation can be derived if the entropy of a pure substance is regarded as a function of T and P; then,

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP,$$

and

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP.$$

But,

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

And, from Maxwell's fourth relation,

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

thus,

$$\boxed{T\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP.} \tag{10.35}$$

Equation (10.35) is the *second T dS equation,* which is more useful than the first $T\,dS$ equation because the partial derivative holds pressure constant rather than volume constant. A third *T dS equation* for hydrostatic systems will be found among the problems at the end of the chapter. Two important applications of the second $T\,dS$ equation follow.

1. *Reversible isothermal change of pressure.* When T is constant,

$$T\,dS = -T\left(\frac{\partial V}{\partial T}\right)_P dP,$$

and

$$Q = -T\int\left(\frac{\partial V}{\partial T}\right)_P dP.$$

Remembering that the volume expansivity is

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

we obtain

$$Q = -T\int V\beta\,dP,$$

which can be integrated when the dependence of V and β on the pressure is known. In the case of a solid or liquid, neither V nor β is very sensitive to a change in pressure. For example, in the case of mercury, as the pressure is increased from zero to a thousand times atmospheric pressure at room temperature, the volume of 1 mol of mercury changes only $\frac{1}{3}$ percent, and the volume expansivity changes about 4 percent. The volume and the expansivity of most solids and liquids behave similarly; therefore, V and β are assumed to be constant and are brought in front of the integral sign. We then have

$$Q = -TV\beta\int_{P_i}^{P_f} dP,$$

or

$$Q = -TV\beta(P_f - P_i).$$

It is seen from this result that, as the pressure is increased isothermally, heat will flow *out* if β is positive but that, for a substance with a negative expansivity (such as water between 0 and 4°C, or a rubber band), an isothermal increase of pressure causes an absorption of heat.

If the pressure on 15 cm^3 of mercury at 20°C is increased reversibly and isothermally from 0 to 1000 atm, the heat transferred will be approximately

$$Q \simeq -TV\beta P_f,$$

where $T = 293$ K, $V = 2\times10^{-5}$ m^3, $\beta = 1.81\times10^{-4}$ K^{-1}, and $P_f = 1.01\times10^8$ Pa. Hence,

$$\begin{aligned}Q &= -(293\,\mathrm{K})(1.5\times10^{-5}\,\mathrm{m}^3)(1.81\times10^{-4}\,\mathrm{K}^{-1})(1.01\times10^{8}\,\mathrm{Pa})\\ &= -80.3\,\mathrm{N\cdot m}\\ &= -80.3\,\mathrm{J}.\end{aligned}$$

In other words, 80.3 J of heat leaves the system in order to hold the temperature constant as the pressure is increased by an enormous amount.

It is interesting to compare the heat liberated by the system with the work done on the system during the compression,

$$W = -\int P\,dV;$$

and, at constant temperature,

$$W = -\int \left(\frac{\partial V}{\partial P}\right)_T P\,dP.$$

Recalling the isothermal compressibility, $\kappa = -(1/V)(\partial V/\partial P)_T$, we get

$$W = \int_{P_i}^{P_f} V\kappa\,P\,dP.$$

The isothermal compressibility is also fairly insensitive to a change of pressure. The isothermal compressibility of mercury at room temperature changes about 2 percent as the pressure is increased from zero to a thousand times atmospheric pressure. Therefore, we may again replace V and κ by constant values and obtain

$$\begin{aligned}W &= \tfrac{1}{2}V\kappa(P_f^2 - P_i^2)\\ &\simeq \tfrac{1}{2}V\kappa\,P_f^2.\end{aligned}$$

For example, taking $\kappa = 4.01\times10^{-11}\,\mathrm{Pa}^{-1}$ for mercury, we get

$$\begin{aligned}W &= \tfrac{1}{2}V\kappa\,P_f^2\\ &= \tfrac{1}{2}(1.5\times10^{-5}\,\mathrm{m}^3)(4.01\times10^{-11}\,\mathrm{Pa}^{-1})(1.01\times10^{8}\,\mathrm{Pa})^2\\ &= 3.07\,\mathrm{J}.\end{aligned}$$

Therefore, it is seen that, if the pressure is increased from 0 to 1000 atm during a compression of 15 cm^3 of mercury maintained at 20°C, then 80.3 J of heat flows from the system but only 3.07 J of work is performed on the system! The extra amount of energy in the form of heat comes, of course, from the store of internal energy, which has changed by an amount

$$\begin{aligned}\Delta U &= Q + W\\ &= -80.3\,\mathrm{J} + 3.1\,\mathrm{J}\\ &= -77.2\,\mathrm{J}.\end{aligned}$$

Whereas isothermal compressibility κ is always a positive quantity, volume expansivity β may be positive or negative. In the foregoing example, β is positive and heat flows out of the system during compression. For a substance with a negative expansivity β, heat is absorbed by the system and the internal energy is increased.

2. *Reversible adiabatic change of pressure.* Since the entropy remains constant in this process,

$$T\,dS = 0 = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP,$$

or

$$dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP = \frac{TV\beta}{C_P}\,dP.$$

In the case of a solid or liquid, an increase of pressure of as much as 1000 atm produces only a small temperature change. Also, experiment shows that C_P hardly changes, even for an increase of 10,000 atm. The equation above, when applied to a solid or a liquid, may, therefore, be written

$$\Delta T = \frac{TV\beta}{C_P}(P_f - P_i).$$

It is clear from the discussion above that a reversible adiabatic increase of pressure will produce an increase of temperature in any substance with a positive expansivity, and a decrease in temperature in a substance with a negative expansivity.

For example, if the pressure on 15 cm^3 of mercury (specific heat $c_P = 139\,\text{J/kg}\cdot\text{K}$ and specific volume $v = 7.38 \times 10^{-5}\,\text{m}^3/\text{kg}$) at 20°C is increased isentropically from 0 to 1000 atm, the temperature change will be approximately

$$\begin{aligned}\Delta T &\simeq \frac{Tv\beta}{c_P}P_f\\ &= \frac{(293\,\text{K})(7.38\times10^{-5}\,\text{m}^3/\text{kg})(1.81\times10^{-4}\,\text{K}^{-1})}{139\,\text{J/kg}\cdot\text{K}}(1.01\times10^{8}\,\text{Pa})\\ &= 2.84\,\text{K}.\end{aligned}$$

In Sec. 2.4, the inverse of this example found that a 10°C change in the temperature of mercury requires approximately 450 atm of pressure. The discrepancy in results arises because the earlier calculation was done at constant volume, thereby eliminating the effect of work being performed. If the system were a substance with negative β, then the adiabatic increase of pressure would have produced a decrease in temperature.

10.7
INTERNAL-ENERGY EQUATIONS

If a pure substance undergoes an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = T\,dS - P\,dV.$$

Dividing by dV, we get

$$\frac{dU}{dV} = T\,\frac{dS}{dV} - P,$$

where U, S, and P are regarded as functions of T and V. If T is held constant, then the derivatives become partial derivatives, and

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

Using Maxwell's third relation, $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, we get

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.} \tag{10.36}$$

We shall call this equation the *first internal-energy equation*. Although holding the volume constant is difficult in an experiment, it is straightforward in an equation of state. Two examples of its usefulness follow.

1. *Ideal gas*:

$$P = \frac{nRT}{V},$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V},$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T\,\frac{nR}{V} - P = 0.$$

Therefore, U does not depend on V, but is a function of only T in an ideal gas.

2. *Van der Waals gas* (1 mol):

$$P = \frac{RT}{v-b} - \frac{1}{v^2},$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b},$$

and

$$\left(\frac{\partial u}{\partial v}\right)_T = T\,\frac{R}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}.$$

Consequently,

$$du = c_V\,dT + \frac{a}{v^2}\,dv,$$

and

$$u = \int c_V\,dT - \frac{a}{v} + \text{const.}$$

It follows, therefore, that the internal energy of a van der Waals gas increases as the volume increases, with the temperature remaining constant.

The second internal-energy equation shows the dependence of internal energy on pressure. We start with Eq. (10.4),

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

and divide by dP. Then,

$$\frac{dU}{dP} = T\frac{dS}{dP} - P\frac{dV}{dP},$$

where U, S, and V are regarded as functions of T and P. If T is held constant, then the derivatives become partial derivatives, and

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

Using Maxwell's fourth relation, $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, we get

$$\boxed{\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T,} \tag{10.37}$$

which is the *second internal-energy equation.*

10.8
HEAT-CAPACITY EQUATIONS

Equating the first and second $T\,dS$ equations,

$$C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV,$$

and solving for dT, we obtain

$$dT = \frac{T\left(\dfrac{\partial P}{\partial T}\right)_V}{C_P - C_V}dV + \frac{T\left(\dfrac{\partial V}{\partial T}\right)_P}{C_P - C_V}dP.$$

But,

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP.$$

Therefore,

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

and

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

Both of the foregoing equations yield the result that

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

It was shown, by Eq. (2.6), that

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T,$$

and, therefore,

$$\boxed{C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T.} \tag{10.38}$$

Equation (10.38) is an important equation in thermodynamics, and it shows that:

1. Since $(\partial P/\partial V)_T$ is always negative for all known substances and $(\partial V/\partial T)_P^2$ must be positive, then $C_P - C_V$ can never be negative; or C_P can never be less than C_V.
2. As $T \rightarrow 0$, $C_P \rightarrow C_V$; or, *at absolute zero, the two heat capacities are equal.*
3. $C_P = C_V$ when $(\partial V/\partial T)_P = 0$. For example, at 4°C, the temperature at which the density of water is a maximum, $C_P = C_V$.

Laboratory measurements of the heat capacity of solids and liquids usually take place at constant pressure and for unit mass, and, therefore, data are reported in terms of specific heat c_P. It would be extremely difficult to measure, with any degree of accuracy, c_V of a solid or liquid, because of thermal expansion. Values of c_V, however, must be known for purposes of comparison with theory. The equation for the difference in the specific heats is very useful in calculating c_V in terms of c_P and other measurable quantities. Remembering that volume expansivity is

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

and isothermal compressibility is

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,$$

we may write Eq. (10.38) in the form

$$c_P - c_V = \frac{Tv\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T},$$

or

$$\boxed{c_P - c_V = P\frac{Tv\beta^2}{\kappa},} \tag{10.39}$$

where v is the specific volume. Equation (10.39) was used in Sec. 9.8 to calculate c_V of crystalline solids. As another example, let us calculate the specific heat at constant volume of mercury at 20°C and atmospheric pressure. From experiment, we have $c_P = 139\,\mathrm{J/kg\cdot K}$, $T = 293\,\mathrm{K}$, $v = 7.38\times 10^{-5}\,\mathrm{m^3/kg}$, $\beta = 1.81\times 10^{-4}\,\mathrm{K^{-1}}$, and $\kappa = 4.01\times 10^{-11}\,\mathrm{Pa^{-1}}$. Hence,

$$139\,\mathrm{J/kg\cdot K} - c_V = \frac{(293\,\mathrm{K})(7.38\times 10^{-5}\,\mathrm{m^3/kg})(1.81\times 10^{-4}\,\mathrm{K^{-1}})^2}{4.01\times 10^{-11}\,\mathrm{Pa^{-1}}}$$

$$= 17.7\,\mathrm{J/kg\cdot K},$$

and

$$c_V = 121.3\,\mathrm{J/kg\cdot K}.$$

Finally, the ratio of specific heats γ is

$$\gamma = \frac{c_P}{c_V} = \frac{139\,\mathrm{J/kg\cdot K}}{121.3\,\mathrm{J/kg\cdot K}} = 1.15.$$

The two $T\,dS$ equations for specific heats are

$$T\,ds = c_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP,$$

and

$$T\,ds = c_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV.$$

At constant S,

$$c_P\,dT_S = T\left(\frac{\partial V}{\partial T}\right)_P dP_S,$$

and

$$c_V\,dT_S = -T\left(\frac{\partial P}{\partial T}\right)_V dV_S.$$

Dividing, we obtain

$$\frac{c_P}{c_V} = -\left[\frac{(\partial V/\partial T)_P}{(\partial P/\partial T)_V}\right]\left(\frac{\partial P}{\partial V}\right)_S.$$

But, the quantity in brackets is equal to $-(\partial V/\partial P)_T$. Therefore,

$$\frac{c_P}{c_V} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T}. \tag{10.40}$$

The *isentropic compressibility* is defined as

$$\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \tag{10.41}$$

and, as usual, the isothermal compressibility is given by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

We have, therefore,

$$\boxed{\gamma = \frac{c_P}{c_V} = \frac{\kappa}{\kappa_S},} \tag{10.42}$$

from which values of κ_S may be calculated, as was done for NaCl in Table 9.5.

PROBLEMS

10.1. Starting with the first Maxwell relation, derive the remaining three by using only the relations:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1,$$

and

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = +1.$$

10.2. Show that, for an ideal gas:

(*a*) $A = \int C_V \, dT - T \int \frac{C_V}{T} dT - nRT \ln V - \text{const.}\, T + \text{const.}$

(*b*) $G = \int C_P \, dT - T \int \frac{C_P}{T} dT + nRT \ln P - \text{const.}\, T + \text{const.}$

(*c*) Apply the above equations to 1 mol of an ideal gas.

10.3. From the differential equation for the thermodynamic potential $A(T, V)$, derive expressions for pressure P, entropy S, internal energy U, heat capacity at constant volume C_V, heat capacity at constant pressure C_P, volume expansivity β, and isothermal compressibility κ.

10.4. Derive the following equations:

(*a*) $U = -T\left(\frac{\partial A}{\partial T}\right)_V = -T^2\left[\frac{\partial (A/T)}{\partial T}\right]_V.$

(*b*) $C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V.$

(*c*) $H = G - T\left(\frac{\partial G}{\partial T}\right)_P = -T^2\left[\frac{\partial (G/T)}{\partial T}\right]_P$ (Gibbs-Helmholtz equation).

(*d*) $C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P.$

10.5. Another set of characteristic functions for a single-substance system can be defined by performing the Legendre transformations on the entropy $S(U, V)$ rather than on the internal energy $U(V, S)$. The thermodynamic potentials turn out to be particularly useful in statistical mechanics and the theory of irreversible thermodynamics, in contrast to equilibrium thermodynamics presented in this book.

(*a*) Show that Legendre transformation of $S(U, V)$ that produces the characteristic function $J(1/T, V)$, known as the *Massieu function*, is given by the transform

$$J = -\frac{U}{T} + S = -\frac{A}{T},$$

and
$$dJ = \frac{U}{T^2}\,dT + \frac{P}{T}\,dV.$$

(*b*) Show that Legendre transformation of $J(1/T, V)$ that produces the thermodynamic potential $Y(1/T, P/T)$, known as the *Planck function*, is defined by the transform

$$Y = -\frac{H}{T} + S = -\frac{G}{T},$$

and
$$dY = \frac{H}{T^2}\,dT - \frac{V}{T}\,dP.$$

10.6. From the fact that dV/V is an exact differential, derive the relation

$$\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P.$$

10.7. By invoking the condition for an exact differential, Eq. (10.30), demonstrate that the reversible heat Q_R is not a thermodynamic property.

10.8. Derive the third $T\,dS$ equation,

$$T\,dS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV,$$

and show that the three $T\,dS$ equations may be written as follows:

(*a*) $T\,dS = C_V\,dT + \dfrac{\beta T}{\kappa}\,dV.$

(*b*) $T\,dS = C_P\,dT - V\beta T\,dP.$

(*c*) $T\,dS = \dfrac{C_V \kappa}{\beta}\,dP + \dfrac{C_P}{\beta V}\,dV.$

10.9. The pressure on 500 g of copper is increased reversibly and isothermally from 0 to 5000 atm at 298 K. (Take the density $\rho = 8.96 \times 10^3\ \mathrm{kg/m^3}$, volume expansivity $\beta = 49.5 \times 10^{-6}\ \mathrm{K^{-1}}$, isothermal compressibility $\kappa = 6.18 \times 10^{-12}\ \mathrm{Pa^{-1}}$, and specific heat $c_P = 385\ \mathrm{J/kg \cdot K}$ to be constant.)

(*a*) How much heat is transferred during the compression?
(*b*) How much work is done during the compression?
(*c*) Determine the change of internal energy.
(*d*) What would have been the rise of temperature if the copper had been subjected to a reversible adiabatic compression?

10.10. The pressure on 0.2 kg of water is increased reversibly and isothermally from atmospheric pressure to 3×10^8 Pa at 20°C. (Numerical values are given in Table 9.6.)

(*a*) How much heat is transferred?

(*b*) How much work is done?
(*c*) Calculate the change in internal energy.

10.11. The pressure on 1 g of water is increased from 0 to 10^8 Pa reversibly and adiabatically. Calculate the temperature change when the initial temperature and other variables have the different values given in the three cases below:

Temperature, °C	**Specific volume** v, $10^{-3}\,\mathrm{m^3/kg}$	β, $10^{-6}\,\mathrm{K^{-1}}$	c_P, $10^3\,\mathrm{J/kg\cdot K}$
0	1.0002	−68	4.217
5	1.0000	+16	4.202
50	1.0121	+458	4.181

10.12. A gas obeys the equation $P(v-b)=RT$, where b is constant and c_V is constant. Show that:
(*a*) u is a function of T only.
(*b*) γ is constant.
(*c*) A relation that holds during an adiabatic process is

$$P(v-b)^{\gamma}=\text{const.}$$

10.13 Show that for a gas obeying the van der Waals equation $(P+a/v^2)\,(v-b)=RT$, with c_V a function of T only, an equation for an adiabatic process is

$$T(v-b)^{R/c_V}=\text{const.}$$

10.14. (*a*) Using the virial expansion

$$Pv=RT(1+BP+CP^2+\cdots)$$

calculate $(\partial u/\partial P)_T$ and its limit as $P\to 0$.
(*b*) Using the same expansion, calculate $(\partial P/\partial v)_T$ and its limit as $P\to 0$.
(*c*) Using parts (*a*) and (*b*), calculate $(\partial u/\partial v)_T$ and its limit as $P\to 0$. (Compare the solution with the results of Rossini and Frandsen given in Sec. 5.2.)

10.15. Show that the differentials of the three thermodynamic potentials U, H, and A may be written

$$dU=(C_P-PV\beta)dT+V(\kappa P-\beta T)dP,$$
$$dH=C_P\,dT+V(1-\beta T)dP,$$
and
$$dA=-(PV\beta+S)dT+PV\kappa\,dP.$$

10.16. (*a*) Derive the equation

$$\left(\frac{\partial C_V}{\partial V}\right)_T=T\left(\frac{\partial^2 P}{\partial T^2}\right)_V.$$

(*b*) Prove that C_V of an ideal gas is a function of T only.
(*c*) In the case of a gas obeying the equation of state

$$\frac{Pv}{RT} = 1 + \frac{\beta}{v},$$

where B is a function of T only, show that

$$c_V = -\frac{RT}{v}\frac{d^2}{dT^2}(BT) + (c_V)_0,$$

where $(c_V)_0$ is the value at very large volumes.

10.17. (*a*) Derive the equation

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P.$$

(*b*) prove that C_P of an ideal gas is a function of T only.

(*c*) In the case of a gas obeying the equation of state

$$Pv = RT + BP,$$

where B is a function of T only, show that

$$c_P = -T\frac{d^2B}{dT^2}P + (c_P)_0,$$

where $(c_P)_0$ is the value at very low pressures.

10.18. In the accompanying table are listed the thermal properties of liquid neon, compiled by Gladun. Calculate the plot against temperature: (*a*) c_V, (*b*) κ_S, and (*c*) γ.

T, K	**ρ, kg/m^3**	**β, 10^{-2} K^{-1}**	**κ, 10^{-8} Pa^{-1}**	**c_P, 10^3 J/kg·K**
25	1240	1.33	0.43	1.81
27	1206	1.46	0.50	1.86
29	1170	1.63	0.62	1.94
31	1131	1.84	0.79	2.04
33	1089	2.12	1.03	2.18
35	1042	2.52	1.40	2.36
37	992	3.14	2.04	2.63
39	932	4.24	3.4	3.07
41	859	6.8	6.9	4.06
42	813	10	11	4.96
43	754	18	26	7.93

10.19. Derive the following equations:

(*a*) $$C_V = -T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_S.$$

(*b*) $$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V\kappa}{\beta T}.$$

(*c*) $$\frac{(\partial V/\partial T)_S}{(\partial V/\partial T)_P} = \frac{1}{1-\gamma}.$$

10.20. Derive the following equations:

(*a*) $C_P = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_S.$

(*b*) $\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V\beta T}.$

(*c*) $\frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{\gamma}{\gamma - 1}.$

10.21. (*a*) A measure of the result of an adiabatic Joule free expansion is provided by the *Joule coefficient* $\eta = (\partial T/\partial V)_U$. Show that

$$\eta = -\frac{1}{C_V}\left(\frac{\beta T}{\kappa} - P\right).$$

(*b*) A measure of the result of the Joule-Thomson expansion (adiabatic throttling process or isenthalpic expansion) is provided by the *Joule-Thomson coefficient* $\mu = (\partial T/\partial P)_H$. Show that

$$\mu = \frac{V}{C_P}(\beta T - 1).$$

10.22. The temperature of 1 kg of mercury at 20°C is increased by 5°C under conditions of constant volume. How much heating is required? (Take the volume expansivity $\beta = 1.81 \times 10^{-4}\,\mathrm{K}^{-1}$, specific heat at constant pressure $c_P = 139\,\mathrm{J/kg \cdot K}$, isothermal compressibility $\kappa = 3.94 \times 10^{-11}\,\mathrm{Pa}^{-1}$ to be constant.)

CHAPTER 11

Open Systems

11.1
JOULE-THOMSON EXPANSION

In this chapter, we shall study the behavior of open systems by means of phase transitions. In the best-known first-order phase transitions, namely, the melting of ice and the vaporization of water, the regions of temperature and pressure are easily accessible without special apparatus. Some of the most interesting materials, however, such as nitrogen, hydrogen, and helium, whose phase transitions are well understood, exist only at low temperatures. It is important, therefore, to learn how these low temperatures are achieved and maintained. The first step is to liquefy nitrogen, which is produced by means of the *Joule-Thomson expansion* or, as it is also called, a throttling process, as discussed in Sec. 10.2.

In the Joule-Thomson expansion, a gas is made to undergo a continuous throttling process. By means of a pump, a constant pressure is maintained on one side of a porous plug and a constant lower pressure on the other side. The experiment is performed in the following way. The pressure P_i and temperature T_i on the high-pressure side of the plug are chosen arbitrarily. The pressure P_f on the other side of the plug is then set at any value less than P_i, and the temperature of the gas T_f is measured. Next, P_i and T_i are kept the same, P_f is changed to another value, and the corresponding T_f is measured. This procedure is repeated for a number of different values of P_f, and the corresponding T_f is measured in each case. The final pressure P_f is the independent variable of the experiment, and T_f is the dependent variable. The results provide a set of discrete points on a phase diagram, one point being (P_i, T_i) and the others being the various corresponding P_f's and T_f's indicated in Fig. 11-1 by numbers (1) to (7). Although the points shown in the figure do not refer to any particular gas, they are typical of most gases. It can be seen

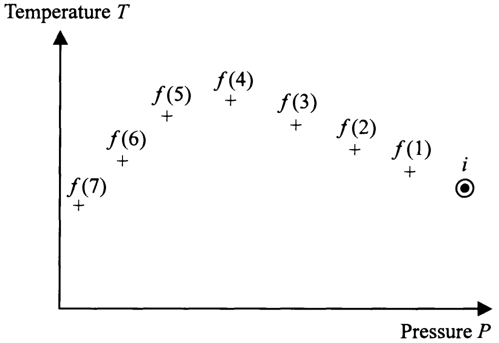

FIGURE 11-1
Isenthalpic states of a gas undergoing the Joule-Thomson expansion.

that, if a throttling process takes place between the states (P_i, T_i) and (P_f, P_f):(4), there is a rise of temperature. Between (P_t, T_i) and (P_f, T_f):(7), however, there is a drop of temperature. In general, the temperature change of a gas upon passage through a porous plug depends on the three quantities P_i, T_i, and P_f, and may be an increase or a decrease; or, there may be no change whatever in the temperature.

According to the discussion of enthalpy in Sec. 10.2, the eight points plotted in Fig. 11-1 represent equilibrium states of a certain amount of the gas (say, 1 mol), for which the gas has the same molar enthalpy at the initial equilibrium state and all the final equilibrium states. All equilibrium states of the gas corresponding to this molar enthalpy must lie on some curve, and it is reasonable to assume that this curve can be obtained by drawing a smooth curve through the discrete points. Such a curve is called an *isenthalpic curve.* Realize that *an isenthalpic curve is not the graph of a throttling process.* No such graph can be drawn, because in any throttling process the intermediate irreversible states traversed by a gas cannot be described by means of thermodynamic coordinates. An isenthalpic curve is the locus of all points representing equilibrium initial and final states of the same molar enthalpy. The throttling experiment is performed to provide a few of these points, and the rest are obtained by interpolation.

The temperature T_i on the high-pressure side is now changed to another value, with P_i being kept the same. The final pressure P_f is again varied, and the corresponding T_f's are measured. Upon plotting the new point (P_i, T_i) and the resulting P_f's and T_f's, another locus of points is obtained, which determines another isenthalpic curve corresponding to a different molar enthalpy. In this way, a series of isenthalpic curves is obtained. Such a series is shown in Fig. 11-2 for nitrogen.

The numerical value of the slope of an isenthalpic curve on a TP diagram, at any point, is called the *Joule-Thomson coefficient* and is denoted by μ. Thus,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h, \tag{11.1}$$

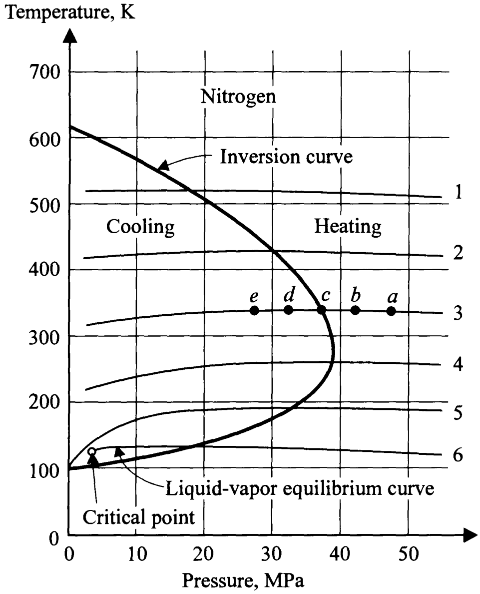

FIGURE 11-2
Isenthalpic curves, labeled 1–6, and inversion curve for nitrogen. In the region below the liquid–vapor curve, the substance is in the liquid phase.

that is, the Joule-Thomson coefficient is the slope at a point on the isenthalpic expansion curve. The locus of all points at which the Joule-Thomson coefficient is zero (the locus of the maxima of the isenthalpic curves) is known as the *inversion curve* and is shown for nitrogen in Fig. 11-2, as a heavy closed curve. The region inside the inversion curve, where μ is positive, is called the *region of cooling*, that is, the final temperature of the gas is less than the initial temperature; whereas outside the inversion curve, where μ is negative, it is called the *region of heating*, that is, the final temperature is more than the initial temperature. For example, expansion represented by movement from point (a) on Fig. 11-2 to either (b) or (c) raises the temperature of the gas, whereas movement from points (c) or (d) to (e) lowers the temperature of the gas.

Since the Joule-Thomson coefficient involves T, P, and h, we seek a relation among the differentials of T, P, and h. In general, the difference in molar enthalpy between two neighboring equilibrium states is

$$dh = T\,ds + v\,dP,$$

and, according to the second $T\,ds$ equation,

$$T\,ds = c_P\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP.$$

Substituting for $T\,ds$, we get

$$dh = c_P\,dT - \left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right] dP,$$

or

$$dT = \frac{1}{c_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right] dP + \frac{1}{c_P}\,dh.$$

Since $\mu = (\partial T/\partial P)_h$,

$$\boxed{\mu = \frac{1}{c_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right].} \tag{11.2}$$

This is the thermodynamic equation for the Joule-Thomson coefficient. The condition for the inversion curve, $\mu = 0$, is met when the quantity in the brackets vanishes. It is evident that, for 1 mol of an ideal gas, the Joule-Thomson coefficient equals

$$\mu = \frac{1}{c_P}\left(T\,\frac{R}{P} - v\right) = 0.$$

In other words, the final temperature equals the initial temperature under all conditions for an ideal gas in the Joule-Thomson expansion. For real gases, the final temperature may be either more or less than the initial temperature. As a result of the latter possibility, the most important application of the Joule-Thomson expansion is cooling of gases and their liquefaction.

11.2

LIQUEFACTION OF GASES BY THE JOULE-THOMSON EXPANSION

An inspection of the isenthalpic curves and the inversion curve of Fig. 11-2 shows that, for the Joule-Thomson expansion to give rise to cooling, the initial temperature of the gas must be below the point where the inversion curve intercepts the temperature axis, that is, below the maximum inversion temperature. Otherwise, the Joule-Thomson expansion raises the temperature of the gas. For many gases, room temperature is already below the maximum inversion temperature, so that no precooling is necessary. Thus, if air is compressed to a pressure of 200 atm and a temperature of 52°C, then, after throttling to a pressure of 1 atm, it will be cooled to 23°C. On the other hand, if helium originally at 200 atm and 52°C is throttled to 1 atm, its temperature will rise to 64°C.

Figure 11-3 shows that, before the Joule-Thomson expansion can produce cooling in hydrogen, the hydrogen must be cooled below 200 K. Liquid nitrogen at 77 K is used for this purpose. To produce Joule-Thomson cooling in helium, the helium needs to be cooled below 43 K. Liquid hydrogen is sometimes used as a refrigerant, with appropriate precautions. Table 11.1 gives the

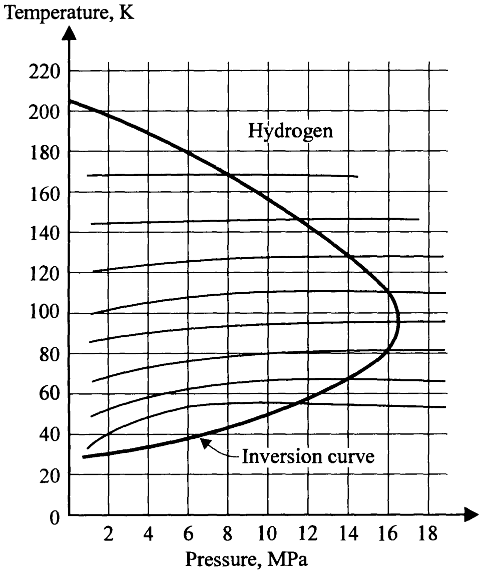

FIGURE 11-3
Isenthalpic curves and inversion curve for hydrogen.

TABLE 11.1
Maximum inversion temperatures

Gas	Maximum inversion temperature, K
Xe	1486
CO_2	1275
Kr	1079
Ar	794
CO	644
N_2	607
Ne	228
H_2	204
^4He	43

maximum inversion temperatures of a few gases. The inversion curve for ^{4}He is shown in Fig. 11-4.

It is clear from Figs. 11-2, 11-3, and 11-4 that, once a gas has been precooled to a temperature lower than the maximum inversion temperature, the optimum pressure from which to start throttling corresponds to a point on the inversion curve. Starting at this pressure and ending at atmospheric pressure, the process produces the largest temperature drop, which may not be large enough to produce liquefaction. Consequently, the gas that has been cooled by throttling is used to cool the incoming gas, which after throttling

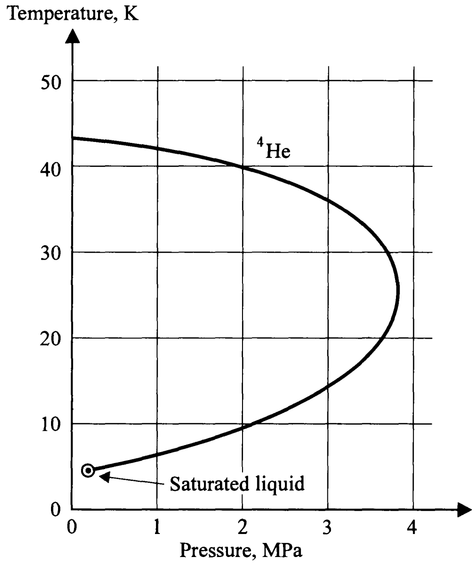

FIGURE 11-4
Inversion curve for ^{4}He.

becomes still cooler. After successive cooling processes, the temperature of the gas is lowered to such a temperature that, after throttling, it becomes partly liquefied. The device used for this purpose, a *countercurrent heat exchanger*, is shown in Fig. 11-5.

The gas, after precooling, is sent through the middle tube of a long coil of double-walled pipe. After throttling, it flows back through the outer annular space surrounding the middle pipe. For the heat exchanger to be efficient, the temperature of the gas as it leaves must differ only slightly from the temperature at which it entered. To accomplish this, the heat exchanger must be quite long and well insulated, and the gas must flow through it with sufficient speed to cause turbulent flow, so that there is good thermal contact between the opposing streams of gas.

When the steady state is finally reached, liquid is formed at a constant rate: for every mass unit of gas supplied, a certain fraction y is liquefied, and the fraction $1 - y$ is returned to the pump. Considering only the heat exchanger and throttling valve to be completely insulated, as shown in Fig. 11-6, we have a process in which the molar enthalpy of 1 mol of entering gas is equal to the molar enthalpy of y units of emerging liquid plus the molar enthalpy of $1 - y$ units of emerging gas. if

$$h_i = \text{molar enthalpy of entering gas at } (T_i, P_i),$$
$$h_L = \text{molar enthalpy of emerging liquid at } (T_L, P_L),$$

and $$h_f = \text{molar enthalpy of emerging gas at } (T_f, P_f),$$

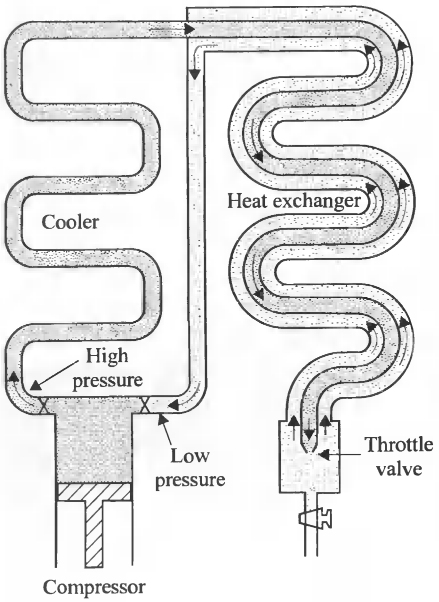

FIGURE 11-5
Apparatus for the liquefaction of a gas by means of the Joule-Thomson expansion.

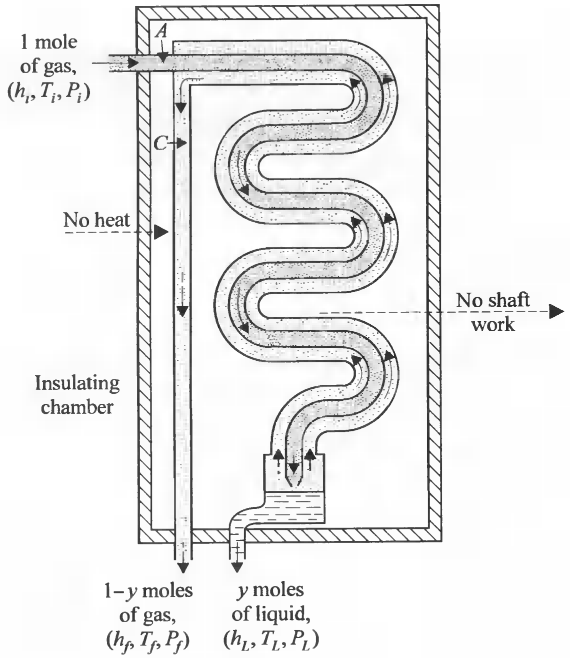

FIGURE 11-6
Throttling valve and heat exchanger in steady state.

then
$$h_i = yh_L + (1 - y)h_f,$$

or
$$y = \frac{h_f - h_i}{h_f - h_L}. \tag{11.3}$$

In the steady state, h_L is determined by the pressure on the liquid, which fixes the temperature, and hence is constant. The final molar enthalpy h_f is determined by the pressure drop in the return tube and the temperature at point C, which is only a little below that at point A; hence, h_f remains constant. The initial molar enthalpy h_i refers to a temperature T_i that is fixed, but at a pressure that may be chosen at will. Therefore, the liquefied fraction y may be varied only by varying h_i. From Eq. (11.3), it is seen that the fraction y that is liquefied will be a maximum when h_i is a minimum; and, since h_i may be varied only by varying the pressure, h_i will be a minimum when

$$\left(\frac{\partial h_i}{\partial P}\right)_{T=T_i} = 0.$$

But, from Eqs. (2.6) and (11.1),

$$\left(\frac{\partial h}{\partial P}\right)_T = -\left(\frac{\partial h}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_h = -c_P\mu;$$

hence, for y to be a maximum,

$$\mu = 0 \qquad \text{at } T = T_i,$$

or *the point* (T_i, P_i) *must lie on the inversion curve* in order to maximize the fraction y of the liquid.

In the design of gas-liquefaction equipment, a *TS* diagram showing isobars and isenthalps is particularly useful. For example, to calculate the fraction y liquefied in the steady state, the three molar enthalpies h_i, h_f, and h_L may be obtained directly from such a diagram. *TS* diagrams for hydrogen and for helium are shown in Figs. 11-7 and 11-8, respectively.

The use of the Joule-Thomson expansion to produce liquefaction of gases has two advantages: (1) There are no moving parts at low temperature that would be difficult to lubricate. (2) The lower the temperature, the larger the drop in temperature for a given pressure drop, as shown by the isenthalps in Figs. 11-2 and 11-3. For the purpose of liquefying hydrogen and helium, however, a disadvantage is that the hydrogen must be precooled with liquid nitrogen, and the helium must be precooled with liquid hydrogen.

An approximately reversible adiabatic expansion against a piston or a turbine blade always produces a decrease in temperature, no matter what the original temperature. Therefore, if a gas like helium could be made to do external work adiabatically through the medium of an engine or a turbine, then, with the aid of a heat exchanger, the helium could be liquefied without precooling. But, this method has the disadvantage that the temperature drop on adiabatic expansion decreases as the temperature decreases.

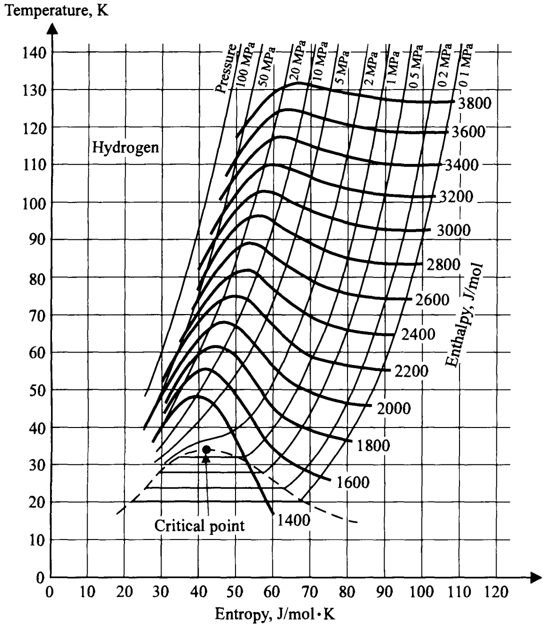

FIGURE 11-7
Temperature–entropy diagram for hydrogen.

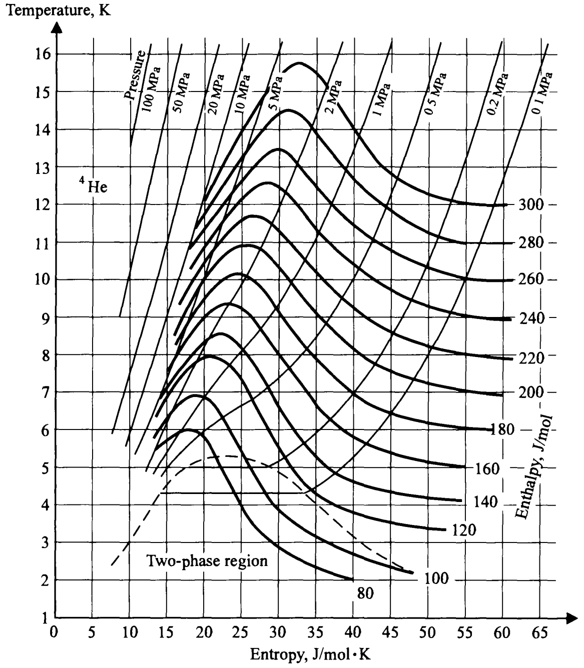

FIGURE 11-8
Temperature–entropy diagram for ^{4}He.

A combination of both methods has been used successfully. Thus, adiabatic reversible expansion is used to achieve a temperature within the inversion curve, and then the Joule-Thomson expansion completes the liquefaction. Kapitza was the first to liquefy helium in this way, with the aid of a small expansion engine that was lubricated by the helium itself. Later, he liquefied air with the aid of a centrifugal turbine only a trifle larger than a watch.

The most significant development in the field of gas liquefaction is the Collins helium liquefier, commonly called a "closed-cycle refrigerator," in which helium undergoes adiabatic expansion in a reciprocating engine. The expanded gas is then used to cool the incoming gas in the usual countercurrent heat exchanger. When the temperature is low enough, the gas passes through a throttling valve, and Joule-Thomson cooling is used to complete the liquefaction. The unit consists of a four-stage compressor, a gasholder, a purifier, and a cryostat containing the engines and heat exchangers, Dewar flasks, vacuum pumps, and gauges.

11.3
FIRST-ORDER PHASE TRANSITIONS: CLAUSIUS-CLAPEYRON EQUATION

In the familiar phase transitions — melting, vaporization, and sublimation — as well as in some less familiar transitions, such as from one polymorph of ice to another, the temperature and pressure remain constant while the entropy and volume change. Consider n_0 moles of material in phase i with molar entropy $s^{(i)}$ and molar volume $v^{(i)}$. Both $s^{(i)}$ and $v^{(i)}$ are functions of T and P, and hence remain constant during the phase transition that ends with the material in phase f with molar entropy $s^{(f)}$ and molar volume $v^{(f)}$. (The different phases are indicated by superscripts in order to reserve subscripts for specifying different states of the same phase or different substances.) Let x equal the fraction of the initial phase that has been transformed into the final phase at any moment. Then, the entropy S and the volume V of the mixture at any moment are given by

$$S = n_0(1 - x)s^{(i)} + n_0 x s^{(f)},$$

and

$$V = n_0(1 - x)v^{(i)} + n_0 x v^{(f)},$$

and S and V are seen to be linear functions of x.

If the phase transition takes place reversibly at constant pressure, the change of enthalpy per mole is given by

$$\Delta h = T(s^{(f)} - s^{(i)}).$$

The change in molar enthalpy, therefore, means that there is a change of molar entropy. Since

$$dg = -s\,dT + v\,dP,$$

then
$$s = -\left(\frac{\partial g}{\partial T}\right)_P,$$

and
$$v = \left(\frac{\partial g}{\partial P}\right)_T.$$

We may characterize the familiar phase transitions by either of the following equivalent statements:

1. There are changes of molar entropy and of molar volume.
2. The first-order derivatives of the molar Gibbs function change discontinuously.

Any phase change that satisfies these requirements is known as a *phase change of the first order*. For such a phase change, the temperature variations of g, s, v, and c_P are shown by four graphs in Fig. 11-9, which shows a phase change from liquid to vapor. The phase transition may be regarded as accomplished reversibly in either direction. Notice that the molar Gibbs function has a single value at the vaporization temperature, but the slope is discontinuous.

The fourth graph, showing the behavior of molar heat capacity c_P, is particularly significant in that *the c_P of a mixture of two phases during the*

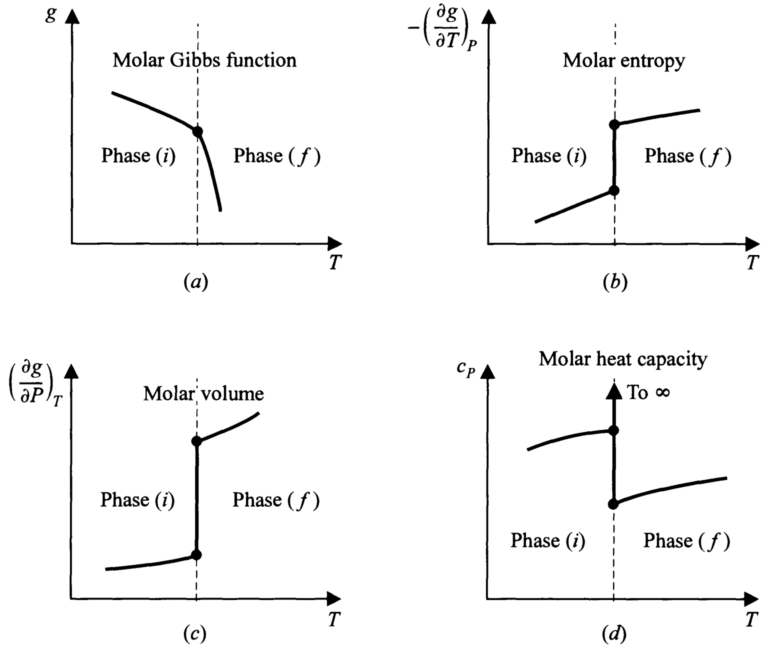

FIGURE 11-9
Characteristics of a first-order phase transition: (a) molar Gibbs function; (b) molar entropy; (c) molar volume; (d) molar heat capacity.

phase transition is infinite. This is true because the transition occurs at constant T and P. When P is constant, $dT = 0$; or when T is constant, $dP = 0$. Therefore,

$$c_P = T\left(\frac{\partial s}{\partial T}\right)_P \to \infty; \qquad \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \to \infty; \qquad \kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \to \infty.$$

It should be noticed, however, that these statements are true only when both phases are present. As shown in Fig. 11-9(d), the c_P of phase (i) remains finite right up to the transition temperature. It does not "anticipate" the onset of a phase transition by starting to rise before this temperature is reached. This is always true of a first-order transition, but not of other transitions, as will be shown in Chap. 14.

The second $T\,dS$ equation provides an indeterminate result when applied to a first-order phase transition. For 1 mol,

$$T\,ds = c_P\,dT - Tv\beta\,dP,$$

where $c_P = \infty$ and $dT = 0$; also, $\beta = \infty$ and $dP = 0$.

The first $T\,dS$ equation, however, may be integrated through the phase transition. When 1 mol of substance is converted reversibly, isothermally, and isobarically from phase (i) to phase (f), the first $T\,dS$ equation,

$$T\,ds = c_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dv,$$

may be integrated with the understanding that the various P's and T's at which a phase transition occurs obey a relation in which P is a function of T only, independent of V, so that $(\partial P/\partial T)_V = dP/dT$. Hence,

$$T\left(s^{(f)} - s^{(i)}\right) = T\,\frac{dP}{dT}\left(v^{(f)} - v^{(i)}\right).$$

The left-hand member of this equation, according to Eq. (10.6), is the isobaric change of molar enthalpy $h^{(f)} - h^{(i)}$. Hence,

$$\boxed{\frac{dP}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{h^{(f)} - h^{(i)}}{T(v^{(f)} - v^{(i)})}.} \tag{11.4}$$

This equation, known as the *Clausius-Clapeyron equation*, applies to any first-order change of phase or any transition that occurs at constant T and P. The difference in molar enthalpies at a fixed pressure $h^{(f)} - h^{(i)}$ is also known as the *molar latent heat.* Intead of molar enthalpies and molar volumes, Eq. (11.4) can also be expressed in terms of *specific* enthalpies and *specific* volumes. Of course, heat is exchanged with the surroundings, but it is the enthalpy of the system that changes.

It is instructive to derive the Clausius-Clapeyron equation in another way. It was shown in Chap. 10 that the Gibbs function remains constant during a reversible process taking place at constant temperature and pressure. Hence, for a change of phase at T and P, the molar (or specific) Gibbs functions are equal at the two end-states

$$g^{(i)} = g^{(f)};$$

and, for a phase change at $T + dT$ and $P + dP$,

$$g^{(i)} + dg^{(i)} = g^{(f)} + dg^{(f)}.$$

Subtracting, we get

$$dg^{(i)} = dg^{(f)},$$

or

$$-s^{(i)}\,dT + v^{(i)}\,dP = -s^{(f)}\,dT + v^{(f)}\,dP.$$

Therefore,

$$\frac{dP}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}},$$

or

$$\frac{dP}{dT} = \frac{h^{(f)} - h^{(i)}}{T(v^{(f)} - v^{(i)})}.$$

In dealing with phase transitions, it is necessary to indicate, in a simple way, the initial and final phases and the corresponding molar (or specific) enthalpy of transition. The notation used in this book is as follows: a symbol representing any property of the solid phase will be identified with a prime; for the liquid phase it will have a double prime, and for the vapor phase a triple prime. Thus, v' stands for the molar volume of a solid, v'' of a liquid, and v''' of a vapor. The change of molar enthalpy of fusion (melting) will be Δh_F, the change of molar enthalpy of vaporization (boiling) Δh_V, and the change of molar enthalpy of sublimation Δh_S.

11.4
CLAUSIUS-CLAPEYRON EQUATION AND PHASE DIAGRAMS

The Clausius-Clapeyron equation is important to the understanding of the coexistence curves in phase diagrams, such as the PT-projections in Fig. 9-4 for H_2O and Fig. 9-5 for CO_2, where the three coexistence curves are the sublimation curve, the fusion curve, and the vaporization curve. When a system is represented by a point on a coexistence curve, but not the critical point or triple point, then the system is made up of two coexisting phases, each with the same temperature and the same pressure for both phases. The Clausius-Clapeyron equation, however, is not concerned with the *coordinates* of a point on the coexistence curve, but, rather, with the *slope* at a point on the coexistence curve.

Consider a sample of ice that has an initial temperature T below the melting temperature and is open to atmospheric pressure P, which remains constant. Heating that increases the enthalpy also raises the temperature. In terms of the phase diagram shown in Fig. 11-10, a point in the solid region

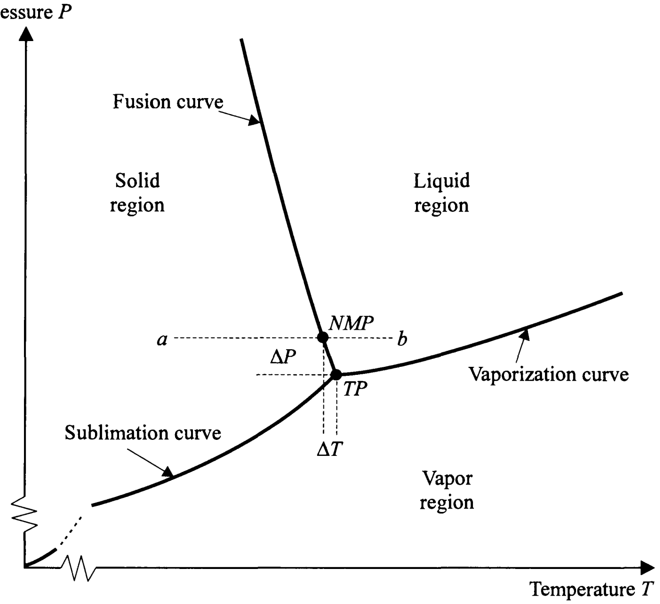

FIGURE 11-10
Phase diagram for H_2O in the region of the triple point and normal melting point.

representing the state, such as (*a*), moves horizontally until it reaches the fusion curve. Additional heating melts the ice to produce liquid water, but with no change of temperature, which is the normal melting point T_{NMP}. After enough heating has melted all the ice, the temperature of the system rises again, which is indicated on the phase diagram by the point representing the state of the system, such as (*b*), moving horizontally away from the fusion curve in the liquid region toward the vaporization curve.

A sample of ice at the normal melting point temperature T_{NMP} coexists with water and air at standard atmospheric pressure. If the sample is placed in a chamber and the air pressure of the system is lowered, then there has been a small change in pressure ΔP and the state of the system would no longer lie on the fusion curve. As a result, the temperature of the system will change by ΔT to return the state to the fusion curve. For a small-order approximation, the change in temperature is $\Delta T = \Delta P/(dP/dT)$, where the denominator is the slope of the fusion curve. Since the slope of the fusion curve for H_2O is negative, a *decrease* in pressure results in an *increase* in the melting temperature, as shown in Fig. 11-10. A few other substances, such as graphite and bismuth, show the same behavior. But, generally, the slope is positive for the fusion curve of almost all substances, so a *decrease* in pressure results in a *decrease* in the melting temperature, and vice versa.

The negative slope of the fusion curve for H_2O partially explains why the triple-point temperature $T_{TP} = 273.16\,\mathrm{K}$ is higher than the normal melting point temperature $T_{NMP} = 273.15\,\text{K}$. At the normal melting point, ice and water are in equilibrium *with air* at a pressure of 101,325 Pa. At the triple point, however, ice and water are in equilibrium with water vapor, which has a vapor pressure of only 612 Pa. Assuming that for small temperature changes the molar enthalpies and molar volumes are constant, we obtain from Eq. (11.4),

$$\Delta T = \frac{T(v'' - v')}{(h'' - h')}\Delta P,$$

where single-primed quantities refer to the solid phase and double-primed quantities to the liquid phase. Since the triple point of water is a defined temperature on the absolute temperature scale, take it to be the initial state of the system. The change in temperature by increasing the pressure from essentially zero for the triple point to atmospheric pressure for the normal melting point can be calculated to three significant figures using $T = 273\,\text{K}$, $v' = 19.64 \times 10^{-6}\,\text{m}^3/\text{mol}$, $v'' = 18.02 \times 10^{-6}\,\text{m}^3/\text{mol}$, $h'' - h' = 6.01\,\text{kJ/mol}$, and $\Delta P = 1.01 \times 10^5\,\text{Pa}$, which yields

$$\begin{aligned}\Delta T &= \frac{(273\,\text{K})(18.02 \times 10^{-6}\,\text{m}^3/\text{mol} - 19.64 \times 10^{-6}\,\text{m}^3/\text{mol})}{6.01 \times 10^3\,\text{J/mol}}(1.01 \times 10^5\,\text{Pa}) \\ &= -7.27 \times 10^{-3}\,\text{K} \\ &= -0.0073\,\text{K}.\end{aligned}$$

That is, the increase of the pressure depresses the temperature from the triple point of ice by 0.0073 K. The lowering of temperature from the triple point of ice to the normal melting point is also affected by the air that is dissolved in a mixture of ice and water. The effect of the dissolved air is to lower the temperature at which ice melts by 0.0023 K with respect to the melting temperature of pure water. Therefore, the two effects combine to lower the temperature of the triple point by 0.0096 K, or approximately 0.01 K. Since the triple point is arbitrarily assigned an exact value of 273.16 K, the result is that the normal melting point is approximately 273.15 K.

The depression of the temperature of the triple point of ice to the temperature of its normal melting point is an example of *regelation*, defined as the phenomenon in which ice (or any substance that expands upon freezing) melts under intense pressure and freezes again when this pressure is removed. It was once thought that regelation melted snow or ice under skis or ice skates to provide a slippery surface, but, in fact, friction is the major cause of melting.†

Unlike fusion curves, the slope of the sublimation and vaporization curves of all substances is always positive, because the molar volume of a vapor is always larger than the molar volume of its liquid. The increase in volume for sublimation and vaporization suggests that the vapor has more disorder than its solid or liquid, that is, the entropy of transition from solid or liquid to

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† Peter V. Hobbs: *Ice Physics*, Clarendon Press, Oxford, 1974, pp. 411–416.

vapor is positive. From the expression of the Clausius-Clapeyron equation given in Eq. (11.4), it is seen that the molar entropy of transition is related to the molar enthalpy of transition by the simple equation, $\Delta s = \Delta h/T$, where T is the temperature at which the transition occurs. The molar entropy of transition for a few common substances is shown in Table 11.2. Notice that Δs_{NBP} is significantly larger than Δs_{NMP} for each substance, because the vapor is significantly more disordered than the liquid, whereas the liquid is only moderately more disordered than the solid.

11.5
CLAUSIUS-CLAPEYRON EQUATION AND THE CARNOT ENGINE

The Clausius-Clapeyron equation may also be derived from a study of a Carnot engine, which operates using a two-phase hydrostatic system. As a result, the Clausius-Clapeyron equation is discussed from the point of view of a PV diagram, rather than a phase diagram (PT diagram).

Consider a Carnot engine operating in the two-phase region of the water-vapor region, as illustrated in Fig. 11-11 (compare with Figs. 7-2 and 9-1). In the reversible cycle shown, processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are adiabatic, and processes $2 \rightarrow 3$ and $4 \rightarrow 1$ are isothermal and isobaric. During the process $2 \rightarrow 3$, at temperature $T + dT$, n moles of liquid are converted to vapor at pressure $P + dP$; while during process $4 \rightarrow 1$, at temperature T, n moles of vapor are converted back to liquid at pressure P. From Eqs. (6.1) and (7.8) for the efficiency η of the Carnot engine, it follows that

$$\eta = \frac{|W|}{|Q_H|}$$

TABLE 11.2
Entropy changes during phase transitions
(All values of normal quantities are obtained at pressure $P = 1.01$ kPa)

Substance	**Δh_{NMP}, kJ/mol**	**T, K**	**Δs_{NMP}, kJ/mol·K**	**Δh_{NBP}, kJ/mol**	**T, K**	**Δs_{NBP}, kJ/mol·K**
H_2O	6.01	273.15	21.00	40.66	373.15	109.0
Bi	11.30	544.5	20.75	151.5	1837	74.3
Mg	8.95	922	9.91	127.4	1363	93.5
Zn	7.38	693	10.66	115.56	1184	97.6

Substance	**Δh_{TP}, kJ/mol**	**T, K**	**Δs_{TP}, kJ/mol·K**	**Δh_{NSP}, kJ/mol**	**T, K**	**Δs_{NSP}, kJ/mol·K**
CO_2 ($P_{TP} = 518$ kPa)	8.33	216.58	38.46	25.23	194.64	129.65

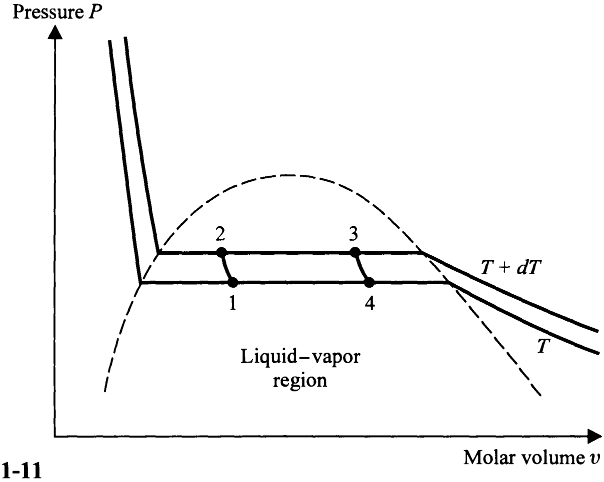

FIGURE 11-11
PV diagram showing a Carnot cycle in the liquid–vapor region.

and
$$\eta = 1 - \frac{T}{T + dT} = \frac{dT}{T},$$

so, we obtain
$$\frac{|W|}{|Q_H|} = \frac{dT}{T}. \tag{11.5}$$

The work done by the system during the Carnot cycle is the area $(dP)(n\,\Delta v)$ enclosed by the cycle, where Δv is the change of molar volume at temperature T. The heat absorbed by the system during the isothermal process 2 → 3 is $n\,\Delta h$, where Δh is the molar enthalpy of vaporization. Thus, Eq. (11.5) can be rewritten as

$$\frac{(dP)(n\,\Delta v)}{n\,\Delta h} = \frac{dT}{T},$$

or, within the coexistence region,

$$\left(\frac{dP}{dT}\right)_{\text{coexist.}} = \frac{\Delta h}{T\,\Delta v}.$$

It is interesting that the Clausius-Clapeyron equation can be derived from a Carnot cycle operating in the two-phase coexistence region of a substance without resorting to the more mathematical first $T\,dS$ equation or the Gibbs function.

11.6
CHEMICAL POTENTIAL

The first law for a *closed* hydrostatic system in terms of temperature and entropy is

$$dU(V,S) = -P\,dV + T\,dS, \tag{11.6}$$

where a closed system is one with boundaries impermeable to the transfer of matter, that is, the number of moles n of the system is constant. Let us permit matter to pass through a permeable membrane or through the channels of a porous plug. In other words, the number of moles n can change, thus becoming a new thermodynamic variable. A system in which the number of moles varies is called an *open system*. Heretofore, all systems that we have discussed have not been open, that is, they were closed to the exchange of matter.†

In Eq (11.6), the internal-energy function U depends upon the thermodynamic variables V and S, but, for an open system, U is a function also of the number of moles $n_1, n_2, \cdots, n_N$ of N different substances. Since $U(V,S,n_1,n_2,\cdots,n_N)$ is a state function, we can expand U as

$$\begin{aligned} dU(V,S,n) = {} & \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial n_1}\right)_{V,S,n'} dn_1 + \cdots + \\ & \left(\frac{\partial U}{\partial n_N}\right)_{V,S,n'} dn_N, \end{aligned} \tag{11.7}$$

where the subscript n' on all but the first two partial derivatives means that all n's, except the one in the partial derivative, are being held constant during the differentiation. From Eqs. (11.6) and (11.7), it is seen that

$$\left(\frac{\partial U}{\partial V}\right)_{S,n} = -P,$$

and

$$\left(\frac{\partial U}{\partial S}\right)_{V,n} = T,$$

in agreement with Eq. (10.11). Let us write the remaining partial derivatives as

$$\left(\frac{\partial U}{\partial n_j}\right)_{V,S,n'} \equiv \mu_j, \tag{11.8}$$

where μ_j is defined as the *chemical potential* of the jth substance (not to be confused with the Joule-Thomson coefficient, which is also written as μ). Then, Eq. (11.7) can be rewritten as

$$dU(V,S,n) = -P\,dV + T\,dS + \mu_1\,dn_1 + \cdots + \mu_N\,dn_N,$$

or, the internal energy for an open system is given by

$$dU(V,S,n) = -P\,dV + T\,dS + \sum_{j=1}^{N} \mu_j\,dn_j. \tag{11.9}$$

The terms in Eq. (11.9) are interpreted as types of energy fluxes that change the internal energy of the system. As before, the first term is the reversible

---

† An open system due to a chemical reaction will be discussed in Sec. 15.7.

work and the second term is the reversible heat. The third term is an energy flux known as the *reversible chemical* work $đW_C$, that is,

$$đW_C = \sum_{j=1}^{N} \mu_j \, dn_j. \tag{11.10}$$

Notice that the chemical potential μ is an intensive quantity, like P and T; n is an extensive quantity, like V and S. So, the formalism that established the differential of work to be the product of extensive and intensive quantities, summarized in Table 3.1, is retained for the chemical work. From Eq. (11.8), notice that the chemical potential μ_j is a function of volume, entropy, and the other $n - 1$ substances in the system. Legendre transformations of Eq. (11.9) yield expressions for the enthalpy, Helmholtz function, and Gibbs function for systems open to the flow of matter, namely,

$$dH(P, S, n) = V\,dP + T\,dS + \sum_{j=1}^{N} \mu_j \, dn_j, \tag{11.11}$$

$$dA(V, T, n) = -P\,dV - S\,dT + \sum_{j=1}^{N} \mu_j \, dn_j, \tag{11.12}$$

and

$$dG(P, T, n) = V\,dP - S\,dT + \sum_{j=1}^{N} \mu_j \, dn_j. \tag{11.13}$$

Phase transitions and chemical reactions, which have the same initial and final pressure and temperature, dictate the common practice of defining the chemical potential μ in terms of the Gibbs function $G(P, T, n)$,

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n'}, \tag{11.14}$$

although μ_j can be defined from the other characteristic functions as well. The chemical potential is a state function because it is derived from another state function.

The chemical potential can be better understood by considering the flow of matter. An isolated system consists of an impermeable rigid adiabatic container, which is partitioned into two chambers separated by a rigid diathermic wall, permeable to one substance n_1, but impermeable to all other substances $n_2, \cdots, n_N$, as shown in Fig. 11-12. In the first chamber, a gas of $n_1^{(1)}$ moles with internal energy $U^{(1)}$ is in equilibrium with $n_1^{(2)}$ moles with internal energy $U^{(2)}$ of the same gas in the second chamber, where superscripts identify the chamber. From Eq. (11.9), the change of internal energy of the entire volume (both chambers) is

$$dU = T\,dS + \mu_1 \, dn_1,$$

where the other dn_j values are zero. So,

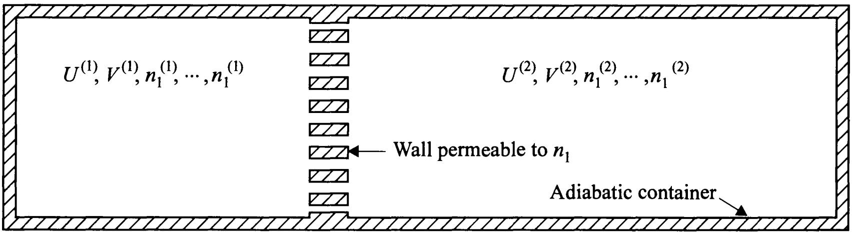

FIGURE 11-12
A rigid, adiabatic container is separated into two chambers by a wall that permits only passage of substance n_1 between the two chambers.

$$dS = \frac{dU}{T} - \frac{\mu_1}{T} dn_1.$$

Taking into account each chamber, we obtain for the composite system

$$dS = dS^{(1)} + dS^{(2)} = \frac{dU^{(1)}}{T^{(1)}} + \frac{dU^{(2)}}{T^{(2)}} - \frac{\mu_1^{(1)}}{T^{(1)}} dn_1^{(1)} - \frac{\mu_1^{(2)}}{T^{(2)}} dn_1^{(2)}. \tag{11.15}$$

Since matter and internal energy are conserved in the isolated composite system,

$$dn_1 = dn_1^{(1)} + dn_1^{(2)} = 0,$$

$$dn_1^{(1)} = -dn_1^{(2)}; \tag{11.16}$$

and

$$dU = dU^{(1)} + dU^{(2)} = 0,$$

$$dU^{(1)} = -dU^{(2)}. \tag{11.17}$$

In other words, the two subsystems are *open* systems capable of exchanging matter between one another, which is a condition heretofore not seen in the closed systems.

Substituting Eqs. (11.16) and (11.17) into Eq. (11.15) yields

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU^{(1)} - \left(\frac{\mu_1^{(1)}}{T^{(1)}} - \frac{\mu_1^{(2)}}{T^{(2)}}\right) dn_1^{(1)}. \tag{11.18}$$

When the two chambers are in equilibrium with each other, any change would be reversible and adiabatic, so there would be no change in entropy, that is, $dS = 0$ in Eq. (11.18). Since $dU^{(1)}$ and dn_1 are nonzero, their coefficients must vanish, so

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}},$$

that is, the temperatures are equal in both chambers at equilibrium. Furthermore,

$$\frac{\mu_1^{(1)}}{T^{(1)}} = \frac{\mu_1^{(2)}}{T^{(2)}},$$

or

$$\boxed{\mu_1^{(1)} = \mu_1^{(2)};} \tag{11.19}$$

that is, the chemical potentials are equal for two open systems in equilibrium. Just as temperature can be thought of as the "driving force" for the process of heating, and pressure can be thought of as the "driving force" for the performance of hydrostatic mechanical work, so, too, can the chemical potential be thought of as the "driving force" for the flow of matter.

The direction of the flow of matter within the composite system can be deduced from Eq. (11.18) in the situation where the system is not in equilibrium, but comes to equilibrium in an *irreversible* process. From the second law, the entropy must increase, or dS must be positive. Furthermore, consider the temperatures of the two subsystems $T^{(1)}$ and $T^{(2)}$ to be equal to T; then, from Eq. (11.18),

$$dS = \frac{\mu_1^{(2)} - \mu_1^{(1)}}{T} dn_1^{(1)} > 0. \tag{11.20}$$

If the chemical potential in the first chamber $\mu_1^{(1)}$ is greater than the chemical potential $\mu_1^{(2)}$ in the second chamber, then the change in the number of moles in the first chamber $dn_1^{(1)}$ is negative; that is, matter flows from the region of higher chemical potential $\mu_1^{(1)}$ to the region of lower chemical potential $\mu_1^{(2)}$.

The chemical potential has important applications in the discussion of chemical equilibrium, ideal-gas reactions, and heterogeneous systems. In the theory of electrons in solids, the chemical potential per particle is known as the *Fermi energy*. If different semiconductors and metals are placed in contact, then electrons flow from a material with higher Fermi energy to a material with lower Fermi energy. As a result, the composite system comes to equilibrium as the materials acquire a common Fermi energy, that is, the same chemical potential, according to Eq. (11.19).

11.7
OPEN HYDROSTATIC SYSTEMS IN THERMODYNAMIC EQUILIBRIUM

Let us restrict the four characteristic functions to a single substance; then,

$$dU(V,S,n) = -P\,dV + T\,dS + \mu\,dn, \tag{11.21}$$

$$dH(P,S,n) = V\,dP + T\,dS + \mu\,dn, \tag{11.22}$$

$$dA(V,T,n) = -P\,dV - S\,dT + \mu\,dn, \tag{11.23}$$

and

$$dG(P,T,n) = V\,dP - S\,dT + \mu\,dn. \tag{11.24}$$

Each of the four thermodynamic functions may be changed by a Legendre transformation of the chemical work term $\mu\, dn$ to produce a new thermodynamic potential, two of which are new to thermodynamics textbooks.[†]

The transform of the internal energy U is

$$L = U - \mu n, \tag{11.25}$$

where the function $L(V, S, \mu)$ is known as the *Hill energy*, named after the chemist Terrell Hill, which in differential form is

$$dL = -P\, dV + T\, dS - n\, d\mu. \tag{11.26}$$

The transform of the enthalpy H is

$$R = H - \mu n, \tag{11.27}$$

where the function $R(P, S, \mu)$, called the *Ray energy*, named after the physicist John Ray, has its differential form as

$$dR = V\, dP + T\, dS - n\, d\mu. \tag{11.28}$$

The Helmholtz function A yields the *grand function* J by means of the Legendre transform

$$J = A - \mu n, \tag{11.29}$$

where $J(V, T, \mu)$ gives

$$dJ = -P\, dV - S\, dT - n\, d\mu. \tag{11.30}$$

Finally, the transform of the Gibbs function G is

$$Z = G - \mu n = 0, \tag{11.31}$$

which gives the *Guggenheim function* $Z(P, T, \mu)$, given in differential form by

$$dZ = V\, dP - S\, dT - n\, d\mu = 0. \tag{11.32}$$

Equation (11.32) is also known as the *Gibbs-Duhem relation.*

The Guggenheim function $Z(P, T, \mu)$ is unique among the eight thermodynamic potentials insofar as it is a null function. Recognizing that $U(V, S, n)$ is a homogeneous function of degree one in the extensive variables V, S, and n, and using Euler's theorem of homogeneous functions on Eq. (11.21), one obtains

$$U = -PV + TS + \mu n.$$

The substitution of the above equation plus Eqs. (10.5) and (10.9) into Eq. (11.31) yields a null result. Physically, the reason that there is no function of P, T, and μ is that three intensive variables cannot be independently specified; only two can be specified and the third is found from the equation of state. Although the Guggenheim function Z is zero, it is still useful to retain a symbol for it in the formalism.

[†] H. W. Graben and John R. Ray: *Molecular Physics*, vol. 80, pp. 1183–1193, 1993.

It is important to realize that the seven functions $H(P, S, n)$, $A(V, T, n)$, $G(P, T, n)$, $L(V, S, \mu)$, $R(P, S, \mu)$, $J(V, T, \mu)$, and $Z(P, T, \mu)$ are all functions that come from Legendre transformations of the fundamental law of the conservation of energy expressed in the internal energy function $U(V, S, n)$ given in Eq. (11.21). The thermodynamic variables of U are successively replaced by other variables using Legendre transformations to produce reformulations of the law of the conservation of energy. The resulting equations are expressed as functions of other thermodynamic variables, which may be more appropriate for the situation under consideration.

Figure 11-13 illustrates the physical meanings of the eight thermodynamic functions. The isolated system with energy U, labeled (*a*), is allowed to interact with its surroundings by means of three reservoirs. The reservoirs maintain the temperature, pressure, chemical potential, or any combination thereof,

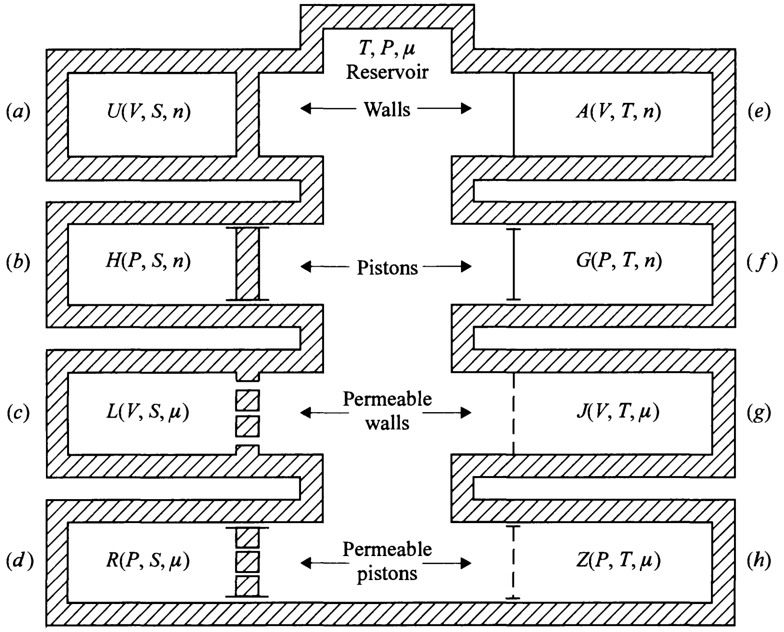

FIGURE 11-13

Eight physical systems of thermodynamics. The four isentropic systems on the left, labeled (*a*) to (*d*), are each entirely enclosed by adiabatic walls and pistons. The four isothermal systems on the right, labeled (*e*) to (*h*), are in thermal contact with temperature reservoir T by means of a diathermic wall or piston. The channels in the walls and pistons allow the exchange of matter with the chemical potential reservoir μ. A piston allows a system to maintain the pressure P of the reservoir. The interior of each system is labeled with the type of energy that is conserved when its three thermodynamic variables are held constant. (H. W. Graben and J. R. Ray, private communication. For alternate details, see their paper in *Molecular Physics*, vol. 80, pp. 1183–1193, 1993.)

constant in the given system depending on the nature of the boundary between the system and the reservoirs. The rigid, adiabatic, impermeable wall of system (*a*) is replaced by boundaries that allow reversible processes to occur. If the rigid wall is replaced by a frictionless piston under an external pressure P, then the pressure of the new system is constrained, but the volume V can vary. If the adiabatic wall is replaced by a diathermic wall in thermal contact with the temperature reservoir, then the temperature T is held constant in the system, but not the entropy S. If the impermeable wall or piston is replaced by a porous rigid or movable boundary open to a reservoir of the same gaseous substance, then the chemical potential μ is held constant, but not the amount of substance n. Thus, the three reservoirs can be used separately or in combination to produce seven reversible processes from $U(V, S, n)$, as shown in Fig. 11-13.

As a result of the reversibility of the processes, the adiabatic processes are also isentropic. Furthermore, the streaming of material through the permeable wall (porous plug) shown in Fig. 11-13(*g*) is *not* the Joule-Thomson expansion, which is an irreversible process.

The octet of formulations of the law of the conservation of energy lays the groundwork for two important applications. The first application is in research on systems of condensed matter using molecular dynamics or Monte Carlo computer simulations, a rapidly growing field called *numerical statistical mechanics*. The second application is to provide the macroscopic thermodynamic systems that correspond to microscopic systems in statistical mechanics.

PROBLEMS

11.1. (*a*) Show that in a Joule-Thomson expansion, no temperature change occurs if $(\partial v/\partial T)_P = v/T$.

(*b*) Show that

$$\mu c_P = T\left(\frac{\partial v}{\partial T}\right)_P - v.$$

In the region of moderate pressures, the equation of state of 1 mol of gas may be written

$$Pv = RT + B'P + C'P^2,$$

where the second and third virial coefficients B' and C' are functions of T only.

(*c*) Show that, as the pressure approaches zero,

$$\mu c_P \to T\frac{dB'}{dT} - B'.$$

(*d*) Show that the equation of the inversion curve is

$$P = -\frac{B' - T(dB'/dT)}{C' - T(dC'/dT)}.$$

11.2. The Joule-Thomson coefficient μ is a measure of the temperature change during a throttling process. A similar measure of the temperature change produced by an isentropic change of pressure is provided by the coefficient μ_S, where

$$\mu_S = \left(\frac{\partial T}{\partial P}\right)_S.$$

Prove that

$$\mu_S - \mu = \frac{V}{C_P}.$$

11.3. According to Hill and Lounasmaa, the equation of the ^{4}He inversion curve is

$$P = -21.0 + 5.44T - 0.132T^2,$$

where P is given in atmospheres.

(*a*) What is the maximum inversion temperature?

(*b*) What point on the inversion curve has the maximum pressure?

11.4. Derive the Clausius-Clapeyron equation from the third Maxwell's relation, namely,

$$(\partial P/\partial T)_V = (\partial S/\partial V)_T.$$

11.5. Show that a substance with a negative slope for its fusion curve, such as ordinary ice or bismuth, contracts upon melting.

11.6. Saturated liquid carbon dioxide at a temperature of 293 K and a pressure of 5.72×10^6 Pa experiences throttling to a pressure of 1.01×10^5 Pa. The temperature of the resulting mixture of solid and vapor is 195 K. What fraction is vaporized? (The enthalpy of saturated liquid at the initial state is 24,200 J/mol, and the enthalpy of saturated solid at the final state is 6750 J/mol. The heat of sublimation at the final state is 25,100 J/mol.)

11.7. The latent heat of fusion for ice I is 3.34×10^5 J/kg at 0°C and atmospheric pressure. If the change in specific volume on melting is -9.05×10^{-5} m^3/kg, then calculate the change of melting temperature due to change of pressure.

11.8. Prove that, during a first-order phase transition:

(*a*) The entropy of the entire system is a linear function of the total volume.

(*b*) The change of internal energy is given by

$$\Delta U = \Delta H\left(1 - \frac{d\ln T}{d\ln P}\right).$$

11.9. When lead is melted at atmospheric pressure, the melting point is 600 K, the density decreases from 11.01 to 10.65 g/cm^3, and the latent heat of fusion ΔH is 24.5 J/g. What is the melting point at the pressure of 1.01×10^7 Pa?

11.10. Water at its freezing point (T_i, P_i) completely fills a strong steel container. The temperature is reduced to T_f at constant volume, with the pressure rising to P_f.

(*a*) Show that the fraction y of water that freezes is given by

$$y = \frac{v_f'' - v_i''}{v_f'' - v_f'}.$$

(*b*) State explicitly the simplifying assumptions that must be made in order that y may be written

$$y = \frac{v''\left[\beta''(T_f - T_i) - \kappa''(P_f - P_i)\right]}{v_f'' - v_f'}.$$

(*c*) Calculate y for $i = 0°\text{C}$, 1.01×10^5 Pa; $f = -5°\text{C}$, 5.98×10^7 Pa; $\beta'' = -67 \times 10^{-6}\,\text{K}^{-1}$; $\kappa'' = 12.04 \times 10^{-11}\,\text{Pa}^{-1}$; $v_f'' - v_f' = -1.02 \times 10^{-4}\,\text{m}^3/\text{kg}$.

11.11. (*a*) Prove that, for a single phase,

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{c_P}{Tv\beta}.$$

(*b*) Calculate $(\partial P/\partial T)_S$ for ice at $-3°\text{C}$, where $c_P = 2.01\,\text{kJ/kg}\cdot\text{K}$, $v = 1.09 \times 10^{-3}\,\text{m}^3/\text{kg}$, and $\beta = 1.58 \times 10^{-4}\,\text{K}^{-1}$.

(*c*) Ice is initially at $-3°\text{C}$ and 1.01×10^5 Pa. The pressure is increased adiabatically until the ice reaches the melting point. At what temperature and pressure is this melting point? (*Hint*: At what point does a line whose slope is $(\partial P/\partial T)_S$ cut a line whose slope is that of the fusion curve, -1.35×10^7 Pa/K?)

11.12. Figure P11-1 shows the surface for the equation of state of water as viewed from the high-temperature end. Consider 1 kg of ice in the state i ($P_i = 1.01 \times 10^5$ Pa, $T_i = 273$ K).

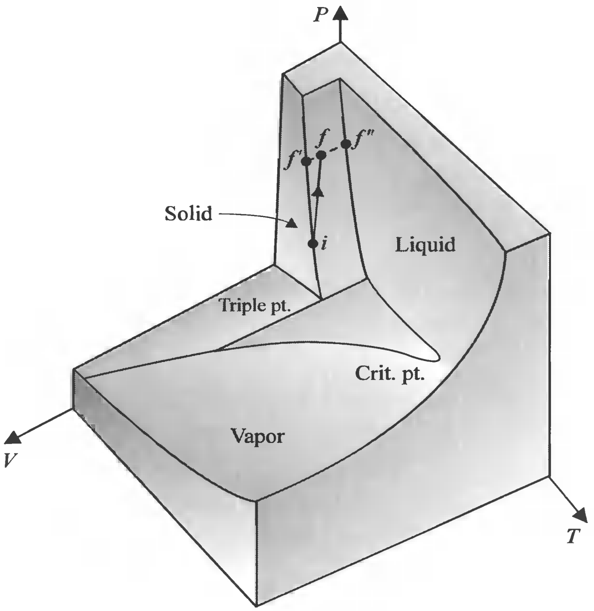

FIGURE P11-1

The ice experiences an isentropic compression to a state f:

(*a*) Why is the state f in the mixture region? In other words, why does some of the ice melt?

(*b*) Show that the fraction x of ice that is melted is given by

$$x = \frac{s_f' - s_i'}{s_f'' - s_f'}.$$

(*c*) State explicitly the simplifying assumptions that must be made in order that x may be written

$$x = -\frac{c_P'(T_f - T_i) - T_f v' \beta' (P_f - P_i)}{\Delta h_F}.$$

(*d*) Calculate x when $T_f = 272\,\mathrm{K}$, $P_f = 1.35 \times 10^7\,\mathrm{Pa}$, $c_P' = 2.01\,\mathrm{kJ/kg \cdot K}$, $v' = 1.09 \times 10^{-3}\,\mathrm{m^3/kg}$, $\beta' = 1.58 \times 10^{-4}\,\mathrm{K^{-1}}$, and $\Delta h_F = 334\,\mathrm{kJ/kg}$.

11.13. A steel bar in the form of a rectangular parallelepiped of height a, breadth b, and length c is embedded in a cake of ice as shown in Fig. P11-2. With the aid of an external magnetic field, a constant force F is exerted downward on the bar. The whole system is at 0°C.

(*a*) Show that the *decrease* in temperature of the ice directly below the bar is

$$\Delta T = \frac{FT(v' - v'')}{bc\,\Delta h_F}.$$

(*b*) Ice melts (see Prob. 11.12) under the bar, and all the water thus formed is forced to the top of the bar, where it refreezes. This phenomenon is known as *regelation*. Heat, therefore, is liberated above the bar, is conducted through the metal and a layer of water under the metal, and is absorbed by the ice under

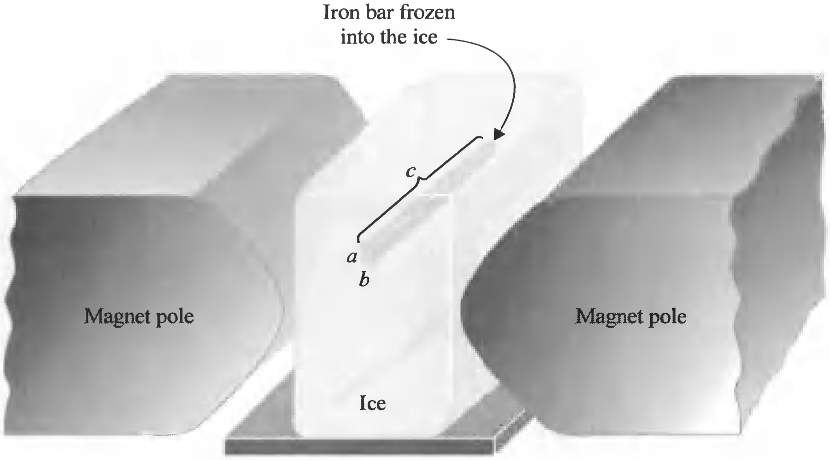

FIGURE P11-2

the layer of water. Show that the speed with which the bar sinks through the ice is

$$\frac{dy}{dt} = \frac{U'T(v' - v'')F}{\rho(\Delta h_F)^2 bc},$$

where U' is the overall heat-transfer coefficient of the composite heat-conducting path consisting of the metal and the water layer. U' is given by

$$\frac{1}{U'} = \frac{x_m}{K_m} + \frac{x_w}{K_w},$$

where x_m and x_w are the thicknesses of the metal and water layer, respectively, and K_m and K_w are their respective thermal conductivities.

(*c*) Assuming that the water layer has a thickness of about 10^{-5} m and a thermal conductivity of about 0.6 W/m · K, and that the bar is 0.1 m long, with a and b each equal to 10^{-3} m, with what speed will the bar descend when $F = 10^2$ N? (Thermal conductivity of steel is 60 W/m · K.)

11.14. (*a*) From Eq. (11.22) derive the relation

$$\left(\frac{\partial S}{\partial P}\right)_{H,n} = -\frac{V}{T}.$$

(*b*) For the ideal gas, the entropy as a function of H, P, n has the form

$$S(H, P, n) = R \ln \frac{f(H, n)}{P^n},$$

where $f(H, n)$ is a function of the enthalpy H and the number of moles n. Using the result from part (*a*), derive the ideal-gas equation of state. (From H. W. Graben and J. R. Ray, *Physical Review*, Ser. A, vol. 43, pp. 4100–4103, 1991.)

PART II

Applications of Fundamental Concepts

CHAPTER 12

Statistical Mechanics

12.1
FUNDAMENTAL PRINCIPLES

In the treatment of kinetic theory given in Sec. 5.9, the particles of an ideal gas could not be regarded as completely independent of one another, for then they could not arrive at an equilibrium distribution of velocities. Therefore, it was assumed that interaction *did* take place, but only during collisions with other particles and with the walls. To describe this limited form of interaction, we refer to the particles as "weakly interacting" or "quasi-independent." The treatment of strongly interacting particles is beyond the scope of the present discussion.

The particles of an ideal gas have another characteristic besides their quasi-independence. They are *indistinguishable*, because they are not localized in space. It was emphasized in Sec. 5.9 that the particles have neither a preferred location nor a preferred velocity. The particles occupying regular lattice sites in a crystal are distinguishable, however, because they are constrained to oscillate about fixed positions; therefore, one particle can be distinguished from its neighbors by its location. The statistical treatment of an ideal crystal as a number of distinguishable, quasi-independent particles will be given in the next chapter. In this chapter, we shall confine our attention to the indistinguishable, quasi-independent atoms of an ideal gas.

Suppose that a closed system contains a monatomic ideal gas consisting of N weakly interacting atoms, where N is an enormous number, say, about 10^{20}. Let the gas be contained in an adiabatic cubical enclosure whose edge has a length L, which could be changed, and let the energy ϵ of any particle, as a first step, be entirely kinetic energy of translation. In the x-direction, the energy ϵ_x is given by

$$\epsilon_x = \tfrac{1}{2}m\dot{x}^2 = \frac{(m\dot{x})^2}{2m} = \frac{p_x^2}{2m},$$

where p_x is the x-component of the momentum. If the particle is assumed to move freely back and forth between two planes a distance L apart, then the Bohr-Sommerfeld form of quantum mechanics provides that, in a complete cycle (from one wall to the other and back again, or a total distance of $2L$), the constant momentum p_x multiplied by the total path $2L$ is an integer n_x times Planck's constant h. Thus,

$$p_x \cdot 2L = n_x h,$$

where n_x is the quantum number of a particle having momentum p_x. Substituting this result into the previous equation, we get

$$\epsilon_x = n_x^2 \frac{h^2}{8mL^2},$$

or

$$n_x = \frac{L}{h}\sqrt{8m\epsilon_x}.$$

The allowed values of kinetic energy ϵ_x are *discrete*, corresponding to integer values of n_x; but, when n_x changes by unity, the corresponding change in ϵ_x is very small, because n_x itself is exceedingly large. To see that a typical value of n_x is very large, consider a cubical box containing gaseous helium at 300 K, whose edge is, say, 10 cm. It was shown at the end of Chap. 5 [Eq. (5.29)] that the average energy of a monatomic ideal gas is $\frac{3}{2}kT$. Since an atom has 3 degrees of freedom, and there is no preferred direction, it follows that the average energy associated with each translational degree of freedom is $\frac{1}{2}kT$. Then, for energy ϵ_x,

$$\begin{aligned}\epsilon_x = \tfrac{1}{2}kT &= \tfrac{1}{2}\left(1.4 \times 10^{-23}\,\frac{\text{J}}{\text{K}}\right)(300\,\text{K})\\ &= 2.1 \times 10^{-21}\,\text{J},\end{aligned}$$

and the number of quantum states for the energy ϵ_x is

$$\begin{aligned}n_x = \frac{L}{h}\sqrt{8m\epsilon_x} &= \frac{0.1\,\text{m}}{6.6 \times 10^{-34}\,\text{J}\cdot\text{s}}\sqrt{8(6.6 \times 10^{-27}\,\text{kg})(2.1 \times 10^{-21}\,\text{J})}\\ &\simeq 10^9;\end{aligned}$$

that is, there are approximately one billion quantum states for a helium atom moving in the x-direction at room temperature. Therefore, the change of energy when n_x changes by unity is so small that, for most practical purposes, the energy may be assumed to vary continuously. This will be of advantage later, when it will be found useful to replace a sum by an integral.

Taking into account all three components of momentum, we get for the *total* kinetic energy of a particle in a cube of side L:

$$\epsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2). \tag{12.1}$$

The specification of the three integers n_x, n_y, and n_z is a specification of a *quantum state* of a particle in a box. All states characterized by values of the n's such that $n_x^2 + n_y^2 + n_z^2 = \text{const.}$ will have the same energy. To use an example given by Guggenheim,† the states corresponding to the values of n_x, n_y, and n_z in Table 12.1 all have the energy $\epsilon_i = 66h^2/8mL^2$. There are twelve quantum states associated with the same *energy level*, and, therefore, we refer to this energy level ϵ_i as having a *degeneracy* g_i of 12. In any actual case, $n_x^2 + n_y^2 + n_z^2$ is an enormous number, so that the degeneracy of an actual energy level is extremely large. Notice that Eq. (12.1) could be written

$$\epsilon = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2), \tag{12.2}$$

where $V^{2/3} = L^2$, so the total kinetic energy is a function of the thermodynamic variable volume.

However close they may be, there is still only a finite number of discrete energy levels for the atoms of an ideal gas. It is the fundamental problem of statistical mechanics to determine, at equilibrium, the *populations* of these energy levels — that is, the number of particles N_1 having energy ϵ_1, the number N_2 having energy ϵ_2, and so on. It is a simple matter to show that (see Prob. 12.4) the number of quantum states g_i corresponding to an energy level ϵ_i (the degeneracy of the level) is very much larger than the number of particles N_i occupying that level at room temperature. Thus,

$$g_i \gg N_i. \tag{12.3}$$

It is very unlikely, therefore, that, at room temperature, more than one particle will occupy the same quantum state at any one time.

At any one moment, some particles are moving rapidly and some slowly, so that the particles are distributed among a large number of different quantum states. As time goes on, the particles collide with one another and with the

TABLE 12.1

An example of 12 distinguishable states of n_x, n_y, and n_z having the same total kinetic energy ϵ equal to $n_x^2 + n_y^2 + n_z^2 = 66$ units of $h^2/8mL^2$

	1	2	3	4	5	6	7	8	9	10	11	12
n_x	8	1	1	7	1	4	7	4	1	5	5	4
n_y	1	8	1	4	7	1	1	7	4	5	4	5
n_z	1	1	8	1	4	7	4	1	7	4	5	5

---

† E. A. Guggenheim: *Boltzmann's Distribution Law*, Interscience Publishers, Inc., New York, 1955.

walls, or emit and absorb photons, so that each particle undergoes many changes from one quantum state to another. The fundamental assumption of statistical mechanics is that *all quantum states have equal likelihood of being occupied.* The probability that a particle may find itself in a given quantum state is the same for all states.

Now, consider the N_i particles in any of the g_i quantum states associated with the energy ϵ_i. Any one particle would have g_i choices in occupying g_i different quantum states. A second particle would have the same g_i choices, and so on. The total number of ways in which N_i *distinguishable* particles could be distributed among g_i quantum states would, therefore, be $g_i^{N_i}$. But, the quantity $g_i^{N_i}$ is much too large, since it holds for distinguishable particles such as A, B, and C in Fig. 12-1. This figure shows six different ways in which three distinguishable particles can occupy three quantum states. If the particles had no identity (were *indistinguishable*), then there would be only one way to occupy these particular quantum states. That is, one must divide by 6 (the number of permutations), which is 3!. The number of permutations of N_i distinguishable objects is $N_i!$. If the quantity $g_i^{N_i}$ is divided by this factor, the resulting expression will then hold for indistinguishable particles. Therefore,

$$\left.\begin{array}{c}\text{No. of ways that } N_i \textit{ indistinguishable} \\ \text{quasi-independent particles can be} \\ \text{distributed among } g_i \text{ quantum states}\end{array}\right\} = \frac{g_i^{N_i}}{N_i!}. \qquad (12.4)$$

It should be pointed out that the N indistinguishable, quasi-independent particles were assumed to be contained within a cubical box only for the sake of simplicity. A rectangular box with three different dimensions could easily have been chosen, and Eq. (12.4) would be unchanged.

A	*B*	*C*
A	*C*	*B*
B	*A*	*C*
B	*C*	*A*
C	*A*	*B*
C	*B*	*A*

FIGURE 12-1
The six ways in which three *distinguishable* particles A, B, and C can be permuted to occupy the three degenerate quantum states of energy ϵ_i.

12.2
EQUILIBRIUM DISTRIBUTION

We have seen that, in the case of an ideal gas, there are many quantum states corresponding to the same energy level and that the degeneracy g_i of each level is much larger than the number of particles which would be found in any one level at any one time. The specification, at any one moment, that there are

N_1 particles in energy level ϵ_1 with degeneracy g_i
N_2 particles in energy level ϵ_2 with degeneracy g_i
. . .
. . .
. . .
N_i particles in energy level ϵ_i with degeneracy g_i
. . .
. . .
. . .

in a container of volume V, when the gas has a total number of particles N and an energy U, is a description of a *macrostate* of the gas. The number of ways Ω in which this macrostate may be achieved is given by a product of terms of the type of Eq. (12.4), or

$$\boxed{\Omega = \frac{g_1^{N_1}}{N_1!}\,\frac{g_2^{N_2}}{N_2!}\cdots.} \tag{12.5}$$

The quantity Ω is called the *thermodynamic probability* of the particular macrostate. Another name for this quantity is the *number of accessible microstates*. Whatever its name, the larger Ω is, the greater the probability of finding the system of N particles in this state. It is assumed that, if V, N, and U are kept constant, *the equilibrium state of the gas will correspond to that macrostate in which Ω is a maximum.* To find the equilibrium populations of the energy levels, therefore, we look for the values of the individual N's that render Ω (or, in anticipation of further results, $\ln \Omega$) a maximum.

Since $\ln \Omega$ contains factorials of large numbers, it is convenient to use Stirling's approximation, which may be derived in the following way: the natural logarithm of x factorial is

$$\ln(x!) = \ln 2 + \ln 3 + \cdots + \ln x.$$

If we draw a series of steps on a diagram, as shown in Fig. 12-2, where the integers are plotted along the x-axis and $\ln x$ along the y-axis, the area under each step is exactly equal to the natural logarithm, since the width of each step equals unity. The area under the steps from $x = 1$ to $x = x$ is, therefore, $\ln(x!)$.

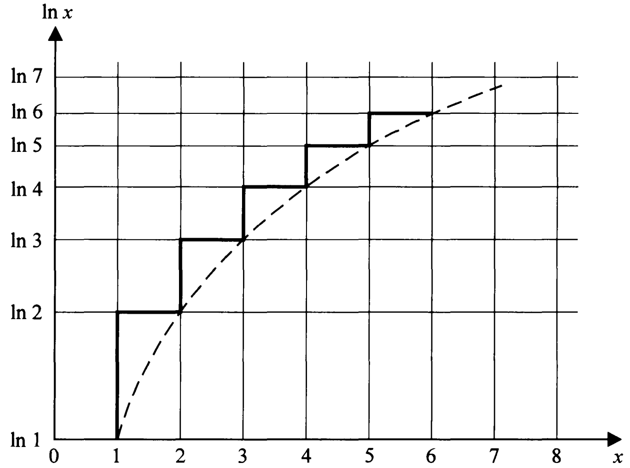

FIGURE 12-2
The area under the dashed curve approximates the area under the steps ($\ln 2 + \ln 3 + \ln 4 + \cdots + \ln x$), when x is large.

When x is large, we may replace the steps by a smooth curve, shown as a dashed curve in Fig. 12-2; therefore, approximately, when x is large,

$$\ln(x!) \approx \int_1^x \ln x \, dx.$$

Integrating by parts, we get

$$\ln(x!) \approx x \ln x - x + 1.$$

Then, if we neglect 1 compared with x,

$$\boxed{\ln(x!) \approx x \ln x - x.} \tag{12.6}$$

This formula is *Stirling's approximation.*

Using Stirling's approximation in Eq. (12.5), we get for $\ln \Omega$,

$$\begin{aligned}\ln \Omega &= N_1 \ln g_i - N_1 \ln N_1 + N_1 + N_2 \ln g_2 - N_2 \ln N_2 + N_2 + \cdots \\ &= \sum N_i \ln g_i - \sum N_i \ln N_i + \sum N_i,\end{aligned}$$

or

$$\ln \Omega = \sum N_i \ln \frac{g_i}{N_i} + N, \tag{12.7}$$

where we have used the fact that $\sum N_i = N$. Our problem now is to render $\ln \Omega$ a maximum, subject to the conditions that

$$\sum N_i = N = \text{const.}, \tag{12.8}$$

and

$$\sum N_i \epsilon_i = U = \text{const.} \tag{12.9}$$

Before we proceed to solve this problem by the method of Lagrangian multipliers, it is important to bear in mind that the ϵ's and g's are constants. The only variables are the populations N_i of the energy levels with the condition $\sum N_i = N$ is constant.

Since $dN = 0$, the differential of $\ln \Omega$ is

$$\begin{aligned} d \ln \Omega &= \sum d\left(N_i \ln \frac{g_i}{N_i}\right) = \sum \ln \frac{g_i}{N_i} dN_i + \sum \frac{N_i^2}{g_i}\left(-\frac{g_i}{N_i^2}\right) dN_i \\ &= \sum \ln \frac{g_i}{N_i} dN_i - d \sum N_i \\ &= \sum \ln \frac{g_i}{N_i} dN_i. \end{aligned} \tag{12.10}$$

Setting the differential of $\ln \Omega$ equal to zero in Eq. (12.10), in order to maximize the thermodynamic probability, and taking the differential of Eqs. (12.8) and (12.9), we get

$$\begin{aligned} \ln \frac{g_i}{N_1} dN_1 + \ln \frac{g_2}{N_2} dN_2 + \cdots + \ln \frac{g_i}{N_i} dN_i + \cdots &= 0, \\ dN_1 + \quad dN_2 + \cdots + \quad dN_i + \cdots &= 0, \end{aligned}$$

and

$$\epsilon_1\, dN_1 + \epsilon_2\, dN_2 + \cdots + \epsilon_i\, dN_i + \cdots = 0.$$

Multiplying the second equation by $\ln \lambda$ and the third by $-\beta$, where $\ln \lambda$ and $-\beta$ are Lagrangian multipliers (see Appendix B), we get, for the three equations above,

$$\begin{aligned} \ln \frac{g_1}{N_1} dN_1 + \ln \frac{g_2}{N_2} dN_2 + \cdots + \ln \frac{g_i}{N_i} dN_i + \cdots &= 0, \\ \ln \lambda\, dN_1 + \ln \lambda\, dN_2 + \cdots + \ln \lambda\, dN_i + \cdots &= 0, \end{aligned}$$

and

$$-\beta\epsilon_1\, dN_1 - \beta\epsilon_2\, dN_2 - \cdots - \beta\epsilon_i\, dN_i - \cdots = 0.$$

If we add these equations, the coefficient of each dN must equal zero, since the dN_i can take any arbitrary value independently of any other dN_j. Taking the ith term,

$$\ln \frac{g_i}{N_i} + \ln \lambda - \beta\epsilon_i = 0,$$

or

$$\ln \frac{N_i}{g_i} - \ln \lambda = -\beta\epsilon_i,$$

or

$$N_i = \lambda g_i e^{-\beta\epsilon_i}. \tag{12.11}$$

The population N_i of any energy level at equilibrium is, therefore, seen to be proportional to the degeneracy g_i of the level and to vary exponentially with the energy of the level ϵ_i.

The next step is to determine the physical significance of the Lagrangian multipliers λ and β.

12.3
SIGNIFICANCE OF LAGRANGIAN MULTIPLIERS λ AND β

The population N_i of the ith energy level ϵ_i is given by

$$N_i = \lambda g_i e^{-\beta\epsilon_i}.$$

Summing over all the energy levels, we get

$$\sum N_i = \lambda \sum g_i e^{-\beta\epsilon_i}$$

and

$$\lambda = \frac{N}{\sum g_i e^{-\beta\epsilon_i}}. \tag{12.12}$$

The sum in the denominator plays a fundamental role in statistical mechanics. It was first introduced by Boltzmann, who called it the *Zustandsumme*, or "sum over states." We retain the first letter of *Zustandsumme* as a mathematical symbol, but the accepted English expression for this sum is the *partition function.* Thus,

$$Z = \sum g_i e^{-\beta\epsilon_i}, \tag{12.13}$$

and the Lagrangian multiplier λ becomes

$$\lambda = \frac{N}{Z}. \tag{12.14}$$

Substituting this result into Eq. (12.11), we get, for the population N_i of the ith energy level,

$$N_i = N\frac{g_i e^{-\beta\epsilon_i}}{Z}. \tag{12.15}$$

It will be shown later that Z is proportional to the volume of the container.

Since the properties of a gas depend on temperature as well as on volume, one would expect a relation between β and the temperature. To introduce the concept of temperature into statistical mechanics, we must go back to the fundamental idea of thermal equilibrium between two systems. Consequently, let us consider a thermally insulated composite system consisting of two samples of ideal monatomic gas separated by a diathermic wall, as shown in Fig. 12-3. Such a closed isothermal system is known as a *canonical ensemble* in statistical mechanics; the conditions for the canonical ensemble are the same as for the Helmholtz function A depicted in Fig. 11-3(*e*). For the sample of gas in the second chamber, the symbols expressing energy levels, populations, etc., are distinguished from the first sample with a circumflex. The thermodynamic probability Ω of the composite system is the product of the separate thermodynamic probabilities, so that the logarithm of Ω is

$$\ln\Omega = \sum N_i \ln\frac{g_i}{N_i} + N + \sum \hat{N}_j \ln\frac{\hat{g}_j}{\hat{N}_j} + \hat{N}.$$

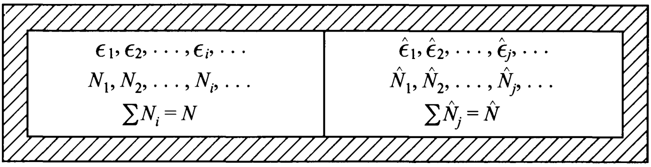

FIGURE 12-3
An isolated composite system of two samples of ideal monatomic gas separated by a diathermic wall. The total internal energy is constant.

Each sample has a constant number of particles, so that

$$\sum N_i = N = \text{const.}$$

and

$$\sum \hat{N}_j = \hat{N} = \text{const.};$$

but the internal energy of each sample is *not constant* because the samples can exchange heat through the diathermic wall in order to maintain the composite system at the same temperature. However, the total internal energy of the *composite* system is constant; thus,

$$\sum N_i\epsilon_i + \sum \hat{N}_j\hat{\epsilon}_j = U = \text{const.}$$

To find equilibrium conditions that maximize the thermodynamic probability, we proceed as before, using the method of Lagrangian multipliers to obtain four equations instead of three:

$$\begin{aligned} \sum \ln\frac{g_i}{N_i}\,dN_i + \sum \ln\frac{\hat{g}_j}{\hat{N}_j}\,d\hat{N}_j &= 0, \\ \ln\lambda \sum dN_i \qquad\qquad\qquad &= 0, \\ \ln\hat{\lambda}\sum d\hat{N}_j &= 0, \end{aligned}$$

and

$$-\beta\sum \epsilon_i\,dN_i - \beta\sum \hat{\epsilon}_j\,d\hat{N}_j = 0.$$

Adding and setting each coefficient of dN_i and $d\hat{N}_j$ equal to zero, we get *two* sets of equations,

$$N_i = \lambda g_i e^{-\beta\epsilon_i}$$

and

$$\hat{N}_j = \hat{\lambda}\hat{g}_j e^{-\beta\hat{\epsilon}_j},$$

where all quantities are different, *except* β. When two systems separated by a diathermic wall come to equilibrium, the temperatures are the same and the β's are the same. The conclusion that β is connected with the temperature is inescapable.

It was shown in Chap. 8 that the entropy of an isolated system increases when the system undergoes a spontaneous, irreversible process. At the conclusion of such a process, when equilibrium is reached, the entropy has the maximum value consistent with its internal energy and volume. The thermodynamic probability also increases and approaches a maximum as equilibrium is approached. Therefore, we look for some correlation between S and Ω. Consider two similar systems A and B in thermal contact — one with entropy S_A and thermodynamic probability Ω_A, the other with values S_B and Ω_B. Since entropy is an extensive variable, the total entropy of the composite system is the sum

$$S = S_A + S_B.$$

The thermodynamic probability, however, is the product, or

$$\Omega = \Omega_A \cdot \Omega_B.$$

If we let the entropy be a function of the thermodynamic probability, that is

$$S = f(\Omega),$$

then the function of the product of the thermodynamic probabilities must equal the sum of the function of each probability,

$$f(\Omega_A \Omega_B) = f(\Omega_A) + f(\Omega_B).$$

The only function that satisfies this relation is the logarithm, which explains the reason for introducing $\ln \Omega$ following Eq. (12.5). Introducing an arbitrary constant k', we may write for the entropy,

$$\boxed{S = k' \ln \Omega} \qquad (12.16)$$

for the relation between entropy and thermodynamic probability.

The first law of thermodynamics applied to any infinitesimal process of a hydrostatic system is

$$đQ = dU + P\,dV.$$

If the process takes place between two neighboring equilibrium states, it may be performed reversibly, in which case $đQ = T\,dS$, and

$$dU = -P\,dV + T\,dS.$$

If we now specify that the reversible process takes place at constant V, we have the important *link between thermodynamics and statistical mechanics*:

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V.} \qquad (12.17)$$

Since both S and U may be calculated by statistical mechanics, *the derivative* $(\partial S/\partial U)_V$ *gives the reciprocal of the Kelvin temperature. This is the way in which the macroscopic concept of temperature is introduced into statistical mechanics.*

In employing the method of Lagrangian multipliers to find the equilibrium values of the energy-level populations [Eqs. (12.10) and (12.11)], we found that

$$d\ln\Omega = \sum \ln\frac{g_i}{N_i}\,dN_i,$$

and

$$\ln\frac{g_i}{N_i} = \beta\epsilon_i - \ln\lambda.$$

Therefore,

$$\begin{aligned} d\ln\Omega &= \sum \beta\epsilon_i\,dN_i - \ln\lambda \sum d\,N_i \\ &= \beta\,d\sum \epsilon_i N_i - \ln\lambda\,d\sum N_i. \end{aligned} \tag{12.18}$$

For a closed system, $d\sum N_i = 0$ and $\sum N_i\epsilon_i$ is just U by Eq. (12.9), yielding

$$d\ln\Omega = \beta\,dU,$$

where U is the total internal energy of the system. Therefore, for constant volume,

$$\beta = \left(\frac{d\ln\Omega}{dU}\right)_V = \frac{1}{k'}\frac{d}{dU}(k'\ln\Omega)_V = \frac{1}{k'}\left(\frac{\partial S}{\partial U}\right)_V.$$

Since $(\partial S/\partial U)_V = 1/T$, we get the beautiful result

$$\boxed{\beta = \frac{1}{k'T}.} \tag{12.19}$$

When the actual values of the ϵ's appropriate to an ideal gas are introduced, it will be seen that k' is none other than Boltzmann's constant k.

12.4
PARTITION FUNCTION FOR CANONICAL ENSEMBLE

We have seen that the population N_i of the ith energy level is

$$N_i = \lambda g_i e^{-\beta\epsilon_i}.$$

Substituting $1/k'T$ for β and N/Z for λ, we get

$$\boxed{N_i = \frac{N}{Z} g_i e^{-\epsilon_i/k'T},} \tag{12.20}$$

where

$$\boxed{Z(V,T) = \sum g_i e^{-\epsilon_i/k'T}.} \tag{12.21}$$

The partition function Z contains the heart of the statistical information about the particles of the closed system. From Eq. (12.21), it is seen that the partition function Z is an explicit function of temperature T and an implicit function of volume V [see Eq. (12.2)]. The partition function $Z(V, T)$ for this system, the canonical ensemble, is the statistical mechanical analog of the Helmholtz function $A(V, T)$. It is worthwhile expressing other properties of the system, such as U, S, and P, in terms of Z. If we differentiate Z with respect to T, holding V constant, we get

$$\begin{aligned}\left(\frac{\partial Z}{\partial T}\right)_V &= \sum g_i\left(\frac{\epsilon_i}{k'T^2}\right)e^{-\epsilon_i/k'T}\\ &= \frac{1}{k'T^2}\sum \epsilon_i g_i e^{-\epsilon_i/k'T}\\ &= \frac{Z}{Nk'T^2}\sum \epsilon_i N_i\\ &= \frac{ZU}{Nk'T^2}.\end{aligned}$$

It follows that

$$\boxed{U = Nk'T^2\left(\frac{\partial \ln Z}{\partial T}\right)_V,} \tag{12.22}$$

and U may be calculated once $\ln Z$ is known as a function of T and V. Also,

$$S = k' \ln \Omega,$$

where, according to Eq. (12.7),

$$\ln \Omega = \sum N_i \ln \frac{g_i}{N_i} + N.$$

Hence,

$$S = -k' \sum N_i \ln \frac{N_i}{g_i} + k'N.$$

Substituting for N_i/g_i the value given in Eq. (12.20), we get

$$S = -k' \sum N_i\left(\ln \frac{N}{Z} - \frac{\epsilon_i}{k'T}\right) + k'N,$$

and, finally,

$$\boxed{S = Nk' \ln \frac{Z}{N} + \frac{U}{T} + Nk',} \tag{12.23}$$

which provides us with a method of calculating S once $\ln Z$ is known.

The Helmholtz function A can also be evaluated in terms of the partition function Z using S from Eq. (12.23). Since

$$A = U - TS,$$

then

$$\begin{aligned}A &= U - T\left(Nk' \ln \frac{Z}{N} + \frac{U}{T} + Nk'\right)\\ &= -k'T(N \ln Z - N \ln N + N);\end{aligned}$$

therefore,

$$\boxed{A = -k'T(N \ln Z - \ln N!).} \tag{12.24}$$

One more useful equation is the relation between pressure and the partition function. Since

$$\begin{aligned} dA &= dU - T\,dS - S\,dT \\ &= -P\,dV - S\,dT, \end{aligned}$$

it follows that

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

Substituting the value for A given in Eq. (12.24), we obtain

$$\boxed{P = Nk'T\left(\frac{\partial \ln Z}{\partial V}\right)_T,} \tag{12.25}$$

so that again the pressure may be calculated once $\ln Z$ is known as a function of T and V.

This is the advantage of statistical mechanics. It provides us with a simple set of rules for obtaining the properties of a system of weakly interacting particles in a closed isothermal container:

1. Use quantum mechanics to find the ϵ values of the quantum states.
2. Find the partition function Z in terms of T and V.
3. Calculate the internal energy by differentiating $\ln Z$ with respect to T.
4. Calculate the pressure by differentiating $\ln Z$ with respect to V.
5. Calculate the entropy from Z and U.
6. Calculate the Helmholtz function A directly from $\ln Z$.

The Helmholtz function calculated from the theoretical partition function can be compared with the Helmholtz function obtained from experimental data for a real substance. In this way, the validity of the assumptions made in calculating the partition function can be tested.

12.5
PARTITION FUNCTION OF AN IDEAL MONATOMIC GAS

To apply the rules laid down in the preceding section to an ideal gas, we must first calculate the appropriate partition function. This was defined to be

$$Z = \sum_{\text{levels}} g_i e^{-\epsilon_i/k'T},$$

where the summation was over all the energy levels. Exactly the same result is obtained if we sum the expression

$$Z = \sum_{\text{states}} e^{-\epsilon_j/k'T}$$

over all quantum states. We at first take into account only the kinetic energy of translation of the particles confined to an adiabatic rectangular box whose x, y, and z sides are, respectively, a, b, and c, which could be changed, thereby changing the volume. The energy of any quantum state j is given by Eq. (12.1) as

$$\epsilon_j = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right),$$

where n_x, n_y, n_z are quantum numbers specifying the various quantum states. The partition function, therefore, is a threefold sum: thus,

$$Z = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-(h^2/8mk'T)(n_x^2/a^2+n_y^2/b^2+n_z^2/c^2)},$$

or $$Z = \sum_{n_x=1}^{\infty} e^{-(h^2/8mk'T)(n_x^2/a^2)} \sum_{n_y=1}^{\infty} e^{-(h^2/8mk'T)(n_y^2/b^2)} \sum_{n_z=1}^{\infty} e^{-(h^2/8mk'T)(n_z^2/c^2)}.$$

Since the values of n_x, n_y, and n_z that give rise to appreciable values of the energy are very large, and since a change of n_x or n_y or n_z by unity produces a change of energy that is exceedingly small, no error is introduced by replacing each sum with an integral and by writing

$$Z = \left[\int_0^{\infty} e^{-(h^2/8mk'T)(n_x^2/a^2)}\,dn_x\right]\left[\int_0^{\infty} e^{-(h^2/8mk'T)(n_y^2/b^2)}\,dn_y\right] \times \left[\int_0^{\infty} e^{-(h^2/8mk'T)(n_z^2/c^2)}\,dn_z\right].$$

Each integral is of the type (see Appendix C)

$$\int_0^{\infty} e^{-ax^2}\,dx = \tfrac{1}{2}\sqrt{\frac{\pi}{a}}.$$

Therefore, $$Z = \left(\frac{a}{2}\sqrt{\frac{8\pi mk'T}{h^2}}\right)\left(\frac{b}{2}\sqrt{\frac{8\pi mk'T}{h^2}}\right)\left(\frac{c}{2}\sqrt{\frac{8\pi mk'T}{h^2}}\right);$$

and since $abc = V$, the partition function for an ideal monatomic gas is given by

$$Z(V, T) = V\left(\frac{2\pi mk'T}{h^2}\right)^{3/2}. \tag{12.26}$$

Thus, $$\boxed{\ln Z(V, T) = \ln V + \tfrac{3}{2}\ln T + \tfrac{3}{2}\ln\left(\frac{2\pi mk'}{h^2}\right).} \tag{12.27}$$

1. *Pressure of an ideal monatomic gas.* From Eq. (12.25),

$$\begin{aligned} P &= Nk'T\left(\frac{\partial \ln Z}{\partial V}\right)_T \\ &= Nk'T\left(\frac{1}{V}\right) \\ &= \frac{N}{V}k'T. \end{aligned} \tag{12.28}$$

Comparing this result with the expression for the pressure $P = NkT/V$ obtained with the kinetic theory of gases, given in Eq. (5.30), where k is Boltzmann's constant, we see that the arbitrary constant k' introduced in the equation $S = k' \ln \Omega$ is none other than the Boltzmann constant, or

$$\boxed{k' = k = \frac{R}{N_A},} \tag{12.29}$$

where N_A is Avogadro's number.

2. *Internal energy of an ideal monatomic gas.* From Eq. (12.22),

$$\begin{aligned} U &= NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \\ &= NkT^2\left(\frac{3}{2T}\right) \\ &= \tfrac{3}{2}NkT. \end{aligned} \tag{12.30}$$

This is exactly the same result that was obtained by the kinetic theory of gases for a monatomic ideal gas and shows that, when particles each having three translational degrees of freedom come to statistical equilibrium, the energy per particle equals $\frac{3}{2}kT$.

3. *Entropy of an ideal monatomic gas.* From Eq. (12.23),

$$\begin{aligned} S &= Nk \ln \frac{Z}{N} + \frac{U}{T} + Nk \\ &= Nk\left[\ln \frac{V}{N} + \tfrac{3}{2}\ln T + \ln\left(\frac{2\pi mk}{h^2}\right)^{3/2}\right] + \tfrac{3}{2}Nk + Nk \\ &= Nk\left[\tfrac{3}{2}\ln T + \ln \frac{V}{N} + \ln\left(\frac{2\pi mk}{h^2}\right)^{3/2} + \tfrac{5}{2}\right]. \end{aligned}$$

If we take 1 mol of gas, then $N = N_A$ and $N_A k = R$. Therefore,

$$s = c_V \ln T + R \ln v + R \ln \frac{(2\pi mk/h^2)^{3/2}}{N_A} + \tfrac{5}{2}R. \tag{12.31}$$

The expression is to be compared with Eq. (8.9), for constant C_V and molar quantities, namely,

$$s = c_V \ln T + R \ln v + s_0,$$

and we see that not only were we able to arrive at this equation by the methods of statistical mechanics, but also we were able to calculate the constant s_0. Equation (12.31), which was first obtained by Sackur and Tetrode, usually bears their names.

12.6
EQUIPARTITION OF ENERGY

Both kinetic theory and statistical mechanics, when applied to the molecules of an ideal gas (each having three translational degrees of freedom), yield the result that, at equilibrium, the energy per particle associated with each degree of translational freedom is $\frac{1}{2}kT$. The methods of kinetic theory could not be applied to rotational and vibrational degrees of freedom, but the simple statistical method just developed is capable of dealing with all types of molecular energy, not just translational kinetic energy.

The property of the partition function which makes it so useful is that, whenever the energy of a molecule is expressed as a sum of independent terms each referring to a different degree of freedom,

$$\epsilon = \epsilon' + \epsilon'' + e''' + \cdots;$$

then,

$$\begin{aligned} Z &= \sum e^{-\epsilon/kT} = \sum e^{-(\epsilon'+\epsilon''+\epsilon'''+\cdots)/kT} \\ &= \sum e^{-\epsilon'/kT} \sum e^{-\epsilon''/kT} \sum e^{-\epsilon'''/kT} \ldots \\ &= Z'Z''Z''' \cdots. \end{aligned} \tag{12.32}$$

If the various types of energy are calculated with classical physics, it is a simple matter to derive the *classical* principle of the equipartition of energy. We take Eq. (12.22), namely,

$$U = NkT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V,$$

and rewrite it thus:

$$\begin{aligned} \langle \epsilon \rangle = \frac{U}{N} &= - \left[\frac{\partial \ln Z}{\partial (1/kT)} \right]_V \\ &= - \left(\frac{\partial \ln Z}{\partial \beta} \right)_V. \end{aligned}$$

Suppose ϵ to consist of terms representing translational kinetic energy of the type $\frac{1}{2}mw^2$, those representing rotational kinetic energy of the type $\frac{1}{2}I\omega^2$, those representing vibrational energy $\frac{1}{2}m\dot{\xi}^2 + \frac{1}{2}k\xi^2$, etc. All these forms of energy are expressed as squared terms of the type $b_i p_i^2$. Let there be f such terms, or

$$\epsilon = b_1 p_1^2 + b_2 p_2^2 + \cdots + b_f p_f^2.$$

Then, since the partition function is the product of the separate partition functions,

$$Z = \int_0^\infty e^{-\beta b_1 p_1^2}\, dp_1 \int_0^\infty e^{-\beta b_2 p_2^2}\, dp_2 \cdots \int_0^\infty e^{-\beta b_f p_f^2}\, dp_f.$$

Let $$y_i = \beta^{1/2} p_i \qquad \text{and} \qquad dy = \beta^{1/2}\, dp_i;$$

then
$$\begin{aligned}\int_0^\infty e^{-\beta b_i p_i^2}\, dp_i &= \int_0^\infty e^{-\beta b_i y_i^2/\beta}\, dy_i/\beta^{1/2}\\ &= \beta^{-1/2}\int_0^\infty e^{-b_i y_i^2}\, dy_i\\ &= \beta^{-1/2} K_i,\end{aligned}$$

where K_i does *not* contain β. The partition function now becomes

$$\begin{aligned}Z &= (\beta^{-1/2}K_1)(\beta^{-1/2}K_2)\cdots(\beta^{-1/2}K_f)\\ &= \beta^{-f/2}K_1K_2\cdots K_f,\end{aligned}$$

where *none of the K's contains* β. Since $\langle\epsilon\rangle = -\partial[(\ln Z)/\partial\beta]_V$,

$$\begin{aligned}\langle\epsilon\rangle &= -\frac{\partial}{\partial\beta}\left(-\frac{f}{2}\ln\beta + \ln K_1 + \ln K_2 + \cdots + \ln K_f\right)_V\\ &= \frac{f}{2\beta};\end{aligned}$$

and since $\beta = 1/kT$,

$$\boxed{\langle\epsilon\rangle = \frac{f}{2}kT.} \tag{12.33}$$

Therefore, it has been proposed that, when a large number of indistinguishable, **quasi-independent** *particles whose energy is expressed as the sum of squared terms come to equilibrium, the average internal energy per particle is f times* $\frac{1}{2}kT$. This is the famous *principle of the equipartition of energy.*

A monatomic ideal gas has only three translational degrees of freedom; therefore, N_A atoms (1 mol) will have a molar internal energy u equal to

$$u = N_A\left(\tfrac{3}{2}kT\right) = \tfrac{3}{2}RT,$$

and $$c_V = \left(\frac{\partial u}{\partial T}\right)_V = \tfrac{3}{2}R.$$

Since $c_P = c_V + R$, then $c_P = \frac{5}{2}R$ and $\gamma = \frac{5}{3}$. These calculations are in agreement with the experimental results listed in Sec. 5.4.

The diatomic gases H_2, D_2, O_2, N_2, NO, and CO, in the neighborhood of *room temperature*, are dumbbell-shaped molecules with three translational degrees of freedom and two rotational degrees of freedom. With five degrees of freedom, the molar internal energy is

$$u = \tfrac{5}{2}RT,$$

and $$c_V = \tfrac{5}{2}R, \qquad c_P = \tfrac{7}{2}R, \qquad \text{and} \qquad \gamma = \tfrac{7}{5},$$

also in agreement with the results of Sec. 5.4.

According to our assumption that particles of gas are quasi-independent, the vibrational degrees of freedom of each atom in the molecule should have been included, which would have increased c_P by R, thereby disagreeing with experiment. But, in the quantum mechanics of interacting particles, various degrees of freedom are, so to speak, turned on as the temperature increases, as shown in Fig. 5-4 for hydrogen gas. At room temperature, only the translational and rotational degrees of freedom are activated; well above 1000 K, the vibrational degrees of freedom are activated. When the principle of the equipartition of energy is applied to solids and liquids, the disagreement is still worse, and this principle must be abandoned in favor of including interactions between particles to calculate the partition function and, hence, the internal energy.

12.7
DISTRIBUTION OF SPEEDS IN AN IDEAL MONATOMIC GAS

Let us consider an ideal monatomic gas. If w denotes the speed of an atom in an ideal gas consisting of N atoms, it is often necessary to calculate the average speed $\langle w \rangle$ or the average square of the speed $\langle w^2 \rangle$, where

$$\langle w \rangle = \frac{1}{N}\int_0^\infty w \, dN_w,$$

and $$\langle w^2 \rangle = \frac{1}{N}\int_0^\infty w^2 \, dN_w,$$

and dN_w is the number of atoms with speeds between w and $w + dw$. In order to evaluate these integrals, one must know the expression for dN_w in terms of w — a relation known as the *Maxwell's law of distribution of speeds* for particles (atoms or molecules) in a gas. In Maxwell's original derivation of this law, it was not necessary to use any physical laws governing the behavior of the particles when colliding with one another or with the wall. These physical laws are hidden within the fundamental assumption that, at or near equilibrium, the particles have no preferred direction of velocity and no preferred location within the container. Since these characteristics of random motion are the same as those involved in the simple treatment of statistical mechanics given in this chapter, we shall derive the Maxwell distribution law from statistical mechanics.

We start with the equation expressing the equilibrium value of the number of atoms N_ϵ with energy ϵ (the equilibrium population of energy level ϵ) given by Eq. (12.20), namely,

$$N_\epsilon = \frac{N}{Z} g_\epsilon e^{-\epsilon/kT}, \tag{12.20}$$

where g_ϵ is the number of quantum states available for atoms of energy ϵ (the degeneracy of the energy level ϵ). These states correspond to positive integer values for each n_x, n_y, and n_z, according to Eq. (12.1), namely,

$$n_x^2 + n_y^2 + n_z^2 = \frac{L^2}{h^2} 8m\epsilon = r^2.$$

In a three-dimensional Euclidian space with coordinates n_x, n_y, and n_z, each unit volume will contain one quantum state. Such a space is shown in Fig. 12-4, where the space containing unit volume elements corresponding to the energy of a particle between ϵ and $\epsilon + d\epsilon$ lies between the positive octant of the spherical surface of radius $r = (L/h)(8m\epsilon)^{1/2}$ and the spherical surface of radius $r + dr$. The volume of this region is dg_ϵ, where

$$\begin{aligned} dg_\epsilon &= \tfrac{1}{8}(4\pi r^2\, dr) \\ &= \tfrac{1}{8}(4\pi)\left(\frac{L^2}{h^2} 8m\epsilon\right) d\left[\frac{L}{h}(8m\epsilon)^{1/2}\right]. \end{aligned}$$

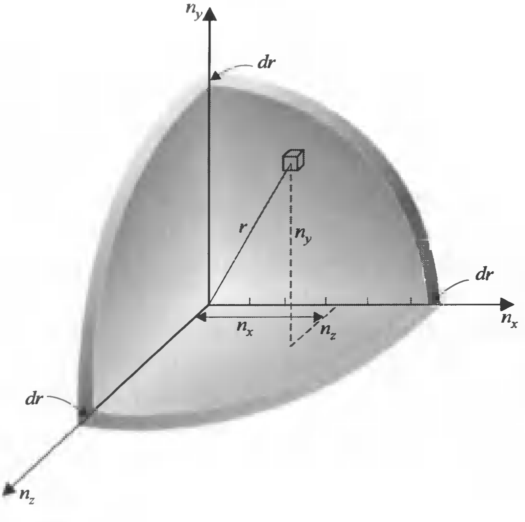

FIGURE 12-4
Quantum number space. All particles contained in a cube of side L, whose energy lies between ϵ and $\epsilon + d\epsilon$, have quantum numbers lying within the spherical shell of inner radius r and outer radius $r + dr$, where $r = (L/h)(8m\epsilon)^{1/2}$.

Simplifying and setting $V = L^3$, we get

$$dg_\epsilon = \frac{2\pi V(2m)^{3/2}}{h^3}\epsilon^{1/2}\,d\epsilon. \tag{12.34}$$

The number of atoms dN_ϵ in the energy range between ϵ and $\epsilon + d\epsilon$ is clearly

$$dN_\epsilon = N\frac{dg_\epsilon}{Z}e^{-\epsilon/kT}. \tag{12.35}$$

We have shown in Eq. (12.26) that the partition function of our ideal gas is

$$Z = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

Hence,

$$\frac{dg_\epsilon}{Z} = \frac{2}{\pi^{1/2}(kT)^{3/2}}\epsilon^{1/2}\,d\epsilon.$$

Substituting dg_ϵ/Z into Eq. (12.35), we get

$$dN_\epsilon = \frac{2N}{\pi^{1/2}(kT)^{3/2}}\epsilon^{1/2}e^{-\epsilon/kT}\,d\epsilon.$$

If the speed of an atom is w, then $\epsilon = \frac{1}{2}mw^2$, and

$$dN_w = \frac{2N}{\pi^{1/2}(kT)^{3/2}}\left(\tfrac{1}{2}mw^2\right)^{1/2}mw\,dw\left(e^{-(1/2)mw^2/kT}\right).$$

Finally,

$$\boxed{\frac{dN_w}{dw} = \frac{2N}{\sqrt{2\pi}}\left(\frac{m}{kT}\right)^{3/2}w^2e^{-(1/2)mw^2/kT}.} \tag{12.36}$$

The expression on the right is the famous *Maxwell's speed-distribution function* and is plotted in Fig. 12-5. Figure 12-6 shows the function for three different temperatures. The higher the temperature, the wider is the spread of values of the speed.

Maxwell's function for the distribution of speeds of the atoms of a gas has been experimentally verified directly as well as indirectly. One of the most convincing experiments was performed by Estermann, Simpson, and Stern in 1947, making use of the apparatus depicted schematically in Fig. 12-7, in which atoms are deflected *by gravity only*. Cesium atoms issue from a thin slit in an oven O at the left of a long, highly evacuated chamber. Most of these atoms are stopped by the diaphragm F, and those which go through the slit constitute a narrow, almost horizontal beam. The slit C, called the *collimating slit*, is halfway between F and the detector D. The atoms are detected by the method of surface ionization, in which nearly every cesium atom striking a hot tungsten wire leaves the wire as a positive ion and is collected by a negatively

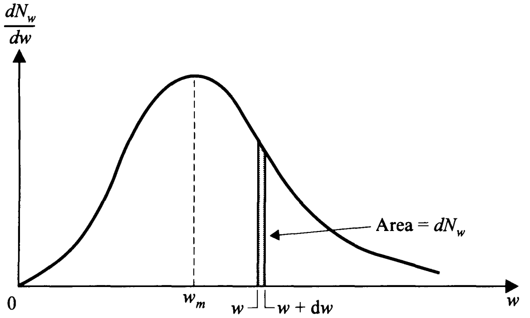

FIGURE 12-5
Graph of Maxwell's speed-distribution function, where the speed w_m is the most probable speed.

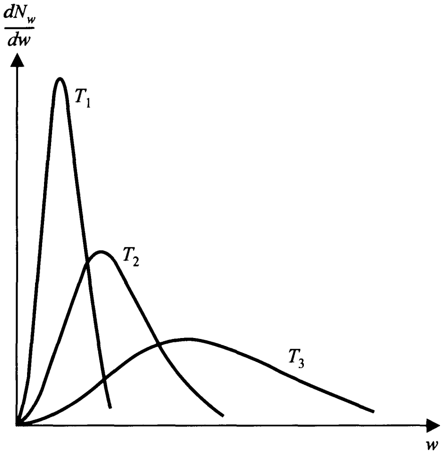

FIGURE 12-6
Maxwell's speed-distribution function at various temperatures; $T_3 > T_2 > T_1$.

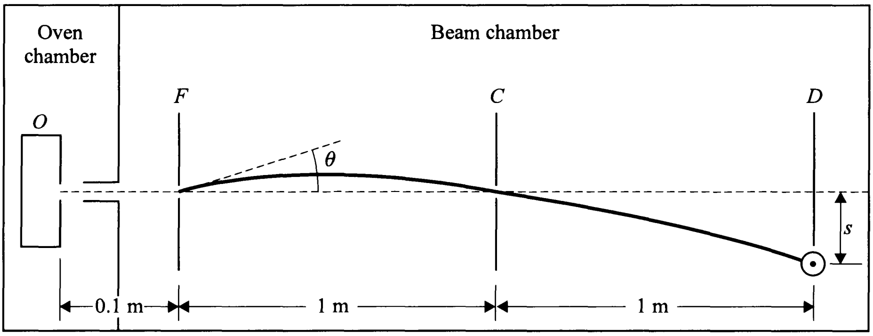

FIGURE 12-7
Apparatus for measuring the deflection of an atomic beam by gravity. *O*, oven; *F* and *C*, slits; *D*, detector.

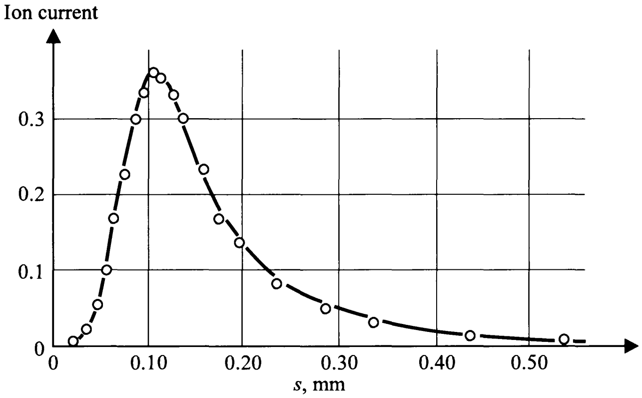

FIGURE 12-8
Distribution of speeds of cesium atoms in an atomic beam deflected by gravity. (The data points are experimental results of I. Estermann, O. C. Simpson, and O. Stern: *Physical Review*, vol. 71, pp. 238–249, 1947. The smooth curve is Maxwell's function.)

charged plate. The plate current is then a measure of the number of cesium atoms striking the detector wire per unit of time.

A simple analysis of the parabolic paths of the atoms that pass through F and C provides a relation between the deflection s and the speed w. The departure angle θ is practically zero. The experimental results are shown in Fig. 12-8, where the smooth curve is a plot of Maxwell's function and the dots are experimental points.

12.8
STATISTICAL INTERPRETATION OF WORK AND HEAT

We have been considering the statistical equilibrium of a large number N of indistinguishable, quasi-independent particles in a cubical container of volume V. The container is a closed cylinder with a piston at one end, permitting variations in the volume. The energy levels ϵ_i of individual particles undergoing translational motion only were given by

$$\epsilon_i = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right).$$

Since $L^3 = V$, then $L^2 = V^{2/3}$, and letting B_i be the sum of the squares of the quantum numbers appropriate to the ith energy level, we get

$$\epsilon_i = \frac{h}{8m} B_i V^{-2/3}.$$

Given the set of quantum numbers that determines B_i, we may say that the *corresponding energy ϵ_i depends on volume only*. Taking the logarithm of ϵ_i,

$$\ln \epsilon_i = \ln \frac{h^2}{2m} + \ln B_i - \tfrac{2}{3}\ln V.$$

The effect of a small change of V on ϵ is given by taking the differential of this equation; whence

$$\frac{d\epsilon_i}{\epsilon_i} = -\tfrac{2}{3}\,\frac{dV}{V}.$$

Therefore,

$$d\epsilon_i = -\tfrac{2}{3}\,\frac{\epsilon_i}{V}\,dV,$$

$$N_i d\epsilon_i = -\tfrac{2}{3}\,\frac{N\epsilon_i}{V}\,dV,$$

and

$$\sum N_i d\epsilon_i = -\tfrac{2}{3}\,\frac{U}{V}\,dV. \tag{12.37}$$

Now, it has been shown both by kinetic theory and by statistical mechanics that the pressure of an ideal gas is given by

$$P = \frac{NkT}{V}.$$

Since the internal energy per particle is translational kinetic energy only, with three degrees of freedom,

$$U = \tfrac{3}{2}NkT,$$

it follows that

$$P = \tfrac{2}{3}\,\frac{U}{V}. \tag{12.38}$$

Substituting this result into Eq. (12.37), we get

$$\sum N_i d\epsilon_i = -P\,dV. \tag{12.39}$$

A change of volume, therefore, causes changes in the energy values of the energy levels, without producing changes in the populations of the levels. In other words, the performance of external work on a system changes *only* the energy values of the energy levels.

When the populations of particles N_i change but the ϵ_i remain constant, we have from Eq. (12.18),

$$d\ln\Omega = \beta \sum \epsilon_i\,dN_i.$$

Since $kd\ln\Omega = dS$, $k\beta\sum \epsilon_i\,dN_i = dS$, and setting $k\beta$ equal to $1/T$, we get, finally,

$$\sum \epsilon_i\,dN_i = T\,dS.$$

We see that a reversible heat transfer changes the populations of the energy levels *without* changing the energy values of the levels themselves. Thus, the equation $dU = \sum N_i \, d\epsilon_i + \sum \epsilon_i \, dN_i$ expresses the first law of thermodynamics, with $\sum N_i \, d\epsilon_i = -P \, dV$ and $\sum \epsilon_i \, dN_i = T \, dS$.

12.9
ENTROPY AND INFORMATION

Whenever work or kinetic energy is dissipated within a system because of friction, viscosity, deformation, electric resistance, or magnetic hysteresis, the disorderly motions of molecules are increased. Whenever different substances are mixed or dissolved or diffused with one another, the spatial positions of the molecules constitute a more disorderly arrangement. Rocks crumble, iron rusts, some metals corrode, wood rots, leather disintegrates, paint peels, and people age. All these processes involve the transition from some sort of "orderliness" to a greater disorder. This transition is expressed in the language of classical thermodynamics by the statement that the entropy of the universe increases. Atomic disorder and entropy go together, and if we measure disorder by the number of ways a particular macrostate may be achieved, then the thermodynamic probability Ω is a measure of disorder. Thus, the equation $S = k \ln \Omega$ is the simple relation between entropy and disorder.

The disordering of microscopic particles during irreversible processes arises from the fact that the motions of individual particles are free from the control of any human activity. However, it is intriguing to speculate on ways to control the particles. Suppose there were a small creature called *Maxwell's demon*, who could control the particles. The demon was proposed by James Clerk Maxwell in 1871 as a challenge to the validity of the second law. The demon is an intelligent being who can supposedly operate a device in such a way that it *reduces* the entropy of the universe, contrary to the second law. Suppose that the demon is situated in an isolated chamber consisting of two compartments connected by a gate that can be either opened or closed. Initially, one compartment is filled with particles and the other compartment is empty. The demon opens the gate only when fast particles approach, thus allowing the fast particles to collect in one compartment and the slow ones to remain in the other. The separation of mixed particles would result in the gas in one compartment becoming hotter and the gas in the other compartment becoming cooler, that is, heat transferred from a lower temperature to a higher temperature without the benefit of external work. This process violates Clausius' statement of the second law for refrigerators. Or, equivalently, the action of the demon would cause a transition from disorder to order in the gas, that is, a decrease in entropy, thus violating the mathematical expression for the second law. If the gate were left open and unattended by Maxwell's demon, then both fast and slow particles would pass through the gate and a separation of particles of different temperatures would not occur.

Since the postulation of Maxwell's demon, there have been attempts to disprove the second law by proposing a perpetual motion machine of the second kind that incorporates the demon, but the attempts have generally failed. Szilard, in 1929, wrote about an "intelligent being" who was incorporated into a perpetual motion machine of the second kind. His intelligent being used a binary decision process, and attention was thereby focused on a fundamental amount of entropy, later known as "information," which is another interpretation for the number of ways in which a particular macrostate may be achieved.

Suppose that you are called upon to guess a person's first name. The number of choices of names of men and women is staggeringly large. With no hint or clue, the number of ways in which one can arrive at a name is very large, and the information at one's disposal is small. Suppose, now, that we are told that the person is a man. Immediately the number of choices of names is *reduced,* whereas the information is *increased.* Information is increased further if we are told that the man's name starts with H, for then the number of choices (or ways of picking a man's name) is reduced very greatly. It is clear that the *fewer* the number of ways a particular situation or a particular state of a system may be achieved, the greater is the information.

A convenient measure of the information I conveyed when the number of choices is reduced from Ω_0 to Ω_1 is given by

$$I = k \ln \frac{\Omega_0}{\Omega_1}.$$

The more the reduction of entropy, the more the information. In other words, information can be defined as *negentropy*. Since $k \ln \Omega$ is the entropy S, then

$$I = S_0 - S_1,$$

or

$$S_1 = S_0 - I,$$

which can be interpreted to mean that the entropy of a system is reduced by the amount of information about the state of a system. In the words of Brillouin, "Entropy measures the lack of information about the exact state of a system."

As an example of the connection between entropy and information, consider the isothermal compression of an ideal gas (N atoms) from a volume V_0 to a volume V_1. We know that the reduction of entropy is equal to

$$S_0 - S_1 = Nk \ln \frac{V_0}{V_1}.$$

But, when we decrease the volume of the gas, we decrease the number of ways of achieving this state, because there are fewer microstates with position coordinates in the smaller volume. Before the compression, each atom is known to be in the volume V_0. The number of locations each atom could occupy is $V_0/\Delta V$, where ΔV is some arbitrary small volume. After the compression, each atom is to be found in volume V_1, with a smaller number of possible locations $V_1/\Delta V$. It follows that

$$I = k \ln \frac{\Omega_0}{\Omega_1} = k \ln \frac{V_0/\Delta V}{V_1/\Delta V} = k \ln \frac{V_0}{V_1},$$

and, for the entire gas of N atoms,

$$I = Nk \ln \frac{V_0}{V_1},$$

in agreement with the result of classical thermodynamics. The increase of information as a result of the compression is seen to be identical with the corresponding entropy reduction.

The connection between entropy and information can be applied to the problem of Maxwell's demon. According to Brillouin, the demon could not tell the difference between one kind of atom and another, because he and the atoms are in an enclosure at a uniform temperature and all are bathed in isotropic blackbody radiation. The demon could not see the individual atoms. However, suppose that we allow the demon, according to the analysis of Rodd,† to use a flashlight whose radiation is not in equilibrium with the enclosure. Then, the demon can get information about the atoms and thereby decrease the entropy of the system. But, other phenomena come into the discussion: (1) the filament of the lamp in the flashlight undergoes an increase of entropy; (2) a photon scattered by an atom is absorbed by the demon and serves to increase his entropy; (3) the action of the demon in opening the trapdoor reduces the number of microstates available to the atoms. (The entropy change of the battery of the flashlight can be ignored.) If all these processes are taken into account and the corresponding entropy changes are calculated from the standpoint of the increase or decrease of information, then Rodd was able to demonstrate that the entropy change of the universe is positive. The second law is not violated.

Advances in information theory were made by Wiener and Shannon in 1948. Subsequently, remarkable progress has been made in deepening the understanding and applicability of the concepts of information storage and information erasure, which are fundamental to computer science and cybernetics. For a fascinating discussion of the history of Maxwell's demon that includes reprints of all the seminal papers, see *Maxwell's Demon: Entropy, Information, Computing*, edited by Leff and Rex (see Bibliography).

PROBLEMS

(Values of constants: $k = 1.38 \times 10^{-23}$ J/K and $h = 6.63 \times 10^{-34}$ J·s.)

12.1. A mercury atom moves in a cubical box whose edge is 1 m long. Its kinetic energy is equal to the average kinetic energy of an atom of an ideal gas at 1000 K. If the quantum numbers n_x, n_y, and n_z are all equal to n, calculate n.

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† P. Rodd: *American Journal of Physics*, vol. 32, pp. 333–335, 1964.

12.2. The quantum states available for gas atoms of energy ϵ in a cubical box of length L correspond to integer values for each n_x, n_y, and n_z, according to Eq. (12.1). In a three-dimensional Euclidean space with coordinates n_x, n_y, and n_z, each unit volume will contain one quantum state. The total number of quantum states g' with energy less than ϵ' is equal to the volume of the positive octant of a sphere of radius $r = L(8m\epsilon_i)^{1/2}/h$.

(*a*) Show that

$$g' = \frac{4\pi V(2m\epsilon')^{3/2}}{3h^3}.$$

(*b*) In a volume of $1\,\text{cm}^3$ of helium gas at 300 K and 1 atm pressure, ϵ' is about 10^{-5} J. Calculate g'.

(*c*) Calculate the number N of helium atoms.

(*d*) Show that $g' \gg N$.

12.3. Take the expression for the kinetic energy of a particle in a cubical box and imagine a space defined by the cartesian coordinates n_x, n_y, and n_z. Note that a single quantum state occupies unit volume in this space.

(*a*) Setting $n^2 = n_x^2 + n_y^2 + n_z^2$, show that the number of quantum states in the small interval dn is $\frac{1}{8}(4\pi n^2\, dn)$.

(*b*) Prove that the number of quantum states dg_ϵ in the energy interval $d\epsilon$ is $(2\pi/h^3)V(2m)^{3/2}\epsilon^{1/2}\, d\epsilon$.

(*c*) Show that the number of ideal-gas particles dN_ϵ occupying these quantum states is given by

$$dN_\epsilon = \frac{2N}{\pi^{1/2}} \frac{1}{(kT)^{3/2}} \epsilon^{1/2} e^{-\epsilon/kT}\, d\epsilon.$$

(*d*) Derive the Maxwell's speed-distribution function, that is, Eq. (12.36).

12.4. Show that, when N ideal-gas atoms come to equilibrium,

$$\frac{g_i}{N_i} = \frac{Z}{N} e^{\epsilon_i/kT},$$

and

$$\frac{Z}{N} = \frac{(kT)^{5/2}}{P}\left(\frac{2\pi m}{h^2}\right)^{3/2}.$$

Taking $\epsilon_i = \frac{3}{2}kT$, $T = 300\,K$, $P = 10^3$ Pa, and $m = 10^{-26}$ kg, calculate g_i/N_i.

12.5. Consider a function f defined by the relation

$$f(\Omega_A\Omega_B) = f(\Omega_A) + f(\Omega_B).$$

First, differentiate partially with respect to Ω_B, and then with respect to Ω_A. Integrate twice to show

$$f(\Omega) = \text{const.} \ln \Omega + \text{const.}$$

12.6. In the case of N *distinguishable* particles, the number of ways Ω, in which a macrostate defined by N_1 particles in g_1 quantum states with energy ϵ_1, N_2 particles in g_2 quantum states with energy ϵ_2, $\cdots$, may be achieved, is given by the Maxwell-Boltzmann expression

$$\Omega_{\mathrm{MB}} = N! \frac{g_1^{N_1} g_2^{N_2} \cdots}{N_1! N_2! \cdots},$$

when $g_i \gg N_i$.

(*a*) Using the Stirling approximation, calculate $\ln \Omega$.

(*b*) Render $\ln \Omega$ a maximum, subject to the equations of constraint $\sum N_i = N = \text{const.}$ and $\sum N_i \epsilon_i = U = \text{const.}$, and explain why U and P should be the same as for indistinguishable particles, but S should be different.

12.7. Given N indistinguishable, quasi-independent particles capable of existing in energy levels $\epsilon_1, \epsilon_2, \cdots$, with degeneracies $g_1, g_2, \cdots$, respectively; in any given macrostate in which there are N_1 particles in energy level ϵ_1, N_2 particles in energy level ϵ_2, $\cdots$, assume the thermodynamic probability to be given by the Bose-Einstein expression,

$$\Omega_{\mathrm{BE}} = \frac{(g_1 + N_1)!(g_2 + N_2)! \cdots}{g_1! N_1! g_2! N_2!}.$$

Using Stirling's approximation and the method of Lagrangian multipliers, render $\ln \Omega_{\mathrm{BE}}$ a maximum, subject to the equations of constraint $\sum N_i = N = \text{const.}$ and $\sum N_i \epsilon_i = U = \text{const.}$, and show that

$$N_i = \frac{g_i}{\lambda e^{-\beta \epsilon_i} - 1}.$$

12.8. Assume the same system as in Prob. 12.7, except that the thermodynamic probability is given by the Fermi-Dirac expression,

$$\Omega_{\mathrm{FD}} = \frac{g_1! g_2! \cdots}{N_1!(g_1 - N_1)! N_2!(g_2 - N_2)! \cdots}.$$

Using Stirling's approximation and the method of Lagrangian multipliers, render $\ln \Omega_{\mathrm{FD}}$ a maximum, subject to the equations of constraint $\sum N_i = N = \text{const.}$ and $\sum N_i \epsilon_i = U = \text{const.}$, and show that

$$N_i = \frac{g_i}{\lambda e^{-\beta \epsilon_i} + 1}.$$

12.9. Given a gaseous system of N_{A} indistinguishable, weakly interacting diatomic molecules:

(*a*) Each molecule may vibrate with the same frequency ν, but with an energy ϵ_i, given by

$$\epsilon_i = (\tfrac{1}{2} + i) h\nu \qquad (i = 0, 1, 2, \cdots).$$

Show that the vibrational partition function Z_ν is

$$Z_\nu = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}.$$

(*b*) Each molecule may rotate, and the rotational partition function Z_r has the same form as that for translation, except that the volume V is replaced by the total solid angle 4π, the mass is replaced by the moment of inertia I, and the exponent $\frac{3}{2}$ (referring to three translational degrees of freedom) is replaced by $\frac{2}{2}$, since there are only two rotational degrees of freedom. Write the rotational partition function.

(*c*) Taking into account translation, vibration, and rotation, calculate the Helmholtz function.

(*d*) Calculate the pressure.

(*e*) Calculate the internal energy.

(*f*) Calculate the molar heat capacity at constant volume.

12.10. Defining the average speed $\langle w \rangle$ by the equation

$$\langle w \rangle = \frac{1}{N}\int_0^\infty w\,dN_w,$$

show that

$$\langle w \rangle = \sqrt{\frac{8kT}{\pi m}}.$$

12.11. (*a*) In Fig. 12-5, let w_m be the value of w at which dN_w/dw is a maximum. Calculate w_m.

(*b*) Choose a new variable $x = w/w_m$, and calculate $dN_x/N\,dx$. What is the maximum value of $dN_x/N\,dx$?

12.12. (*a*) Calculate $\langle 1/w \rangle$ and compare the result with $1/\langle w \rangle$.

(*b*) Show that the number of particles striking a unit area of a wall per unit time is equal to

$$\frac{P}{\sqrt{2\pi mkT}}.$$

12.13. The Doppler broadening of a spectral line increases with the rms speed of the atoms in the source of light. What should give narrower spectral lines: a mercury-198 lamp at 300 K or a krypton-86 lamp at 77 K?

12.14. At what temperature is the mean translational kinetic energy of an atom equal to that of a singly charged ion of the same mass which has been accelerated from rest through a potential difference of: (*a*) 1 V? (*b*) 1,000 V? (*c*) 1,000,000 V? (*Note*: Neglect relativistic effects.)

12.15. An oven contains cadmium vapor at a pressure of 2.28 Pa and at a temperature of 550 K. In one wall of the oven there is a slit with a width of 10^{-5} m and a length of 10^{-2} m. On the other side of the wall is a very high vacuum. If one assumes that all the atoms arriving at the slit pass through, what is the atomic beam current?

12.16. A vessel of volume V contains a gas that is kept at constant temperature. The gas slowly leaks out of a small hole of area A. The outside pressure is so low that no atoms leak back.

(*a*) Prove that the pressure at any time t is given by

$$P = P_0 e^{-k't},$$

where P_0 is the initial pressure.

(*b*) Calculate k' in terms of V, A, and $\langle w \rangle$. (*Note*: Assume that all the atoms arriving at the hole pass through.)

12.17. A spherical glass bulb of 0.1 m radius is maintained at 300 K, except for an appendix with a cross-sectional area of $10^{-4}\,\text{m}^2$ immersed in liquid nitrogen, as shown in Fig. P12-1. The bulb contains water vapor originally at a pressure of 13.3 Pa. Assuming that every water molecule that enters the appendix condenses on the wall and stays there, find the time required for the pressure to decrease to 1.33×10^{-4} Pa.

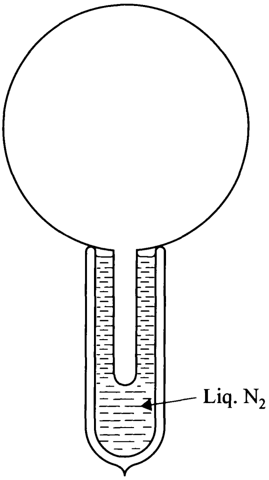

FIGURE P12-1

12.18. A vessel partially filled with mercury, and closed except for a hole of area $10^{-7}\,\text{m}^2$ above the liquid level, is kept at 0°C in a continuously evacuated enclosure. After 30 days, it is found that 2.4×10^{-5} kg of mercury has been lost. What is the vapor pressure of mercury at 0°C?

CHAPTER 13

Thermal Properties of Solids

13.1
STATISTICAL MECHANICS OF A NONMETALLIC CRYSTAL

We concluded Chap. 9 with a discussion of the molar heat capacity at constant volume of nonmetallic crystalline solids. Experimental values for c_P and c_V at low temperatures showed practically the same temperature variation. At higher temperatures, however, c_P continued to rise, while c_V approached a constant value of $3R$, known as the *rule of Dulong and Petit.*

The reason that c_V of a solid is of more theoretical interest than c_P is that $c_V = (\partial u/\partial T)_V$, where u is the molar internal energy, may be calculated with the aid of statistical mechanics. In general, this calculation is extremely complicated, because many different phenomena contribute to the internal energy of the solid. Suppose, for example, that the solid is a crystal having a lattice composed of molecules, each of which consists of several atoms; and, furthermore, suppose that there is about one free electron per molecule. Then, the total internal energy may be due to:

1. Translational motions of the free electrons.
2. Vibrations of the molecules about their equilibrium positions, called briefly *lattice vibrations.*
3. Internal vibrations of atoms within each molecule.
4. Partial rotation of the molecules.
5. Excitation of upper energy levels of the molecules.
6. Anomalous effects.

It is fortunate that all these effects do not take place in all solids. For example, in the case of nonmetals, motions of free electrons do not exist; and, in the case of metals, the lattice consists of single atoms whose component parts do not rotate or vibrate. Furthermore, all effects do not take place in all temperature ranges. Thus, the motions of the free electrons of metals have an appreciable effect on the molar heat capacity only at very low temperatures, below about 20 K. Above this temperature, other contributions are more important. Similarly, excitation of upper energy levels takes place only at very high temperatures and can, therefore, be ignored at moderate temperatures.

In this section, let us limit ourselves to a nonmetallic crystal in which the lattice sites are occupied either by a single atom or ion, or by a rigid molecule whose internal vibrations, rotations, excitations, etc., may be ignored. We shall refer to the particles occupying lattice sites as *lattice points* and we shall assume that there are N of them. These lattice points are localized in space and, therefore, are distinguishable by their positions; furthermore, they are closely packed and interact very strongly with their neighbors. It would seem, at first glance, that the statistical methods described in Chap. 12 as appropriate to indistinguishable, weakly interacting particles are useless here. But, this is not the case. Since each lattice point has three coordinates x, y, and z, the system of N lattice points has $3N$ coordinates. If each lattice point undergoes a displacement from its equilibrium position that is small compared with the space between lattice points, the change in potential energy of the crystal would entail many terms involving not only squares of these displacements but product terms as well. In the theory of small oscillations, it is shown that there *always* exists a new set of $3N$ coordinates (linear functions of the original coordinates) such that the potential energy is the sum of exactly $3N$ squared terms. Corresponding to these new coordinates, called *normal coordinates*, there are $3N$ momenta, and the kinetic energy is the sum of $3N$ terms that each contains the square of a momentum.

A particle undergoing simple harmonic motion in the x-direction has an energy equal to $\frac{1}{2}kx^2 + \frac{1}{2m}p_x^2$. The fact that the energy of N vibrating lattice points is given by $3N$ expressions of this type enables us to conclude that, when N lattice points undergo small displacements, *the vibrations in the crystal may be described as those of 3N independent simple harmonic oscillators.*

These harmonic oscillators (or *normal modes*) are *not associated with individual lattice points*; each mode involves motion of the entire crystal. This conclusion is independent of the type of crystal lattice and is true only when displacements from equilibrium positions are small. When the vibrations become large enough, anharmonic effects take place and the oscillators are no longer independent. Actually, to determine the normal coordinates of a given crystal and to calculate the various frequencies of vibration of the $3N$ normal modes is a very complicated problem in mechanics. It is a fortunate circumstance that considerable information may be obtained by applying statistical mechanics to these normal modes, along with either of two simplifying assumptions: one due to Einstein and the other due to Debye.

Our problem in statistical mechanics has now been reduced to calculating the partition function of $3N$ independent (weakly interacting) but *distinguishable* simple harmonic oscillators. Suppose we have N_ν such oscillators, *each* *vibrating with the same frequency* ν. According to the quantum theory, the energy ϵ of any such oscillator may take on only discrete values:

$$\epsilon_i = (i + \tfrac{1}{2})h\nu \qquad (i = 0, 1, 2, \cdots) \tag{13.1}$$

where h is Planck's constant, 6.63×10^{-34} J · s. Suppose that, at any moment, a macrostate of the crystal is specified by:

N_0 oscillators with energy $\epsilon_0 = \frac{1}{2}h\nu$
N_1 oscillators with energy $\epsilon_1 = \frac{3}{2}h\nu$
N_2 oscillators with energy $\epsilon_2 = \frac{5}{2}h\nu$

……………………………………

These energy states are *not* degenerate; that is, not more than one quantum state has the same energy. The number of ways in which N_ν oscillators may be distributed among the energy states according to the macrostate specified is the same as the number of ways in which N_ν *distinguishable* objects (colored balls, marked objects, etc.) can be distributed in boxes so that there are N_0 objects in box 0, N_1 objects in box 1, etc. To fix our ideas, suppose that we have only four objects, a, b, c, and d, to be distributed between two boxes so that one object will be in one box and three in the other box. The number of different ways in which four lettered objects may be arranged in sequence is $4! = 24$, as shown in Fig. 13-1. Consider the arrangement (microstate) depicted in the upper left-hand corner, where a is in the left box and b, c,

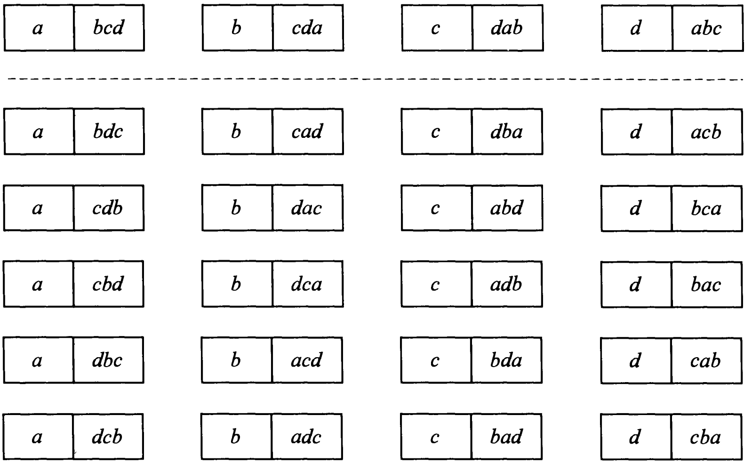

FIGURE 13-1
The number of different microstates corresponding to the macrostate in which one oscillator is in one energy state and three oscillators are in the other energy state is equal to $4!/3! = 4$. The four different microstates lie above the dashed line; those below are superfluous.

and *d* are in the right one. All the other microstates with *a* in the left box (depicted beneath the dashed line) are superfluous, since they involve merely a shift of position *within* a box. Of the six arrangements on the left, only one-sixth need be counted, or 1/3!. The same is true of the arrangements involving *b* in the left box, and so on. The total number of different arrangements, therefore, is $4!/3! = 4$.

In the general case where N_v oscillators are distributed among energy states with N_0 oscillators in the state with energy ϵ_0, N_1 in the state with energy ϵ_1, etc., the total number of nondegenerate microstates, or the thermodynamic probability Ω, is given by

$$\Omega = \frac{N_v!}{N_1!N_2!\cdots}, \tag{13.2}$$

which is the expression given in Prob. 12.6, where degeneracy was included. The entropy S is expressed as

$$\begin{aligned} S &= k \ln \Omega \\ &= k(\ln N_v! - \ln N_1! - \ln N_2! - \cdots) \\ &= k(N_v \ln N_v - N_v - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 - \cdots) \\ &= k(N_v \ln N_v - \sum N_i \ln N_i), \end{aligned}$$

which must be maximized subject to the usual conditions:

$$\sum N_i = N_v = \text{const.},$$

and

$$\sum N_i \epsilon_i = U_v = \text{const.}$$

The details of this calculation are identical with those given in Chap. 12, and only the results will be given. We get

$$N_i = N_v \frac{e^{-\epsilon_i/kT}}{Z_v}, \tag{13.3}$$

where Z_v is the partition function

$$Z_v = \sum e^{-\epsilon_i/kT}, \tag{13.4}$$

and $e^{-\epsilon_i/kT}$ is known as the Boltzmann factor.

The expressions for internal energy U_v and pressure P are the same as for indistinguishable particles, namely,

$$U_v = N_v k T^2 \left(\frac{\partial \ln Z_v}{\partial T}\right)_V, \tag{13.5}$$

and

$$P = N_v k T \left(\frac{\partial \ln Z_v}{\partial V}\right)_T. \tag{13.6}$$

But, the expression for the entropy is simpler:

$$S_\nu = N_\nu k \ln Z_\nu + \frac{U_\nu}{T}. \tag{13.7}$$

The evaluation of the partition function is particularly simple, since it is merely a geometric progression with a ratio less than 1 and an infinite number of terms:

$$\begin{aligned} Z_\nu &= e^{-h\nu/2kT} + e^{-3h\nu/2kT} + e^{-5h\nu/2kT} + \cdots \\ &= e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \cdots\right), \end{aligned}$$

or

$$Z_\nu = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}, \tag{13.8}$$

and

$$\boxed{\ln Z_\nu = -\tfrac{1}{2}\frac{h\nu}{kT} - \ln\left(1 - e^{-h\nu/kT}\right).} \tag{13.9}$$

The internal energy U_ν of N_ν simple harmonic oscillators is

$$\begin{aligned} U_\nu &= N_\nu k T^2 \frac{\partial}{\partial T}(\ln Z_\nu)_V \\ &= N_\nu k T^2 \left[\tfrac{1}{2}\frac{h\nu}{kT^2} - \frac{-e^{-h\nu/kT}(h\nu/kT^2)}{1 - e^{-h\nu/kT}}\right] \\ &= N_\nu\left(\tfrac{1}{2}h\nu + \frac{h\nu}{e^{h\nu/kT} - 1}\right); \end{aligned}$$

therefore, the average energy per oscillator is

$$\langle\epsilon\rangle = \frac{U_\nu}{N_\nu} = \frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}. \tag{13.10}$$

In general, the $3N$ equivalent simple harmonic oscillators do *not* all have the same frequency. Let dN_ν be the number of oscillators whose frequency lies between ν and $\nu + d\nu$. Then,

$$dN_\nu = g(\nu)\, d\nu, \tag{13.11}$$

where $g(\nu)$, the number of oscillators per unit frequency band, must be determined for a given crystal or class of crystals and must satisfy the condition

$$\int dN_\nu = \int g(\nu)\, d\nu = 3N. \tag{13.12}$$

The internal energy of N particles of the crystal is then

$$U = \int \langle\epsilon\rangle dN_\nu = \int\left(\frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}\right) g(\nu)\, d\nu, \tag{13.13}$$

and the heat capacity at constant volume of this amount of crystal is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \int \frac{k(h\nu/kT)^2 e^{h\nu/kT} g(\nu)\, d\nu}{\left(e^{h\nu/kT} - 1\right)^2}. \tag{13.14}$$

The integral can be calculated after some assumption is made for the number of quantum states $g(\nu)$.

13.2
FREQUENCY SPECTRUM OF CRYSTALS

The simplest assumption concerning the vibrational characteristics of a crystal was that of Einstein, namely, that all the $3N$ equivalent harmonic oscillators had the same frequency ν_E (subscript E for Einstein), as depicted in Fig. 13-2(*a*). Equation (13.14), which is open to experimental verification, then reduces to the following simple form:

$$C_V = 3N\frac{k(h\nu_\mathrm{E}/kT)^2 e^{h\nu_\mathrm{E}/kT}}{(e^{h\nu_\mathrm{E}/kT}-1)^2}.$$

If we define the *Einstein characteristic temperature* Θ_E by the expression

$$\Theta_\mathrm{E} = \frac{h\nu_\mathrm{E}}{k} \tag{13.15}$$

and let $N = N_\mathrm{A}$ (Avogadro's number), remembering that $N_\mathrm{A}k = R$ (the molar gas constant), then we get

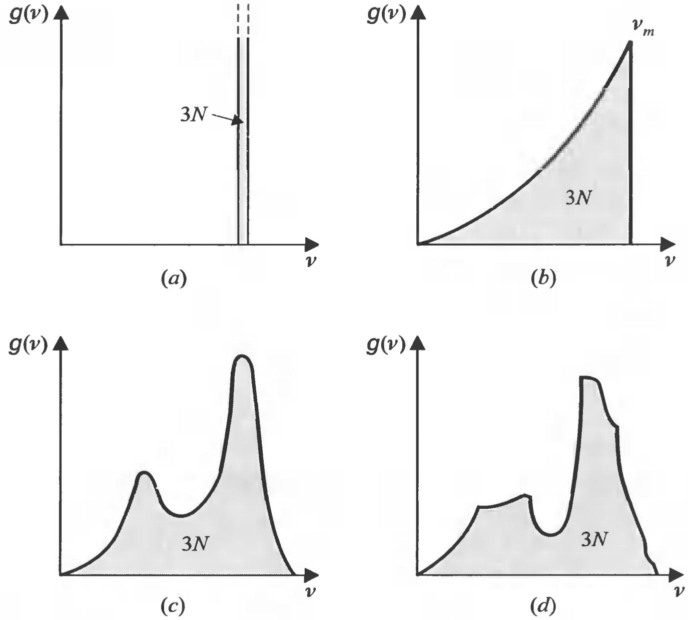

FIGURE 13-2
Frequency spectra of crystal vibrations: (*a*) Einstein approximation; (*b*) Debye approximation; (*c*) Blackman approximation; (*d*) more rigorous calculation.

$$\frac{c_V}{3R} = \left(\frac{\Theta_{\mathrm{E}}}{T}\right)^2 \frac{e^{\Theta_{\mathrm{E}}/T}}{(e^{\Theta_{\mathrm{E}}/T} - 1)^2}. \tag{13.16}$$

This was the first attempt to apply quantum theory to the molar heat capacity of solids, and, although the assumption of equal frequencies for all equivalent harmonic oscillators is far from justified, the Einstein expression has the same general shape as the curves in Fig. 9-14. As $T \rightarrow \infty$, then $c_V/3R \rightarrow 1$, in agreement with the rule of Dulong and Petit. As $T \rightarrow 0$, then $c_V/3R$ approaches zero, in agreement with experiment; but it approaches zero exponentially, which is faster than experiment indicates. However, in spite of the weakness in Einstein's theory, his pioneering work opened the way for the application of quantum theory to the specific heat of solids.

The next approximation was made by Debye. From the point of view of the wave whose wavelength is large compared with the interatomic distances, a crystal appears like a *continuous* medium supporting standing (or stationary) longitudinal and transverse waves. Debye limited the total number of vibrational modes to $3N$. Consequently, a crystal supports a continuous spectrum of frequencies, starting with zero and terminating at a maximum cutoff frequency ν_m. The number of quantum states $g(\nu)$ is given by

$$g(\nu) = \frac{9N}{\nu_m^3} \nu^2. \tag{13.17}$$

It may be seen by inspection that $\int g(\nu)\, d\nu$ is equal to $3N$. The Debye approximation for the frequency spectrum is depicted in Fig. 13-2(*b*).

Substituting the Debye approximation into Eq. (13.14), we get

$$\frac{C_V}{3Nk} = \int_0^{\nu_{\mathrm{D}}} \frac{(3\nu^2/\nu_0^3)(h\nu/kT)^2 e^{h\nu/kT}\, d\nu}{(e^{h\nu/kT} - 1)^2}.$$

It is convenient to define a new variable of integration x, where

$$x = \frac{h\nu}{kT} \quad \text{and} \quad x_m = \frac{h\nu_m}{kT} = \frac{\Theta}{T},$$

and the *Debye characteristic temperature*

$$\Theta = \frac{h\nu_m}{k}. \tag{13.18}$$

With these new quantities and with $N = N_{\mathrm{A}}$,

$$\frac{c_V}{3R} = \frac{3}{(\Theta/T)^3} \int_0^{\Theta/T} \frac{x^4 e^x\, dx}{(e^x - 1)^2}, \tag{13.19}$$

where c_V is the isochoric molar heat capacity due to lattice vibrations. As $T \rightarrow \infty$, the upper limit of the integral becomes small, and the integrand evaluated at small values of x reduces to x^2 and, when integrated, yields $\frac{1}{3}(\Theta/T)^3$. Therefore, $c_V/3R \rightarrow 1$, as required by the rule of Dulong and Petit.

To find the limiting value of $c_V/3R$ as $T \to 0$, it is convenient to express Eq. (13.19) in a different form by integrating by parts:

$$\begin{aligned}\frac{3}{(\Theta/T^3)}\int_0^{\Theta/T}\frac{x^4 e^x\,dx}{(e^x-1)^2} &= \frac{3}{(\Theta/T)^3}\int_0^{\Theta/T} x^4\,d\left(\frac{-1}{e^x-1}\right)\\ &= \frac{3}{(\Theta/T)^3}\left[\int_0^{\Theta/T}\frac{4x^3\,dx}{e^x-1} - \frac{(\Theta/T)^4}{e^{\Theta/T}-1}\right];\end{aligned}$$

therefore,

$$\frac{c_V}{3R} = 4\cdot\frac{3}{(\Theta/T)^3}\int_0^{\Theta/T}\frac{x^3\,dx}{e^x-1} - \frac{3(\Theta/T)}{e^{\Theta/T}-1}. \tag{13.20}$$

In the limit as $T \to 0$,

$$\frac{3(\Theta/T)}{e^{\Theta/T}-1} \to 0,$$

and

$$\int_0^{\Theta/T}\frac{x^3\,dx}{e^x-1} \to \int_0^{\infty}\frac{x^3\,dx}{e^x-1} = 3!\zeta(4),$$

where $\zeta(4)$ is a *Riemann zeta function*,[†] equal to

$$\zeta(4) = 1 + \frac{1}{2^4} + \frac{1}{3^4} + \cdots = \frac{\pi^4}{90}.$$

Hence,

$$\frac{c_V}{3R} \to 4\cdot\frac{3}{(\Theta/T)^3}\,\frac{3!\pi^4}{90} = \frac{4\pi^4}{5}\left(\frac{T}{\Theta}\right)^3.$$

Since $4\pi^4/5 = 77.9$, and, according to Eq. (10.39), at low temperatures $c_V = c_P = c$, we may write *Debye's T^3-law* in either of these two forms:

$$\left.\begin{aligned}\frac{c}{3R} &= 77.9\left(\frac{T}{\Theta}\right)^3\\ \text{or}\qquad c &= \frac{(125)^3\text{mJ}}{\text{mol}\cdot\text{K}}\left(\frac{T}{\Theta}\right)^3\end{aligned}\right\}\left(\text{for } \frac{T}{\Theta} < 0.02\right). \tag{13.21}$$

The evaluation of the integrals for $c_V/3R$ given by Eqs. (13.19) or (13.20) cannot be reduced to a simple analytical form, but must be calculated numerically. The results of this calculation are listed in Table 13.1 and are plotted in Fig. 13-3. The predictions of Debye's theory agree quite well with experimental values of the specific heat of crystals.

[†] See Appendix D.

TABLE 13.1
Debye's molar heat capacity

$\frac{T}{\Theta}$	$\frac{c_V}{3R}$	$\frac{T}{\Theta}$	$\frac{c_V}{3R}$	$\frac{T}{\Theta}$	$\frac{c_V}{3R}$
0	0	0.175	0.293	0.7	0.916
0.025	0.00122	0.20	0.369	0.8	0.926
0.050	0.00974	0.25	0.503	0.9	0.942
0.075	0.0328	0.3	0.613	1.0	0.952
0.100	0.0758	0.4	0.746	1.2	0.963
0.125	0.138	0.5	0.825	1.5	0.980
0.150	0.213	0.6	0.869	2.0	0.988

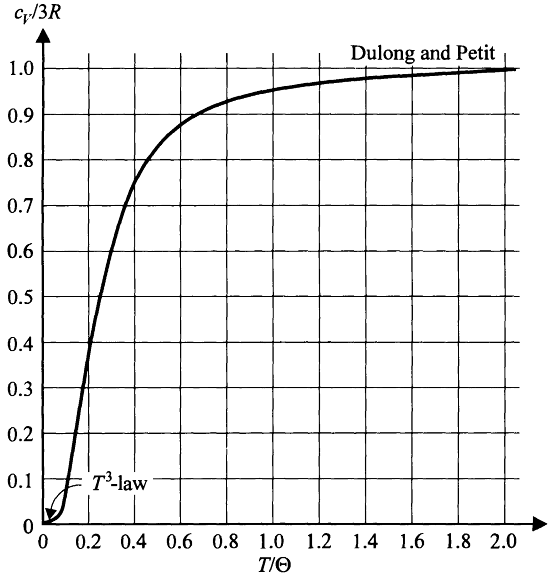

FIGURE 13-3
Temperature variation of the isochoric molar heat capacity, according to the Debye theory of lattice vibrations.

13.3
THERMAL PROPERTIES OF NONMETALS

The fundamental assumption of the Debye theory, leading to a simple quadratic function for $g(\nu)$, as shown in Fig. 13-2(*b*), is quite crude compared with theoretically derived functions such as that of Blackman, shown in Fig. 13-2(*c*). It is quite astonishing that the Debye curve in Fig. 13-3 is in such good agreement with experiment. Only when molar heat capacities are measured with great accuracy do departures from Debye's curve appear. These departures are obtained as follows: the accurate experimental value of $c_V/3R$

at a known T is compared with the theoretical Debye curve of Fig. 13-3, and the corresponding value of T/Θ is obtained; from the ratio, the value of Θ is derived at a number of temperatures. If all values of Θ so obtained were the same, then the Debye theory would hold perfectly. Such is not the case, however, as the experimental points in Fig. 13-4 show. The exact calculation of the frequency spectrum of lattice vibrations is a very complicated task, but the use of computers accomplishes the numerical calculations.

Debye's model, although crude in the medium-temperature range, is quite rigorous at very low temperatures, below $\Theta/100$, well within the T^3-region. The reason may be seen in curves (*b*), (*c*), and (*d*) of Fig. 13-2. At very low temperatures, only the low frequencies of lattice vibration are excited, so that only the beginning segments of the curves play a role. No matter how rigorously the calculation of $g(\nu)$ is carried out, the beginning segment of $g(\nu)$ is always quadratic. Therefore, one would expect that, at very low temperatures, the Debye T^3-law should be strictly obeyed and also that the value of Θ obtained from such measurements should be the correct value of Θ at absolute zero. Using the T^3-law in the form

$$c_V = \left(\frac{125}{\Theta}\right)^3 T^3 \,\frac{\text{mJ}}{\text{mol}\cdot\text{K}},$$

and dividing both sides by T, we get

$$\frac{c_V}{T} = \left(\frac{125}{\Theta}\right)^3 T^2 \,\frac{\text{mJ}}{\text{mol}\cdot\text{K}^2}.$$

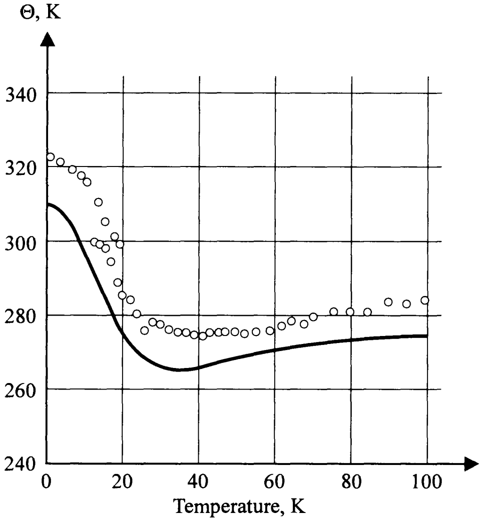

FIGURE 13-4
Variations of Θ with T for NaCl. (Curve calculated by S. O. Lundqvist, V. Lundstrom, E. Tenerz, and I. Waller: *Arkiv foer Fysik (Stockholm)*, vol. 15, pp. 193–206, 1959.)

The graph in Fig. 13-5 shows how well the law is obeyed between 0 and 4.5 K for KCl. Values of Θ near absolute zero are given for a number of nonmetals in Table 13.2.

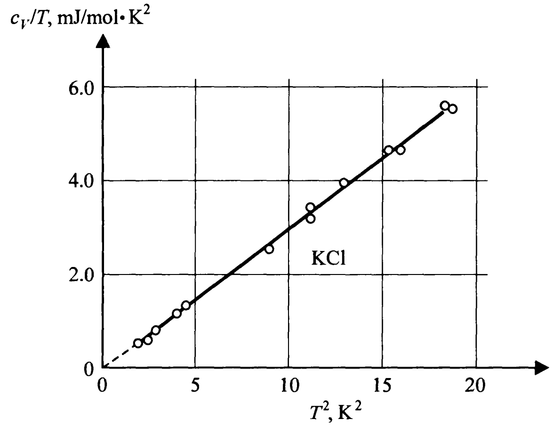

FIGURE 13-5
Verification of Debye's T^3-law for KCl. (P. H. Keesom and N. Pearlman: *Physical Review*, vol. 91, pp. 1354–1355, 1953.)

TABLE 13.2
Debye temperatures for nonmetals

Nonmetal	Θ, K	Nonmetal	Θ, K
^{3}He (bcc)†	16	KBr	174
^{4}He (hcp)†	26	KCl	235
Ne	75	KF	336
A	93	KI	132
Kr	72	RbBr	131
Xe	64	RbCl	165
Se	90	RbI	103
Te	153	InSb	202
As	282	CaF_2	510
Ge	370	SiO_2	470
Si	640	Fe_2O_3	660
C (graphite)	420	$FeSe_2$	366
C (diamond)	2230	FeS_2	637
LiF	422	MgO	946
LiCl	732	ZnS	315
NaBr	225	TiO_2	760
NaCl	321	$NiSe_2$	297
NaF	492	Bi_2Te_3	155
NaI	164	H_2O	192

† Crystal structure: bcc, body-centered cubic; hcp, hexagonal close-packed.

13.4

THERMAL PROPERTIES OF METALS

In a metal crystal, the lattice sites are occupied by single metal atoms whose vibrations obey the same laws that have been found to hold for nonmetals. In addition to the lattice vibrations, however, there are free electrons whose number is of the same order of magnitude as the number of atoms and whose motions resemble those of the molecules of a gas. If the classical theory of an ideal gas were valid for the electron gas in a metal, then the molar heat capacity at constant volume should be augmented *at all temperatures* by the constant value $\frac{3}{2}R$. Hence, at high temperatures, instead of reaching the Dulong and Petit value $3R$, it should reach the value $\frac{9}{2}R$, or about 37 J/mol · K; and, at low temperatures, c_V should not approach zero as T approaches zero, but should approach $\frac{3}{2}R$. The fact that the temperature variation of c_V of metals had the same general features as that of nonmetals remained a puzzle until Sommerfeld applied quantum statistics (Fermi-Dirac statistics) to the free electrons in a metal, and showed that the contribution of the electrons to the molar heat capacity of the metal is linear in T and is appreciable only at low temperatures when the Debye T^3-term becomes small. At higher temperatures, the linear term is small compared with the effect of lattice vibrations. We shall return to this point later, after we have studied other thermal properties of metals.

The molar heat capacity at constant pressure c_P and the volume expansivity β of metals are insensitive to moderate changes of pressure and vary with temperature in the same way as nonmetals. The graphs for copper (as typical of all metals) in Fig. 13-6, which should be compared with those of NaCl in Fig. 9-10, show that both c_P and β are zero at absolute zero, and, from 0 to 50 K, they rise rapidly. At higher temperatures, the curves flatten out but do not approach asymptotic values. The temperature dependence of the β of metals shows a curious regularity, as shown in Fig. 13-7, where it may be seen that the higher the melting point, the lower the volume expansivity. As a result, in the temperature interval from absolute zero to the melting point, all metals expand approximately the same fraction of their original volumes. It seems almost as if a metal like tin, realizing it is going to melt soon, expands rapidly with the temperature, whereas platinum, with a high melting point, slows down its rate.

In Fig. 13-8, it may be seen that the isothermal and adiabatic compressibilities of copper vary with the temperature like those of NaCl in Fig. 9-11. The complete temperature dependence of the thermal properties of copper is given in Table 13-3, and c_V is compared with c_P in Fig. 13-9. Notice that the c_V of copper goes somewhat beyond the Dulong and Petit value above 700 K. We shall see later that this additional heat capacity may be attributed to the free-electron gas inside the metal.

The free-electron gas in a metal differs from an ordinary gas in two main respects. In an ordinary gas, the number of quantum states accessible to the gas atoms is very much larger than the number of atoms ($g \gg N_i$); whereas, in

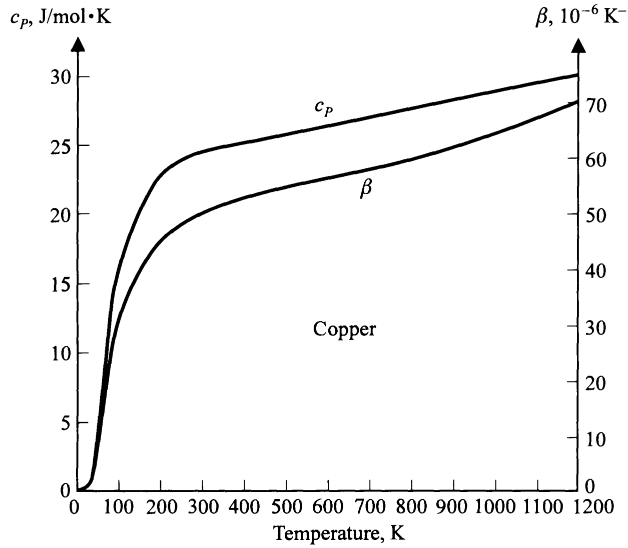

FIGURE 13-6
Temperature variation of isobaric molar heat capacity c_P and volume expansivity β of copper is similar to that of nonmetals. (Compare with Fig. 9-10.)

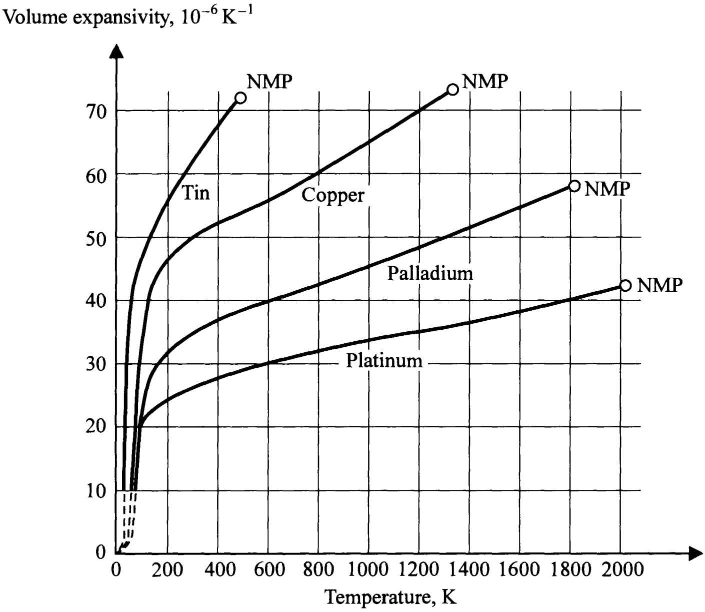

FIGURE 13-7
Normal temperature variation of volume expansivity β of metals. (NMP, normal melting point.)

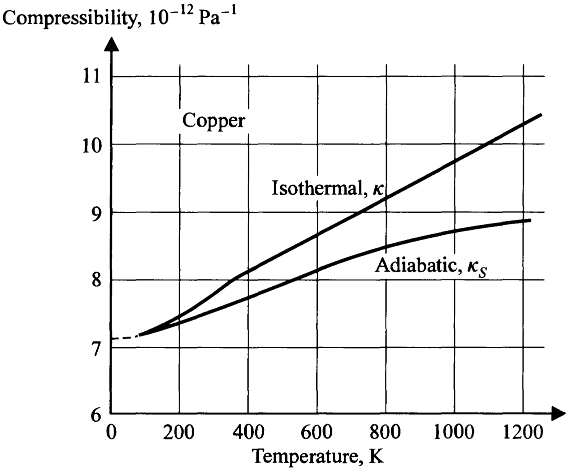

FIGURE 13-8
Temperature variation of isothermal and adiabatic compressibilities of copper with temperature. (Compare with Fig. 9-11.)

TABLE 13.3
Thermal properties of copper

T, K	c_P, J/mol · K	β, 10^{-6} K^{-1}	κ, 10^{-12} Pa^{-1}	v, 10^{-6} m^3/mol	c_V, J/mol · K	κ_S, 10^{-12} Pa^{-1}
50	6.25	11.4	7.13	7.00	6.24	7.12
100	16.1	31.5	7.21	7.01	16.0	7.19
150	20.5	40.7	7.34	7.02	20.3	7.27
200	22.63	45.3	7.49	7.03	22.4	7.34
250	23.77	48.3	7.63	7.04	23.5	7.44
300	24.48	50.4	7.78	7.06	23.8	7.54
500	25.91	54.9	8.39	7.12	24.5	7.95
800	27.7	60.0	9.23	7.26	25.4	8.49
1200	30.2	70.2	10.31	7.45	26.0	8.89

a metal, the number of quantum states is comparable, but again is less than the number of electrons; otherwise, it is an insulator. Let us see how this comes about. An electron moving more or less freely in a cubical metal of length L and volume $V = L^3$ has a kinetic energy ϵ given by exactly the same expression as that developed in Chap. 12 for a particle moving in a cubical box, namely,

$$\epsilon = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2),$$

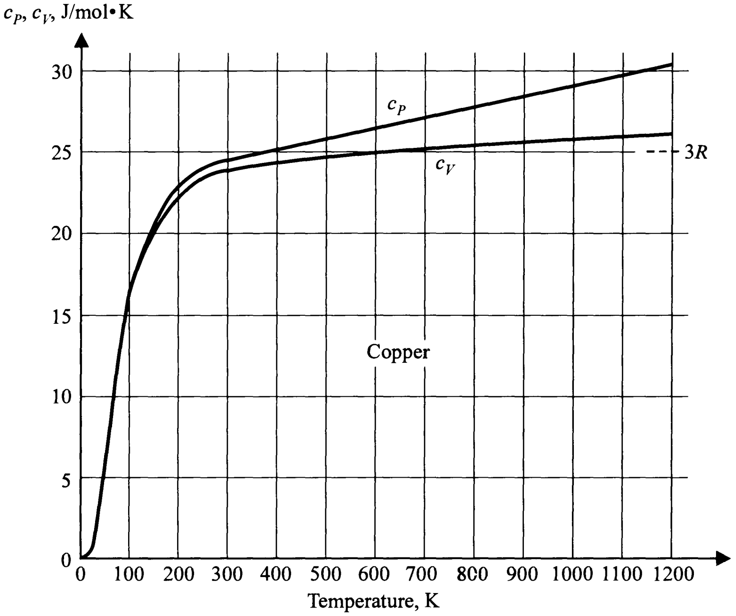

FIGURE 13-9
Temperature variation of c_P and c_V of copper. (Compare with Fig. 9-13.)

where m is the mass of an electron, and the quantum numbers n_x, n_y, and n_z are very large integers. Each triplet of values of n_x, n_y, and n_z refers to one quantum state, and all the quantum states referring to one energy ϵ lie on the surface of a sphere of radius r in a space where n_x, n_y, and n_z are cartesian coordinates and

$$r^2 = n_x^2 + n_y^2 + n_z^2.$$

The quantum states referring to an energy interval between ϵ and $\epsilon + d\epsilon$ lie between the spheres of radius r and $r + dr$, and the number of these states is the volume of the positive part of this spherical shell. Since

$$r^2 = \frac{8mL^2}{h^2}\,\epsilon,$$

then

$$2r\,dr = \frac{8mL^2}{h^2}\,d\epsilon,$$

and the volume of the spherical shell between r and $r + dr$ is $4\pi r^2\,dr$. Therefore, the number of quantum states $g\,d\epsilon$ with energy between ϵ and $\epsilon + d\epsilon$ is one-eighth of this volume, or

$$g\,d\epsilon = \tfrac{1}{8}\cdot 4\pi r^2\,dr = \frac{\pi}{4}r\cdot 2r\,dr$$

$$= \frac{\pi}{4}\sqrt{\frac{8mL^2}{h^2}}\epsilon^{1/2}\frac{8mL^2}{h^2}d\epsilon,$$

or

$$g = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\epsilon^{1/2}. \tag{13.22}$$

The number of quantum states per unit energy interval, g, is seen to depend on $m^{3/2}$. Since an electron has a mass only about 1/10,000 that of, say, a helium atom, it follows that, for a given energy, there may be $(10^{-4})^{3/2}$, or 10^{-6}, fewer quantum states for an electron gas than for an ordinary gas. Also, in a given volume (say, $1\,\text{cm}^3$), there may be 10^{19} atoms of helium; but, in a metal of the same volume, there might be about 10^{23} free electrons, assuming about one free electron per atom of metal. With 10^4 more electrons and about 10^{-6} fewer quantum states, it is clear that the number of electrons and the number of quantum states may be comparable.

Now, according to the Pauli exclusion principle, only two electrons (with opposite spin) can occupy the same quantum state. At a temperature of absolute zero, the electrons cannot all be in the lowest energy state; instead, all energy states are filled to an energy ϵ_F, known as the *Fermi energy*. Notice that the Fermi energy is the chemical potential of the electron gas at $T = 0\,\text{K}$. Suppose that a volume V of metal contains N free electrons. At absolute zero, the number of states occupied by these electrons is $N/2$, where, from Eq. (13.22),

$$\frac{N}{2} = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^{\epsilon_F}\epsilon^{1/2}\,d\epsilon,$$

or

$$\frac{N}{V} = \frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2}\epsilon_F^{3/2}. \tag{13.23}$$

To appreciate how large the Fermi energy is, it is instructive to calculate the temperature of an ordinary gas at which an atom would have the energy ϵ_F. The temperature corresponding to ϵ_F is called the *Fermi temperature*, defined as

$$T_F = \frac{\epsilon_F}{k}, \tag{13.24}$$

where k is Boltzmann's constant. From Eq. (13.23), we get

$$T_F = \left(\frac{3}{8\pi}\right)^{2/3}\frac{h^2}{2mk}\left(\frac{N}{V}\right)^{2/3}. \tag{13.25}$$

The molar volume of copper is $7.1 \times 10^{-6}\,\text{m}^3/\text{mol}$; and, assuming one free electron for every two copper atoms, $N = 3.0 \times 10^{23}$ electrons per mole. Hence,

$$T_F = 0.24\frac{(6.6\times10^{-34}\,\mathrm{J\cdot s})^2(42\times10^{27}\,\mathrm{m^{-3}})^{2/3}}{2(9.1\times10^{-31}\,\mathrm{kg})(1.4\times10^{-23}\,\mathrm{J/K})},$$

or

$$T_F \approx 50{,}000\,\mathrm{K}.$$

This means that the closely packed electrons in a metal *at absolute zero* have the energy that an ordinary gas would have at 50,000 K! This energy, known as the *zero-point energy* of the electron gas, may be several hundred thousand joules per mole of electrons, which is several electron-volts per electron.

When the temperature of the metal is raised to a value T, only electrons whose energies are near ϵ_F can be raised to higher states, so that the increase of energy per unit temperature rise dU/dT, which is the electronic heat capacity, is small. In order to calculate the electronic contribution, c_e, to the total molar heat capacity of the metal, it is necessary to develop a statistics of indistinguishable particles obeying the Pauli exclusion principle where $g_i \approx N_i$. First formulated by Fermi and Dirac, the statistics for two electrons per quantum state is called *Fermi-Dirac statistics* (see Prob. 12.8). When an open system obeying this type of statistics comes to equilibrium, it is a simple matter to show that the number of particles N_i with energy ϵ_i is given by

$$N_i = \frac{g_i}{e^{(\epsilon_i-\epsilon_F)/kT}+1}.$$

Notice that this system, known as the grand canonical ensemble, is the (microscopic) statistical mechanical analog of the (macroscopic) thermodynamic grand function $J(V, T, \mu)$, shown in Fig. 11-13(g), where $\mu = \epsilon_F$ in this case. The internal energy U_e of the system of N electrons is

$$U_e = \frac{3N/V}{2\epsilon_F^{3/2}}\int_0^\infty \frac{\epsilon^{3/2}\,d\epsilon}{e^{(\epsilon-\epsilon_F)/kT}+1}.$$

The evaluation of this integral is difficult. When T/T_F is small, the integrand may be expanded in a series and integrated term by term. When only the first two terms are retained,

$$U_e = \tfrac{3}{5}N\epsilon_F\left[1+\frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 - \cdots\right],$$

where the Fermi energy ϵ_F is the energy of the highest filled quantum state at absolute zero, the terms in the brackets are the temperature dependence of the Fermi energy, and the factor $\frac{3}{5}$ arises because the internal energy is associated with the average kinetic energy per electron. Thus, the electronic heat capacity C_e is

$$C_e = Nk\frac{\pi^2}{2}\,\frac{kT}{\epsilon_F} - \cdots.$$

Calling the constant terms γ', we may write, for the molar electronic heat capacity,

$$\boxed{c_e = \gamma' T} \qquad \text{(for } T \ll T_F\text{)}. \tag{13.26}$$

The entire course of c_e is shown in Fig. 13-10, where it may be seen that, when $T \approx T_F$, then $c_e \approx \frac{3}{2}R$. In the linear region of the curve,

$$c_e = \left(\frac{31}{T_F}\right) T \frac{\text{J}}{\text{mol}\cdot\text{K}} \qquad \left(\text{for } \frac{T}{T_F} < 0.2\right).$$

It was mentioned previously that the c_V of copper at 1200 K exceeds the Dulong and Petit value, as shown in Fig. 13-9. The electronic contribution at this temperature is

$$c_e = (31)\left(\frac{1200}{50,000}\right) \frac{\text{J}}{\text{mol}\cdot\text{K}} = 0.74\,\text{J/mol}\cdot\text{K},$$

and when this is added to the molar specific heat of 25 J/mol · K (due to vibrations in the crystal), the result of 25.8 J/mol · K is in good agreement with the high-temperature value of 26 J/mol · K shown in Fig. 13-9.

The region of greatest interest in the study of the electron gas in a metal is at low temperatures ($T/\Theta < 0.04$), where Debye's T^3-law holds. In this region, the total molar specific heat in mJ/mol · K for a metal is given by

$$c = \gamma' T + \left(\frac{125}{\Theta}\right)^3 T^3,$$

a relation first derived by Sommerfeld in 1928. Dividing by T, we get

$$\frac{c}{T} = \gamma' + \left(\frac{125}{\Theta}\right)^3 T^2; \tag{13.27}$$

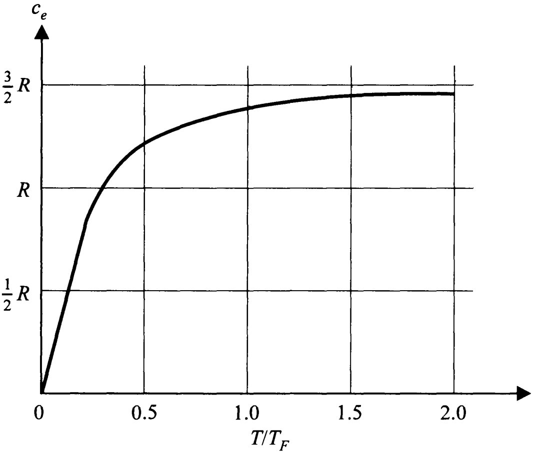

FIGURE 13-10
Temperature variation of molar electronic heat capacity c_e of an electron gas.

therefore, a graph of c/T plotted against T^2 should yield a straight line with a slope equal to $(125/\Theta)^3$ and an intercept γ'. The experimental measurements on copper made at the Westinghouse laboratories, and plotted in Fig. 13-11, verify Eq. (13.27) very well and yield reliable values of Θ and γ'. Values of Θ and γ' of other metals are listed in Table 13.4.

It is an interesting fact that conduction electrons in a metal contribute to the thermal expansivity, as well as to the molar specific heat, and, according to the same relation,

$$\beta = aT + bT^3, \tag{13.28}$$

where the linear term represents the electronic contribution and the cubic term is due to the lattice. A verification of this equation in the case of palladium is shown in Fig. 13-12, and numerical values of a and b are listed in Table 13.5.

TABLE 13.4

Debye temperatures and electronic constants for metals

Metal†	**Θ, K**	**γ', $\frac{\text{mJ}}{\text{mol}\cdot\text{K}^2}$**	**Metal**†	**Θ, K**	**γ', $\frac{\text{mJ}}{\text{mol}\cdot\text{K}^2}$**	**Metal**†	**Θ, K**	**γ', $\frac{\text{mJ}}{\text{mol}\cdot\text{K}^2}$**
3 Li	344	1.63	37 Rb	56	2.4	70 Yb	120	2.9
4 Be	1440	0.17	38 Sr	147	3.6	71 Lu	210	11.3
11 Na	158	1.4	39 Y	280	10.2	72 Hf	252	2.16
12 Mg	400	1.3	40 Zr	291	2.80	73 Ta	240	5.9
13 Al	428	1.35	41 Nb	275	7.79	74 W	400	1.3
19 K	91	2.1	42 Mo	450	2.0	75 Re	430	2.3
20 Ca	230	2.9	44 Ru	600	3.3	76 Os	500	2.4
21 Sc	360	10.7	45 Rh	480	4.9	77 Ir	420	3.1
22 Ti	420	3.5	46 Pd	274	9.42	78 Pt	240	6.8
23 V	380	9.8	47 Ag	225	0.650	79 Au	165	0.69
24 Cr	630	1.40	48 Cd	209	0.69	80 Hg	72	1.79
25 Mn	410	14	49 In	108	1.6	81 Tl	79	1.47
26 Fe	420	3.1	50 Sn	199	1.78	82 Pb	105	3.0
27 Co	445	4.7	51 Sb	211	0.112	83 Bi	119	0.021
28 Ni	450	7.1	55 Cs	38	3.2	90 Th	163	4.3
29 Cu	343	0.688	56 Ba	110	2.7	92 U	207	10.0
30 Zn	327	0.65	57 La	142	10	94 Pu	160	13
31 Ga	320	0.60	66 Dy	210	(10)			
33 As	282	0.19	69 Tm	200	10.5			

† Atomic number and spacing.

TABLE 13.5

Expansivity of metals at low temperatures

($\beta = aT + bT^3$, compiled by K. Andres, 1963, private communication.)

Metal	a, 10^{-9} K^{-2}	b, 10^{-9} K^{-1}	Metal	a, 10^{-9} K^{-2}	b, 10^{-9} K^{-1}
Mo	1.29	0.0114	Al	3.3	0.072
W	0.09	0.0135	Pb	3	4.20
Re	2.7	0.0204	Mg	3.6	0.126
Pt	6.6	0.177	Ta	3.1	0.096
Cd	0.6	1.14	Pd	10.8	0.129

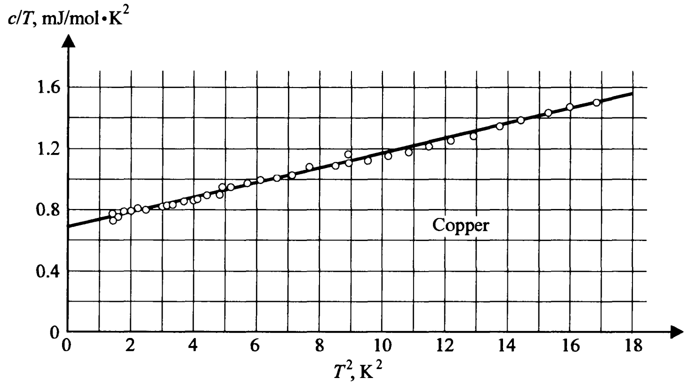

FIGURE 13-11

Molar heat capacity measurements of copper. (W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler: *Physical Review*, vol. 98, pp. 1699–1707, 1955.)

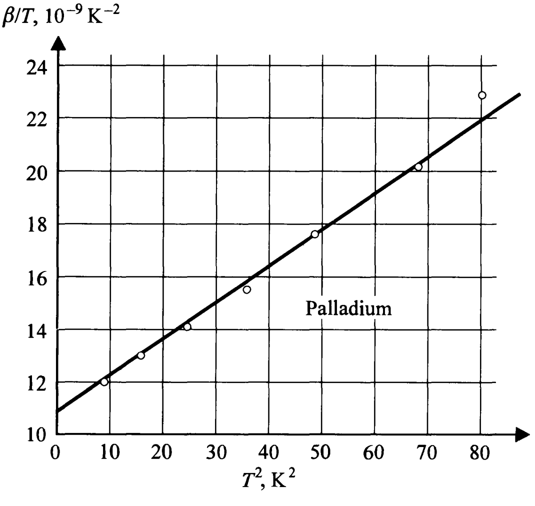

FIGURE 13-12

Thermal expansion of palladium to show the effect of conduction electrons. (G. K. White: *Philosophical Magazine*, vol. 6, pp. 815–818, 1961.)

PROBLEMS

13.1. It was shown in Eq. (13.8) that the partition function of a crystal is given by

$$Z = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}.$$

If the crystal consists of N_A lattice points:
(*a*) Calculate the Helmholtz function A.
(*b*) Calculate the pressure P.
(*c*) Calculate the entropy S.
(*d*) Express the zero-point energy in terms of Θ_E.

13.2. Using the Debye approximation, show that the total internal energy U of N_A lattice points ($3N_A$ independent harmonic oscillators) is

$$U = \tfrac{9}{8}R\Theta + \frac{9RT}{(\Theta/T)^3}\int_0^{\Theta/T} \frac{x^3\,dx}{e^x - 1}.$$

What is the interpretation of the term $\frac{9}{8}R\Theta$?

13.3. Plot the Einstein $c_V/3R$ curve against T/Θ_E on the same graph as the Debye $c_V/3R$ curve against T/Θ, and then compare the two curves.

13.4. A system consists of N_A distinguishable, independent particles, each of which is capable of existing in only two nondegenerate energy states 0 and ϵ.
(*a*) What is the partition function?
(*b*) Calculate the internal energy.
(*c*) Calculate c_V.
(*d*) Plot c_V/R as a function of kT/ϵ from $kT/\epsilon = 0$ to 1.

13.5. Given a crystal obeying Debye's approximation with Θ a function of V only, assume the entropy S to be a function of T/Θ. The Grüneisen constant Γ is defined by the equation

$$\Gamma = -\frac{d\ln\Theta}{d\ln V}.$$

(*a*) Show that

$$\Gamma = \frac{\beta V}{C_V\kappa}.$$

(*Hint*: Use Maxwell's third relation.)
(*b*) Calculate Γ of NaCl at a few temperatures using Table 9.5, and plot Γ against T.
(*c*) Show that

$$\gamma = 1 + \Gamma\beta T.$$

13.6. The partition function of a Debye crystal is

$$\ln Z = -\frac{9}{(\Theta/T)^3}\int_0^{\Theta/T} x^2\ln(1 - e^{-x})dx.$$

(*a*) Show that

$$\ln Z = -3\ln(1 - e^{-\Theta/T}) + \frac{9}{(\Theta/T)^3}\int_0^{\Theta/T} \frac{x^3\,dx}{e^x - 1}.$$

(*b*) Calculate the Helmholtz function.

(*c*) Show that the equation of state of the crystal is given by

$$PV + f(V) = \Gamma(U - U_0),$$

where U_0 is the zero-point energy.

13.7. Show that the partition function Z_{FD} for particles of half integral spin, called "fermions," is given by

$$Z_{\mathrm{FD}}(T, V, \mu) = \prod_{i=0}^{\infty}(1 + e^{-(\epsilon_i - \mu)/kT})^2,$$

where the Fermi energy $\epsilon_{\mathrm{F}} = \mu$, the chemical potential.

13.8. Show that the partition function Z_{BE} for particles of integral spin, called "bosons," is given by

$$Z_{\mathrm{BE}}(T, V, \mu) = \prod_{i=0}^{\infty}\left(\frac{1}{1 - e^{-(\epsilon_i - \mu)/kT}}\right),$$

where μ is the chemical potential.

CHAPTER 14

Critical Phenomena; Higher-Order Phase Transitions

14.1

CRITICAL STATE

The liquid and vapor phases of a substance may coexist in equilibrium at a constant temperature and pressure over a wide range of volumes from v'', where there is practically all liquid, to v''', where there is practically all vapor. At a higher temperature and pressure, v'' increases and v''' decreases. At the critical point, the two volumes (and, therefore, also the two densities) coincide. On a Pv diagram, the critical point is the limiting position as two points lying on a horizontal line approach each other. Hence, at the critical point, the critical isotherm has a horizontal tangent, or $(\partial P/\partial V)_T = 0$. As is evident from Fig. 14-1 for xenon, the critical isotherm must have a point of inflection at the critical point, and, therefore, $(\partial^2 P/\partial V^2)_T = 0$.

At all points within the region of coexistence of the liquid and vapor phases, including the critical point, the three physical properties $c_P = T(\partial S/\partial T)_P$, $\beta = (1/v)(\partial v/\partial T)_P$, and $\kappa = -(1/v)(\partial v/\partial P)_T$ *are all infinite*. On the other hand, c_V is finite, so that $\gamma = c_P/c_V$ is also infinite.

To measure precise values of P_C, v_C, and T_C, it is necessary to determine exactly *when* the critical state is reached. For this purpose, the temperature of the material is increased slowly and uniformly in a sealed tube of constant volume. Consider the tube filled so that the meniscus separating the phases is initially near the top of the tube. When the temperature is increased, the liquid will expand and the meniscus will rise to the top of the tube as the last of the vapor condenses, according to the dashed line 1 → 2 in Fig. 14-1. If the tube is filled so that the initial position of the meniscus is near the bottom, then the meniscus will fall to the bottom as the last of the liquid vaporizes, according to the dashed line 3 → 4 of Fig. 14-1. To observe the critical point, the tube must be filled so that the meniscus will remain in about the middle of the tube, as

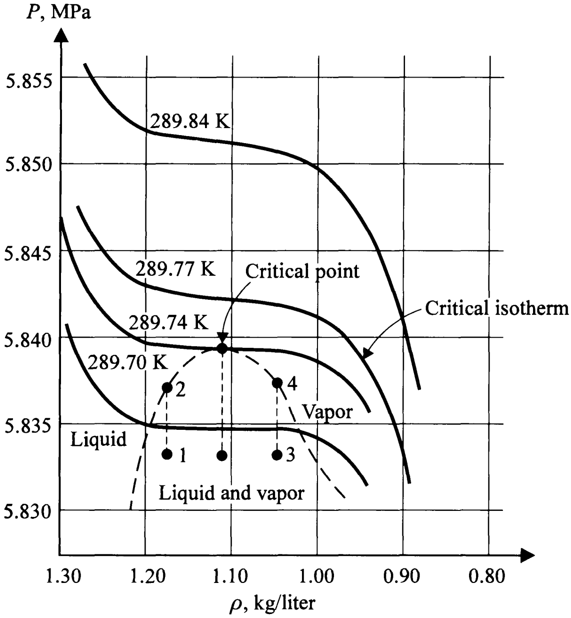

FIGURE 14-1
Measurements of pressure P as a function of density ρ showing isotherms of xenon near the critical point. (H. W. Habgood and W. G. Schneider: *Canadian Journal of Chemistry*, vol. 32, pp. 98–112, 1954.)

shown by the dashed line passing through the critical point. As the critical point is approached, observation becomes difficult because of the following factors:

1. Since the compressibility is infinite, the gravitational field of the earth causes large density gradients from top to bottom. These may be offset somewhat by taking observations of the tube in both vertical and horizontal positions.
2. Since the heat capacity is infinite, thermal equilibrium is difficult to achieve. It is necessary to keep the system at a constant temperature (within 10^{-6} K) for a long time and to stir constantly.
3. Since the thermal expansivity is infinite, small temperature changes of a local mass element within the system produce large volume changes, and, therefore, there are violent density fluctuations, which give rise to a large amount of light scattering, so that the material becomes almost opaque. This phenomenon is called *critical opalescence.*

The critical pressure may be measured at the same time as the critical temperature by noting the pressure at which the meniscus disappears. The critical volume, however, is much more difficult to determine. This measurement is carried out most commonly by measuring the densities of both saturated liquid and saturated vapor as a function of temperature to as close to the critical temperature as possible. The vapor and liquid densities are then plotted against temperature, and a line representing the arithmetic average of these densities is constructed, as shown in Fig. 14-2. This last line is usually called the *rectilinear diameter*, and experiment shows it to be virtually linear. Extrapolation to the critical temperature yields the critical density, that is, $\rho_C \sim \frac{1}{2}(\rho'' + \rho''')$, where ρ'' is the density of the liquid and ρ''' is the density of the gas.

The difference of liquid and gaseous densities $\rho'' - \rho'''$ is called the *order parameter* and is a measure of the microscopic interactions of the particles in a hydrostatic system below the critical point. At temperatures above the critical temperature T_C, the order parameter $\rho'' - \rho'''$ is zero, because the system is in the gaseous phase and presumably little interaction or ordering occurs between the particles. However, as the temperature is lowered toward the critical temperature, particles coalesce to form small "droplets" and "bubbles" that are smaller than the wavelength of visible light. At temperatures just above T_C, the droplets grow to a size comparable to the wavelength of light and light is strongly scattered by the droplets, producing the phenomenon of critical opalescence. At temperatures below T_C, the droplets of higher density precipitate out of the vapor phase to form a liquid. In the region of the coexisting phases, some ordering occurs among the particles, so the order parameter is nonzero.

According to the principle of corresponding states, which was introduced by van der Waals (see Prob. 9.5) and further developed by Guggenheim, the reduced pressure $\tilde{P} = P/P_C$ and reduced density $\tilde{\rho} = \rho/\rho_C$ should be common

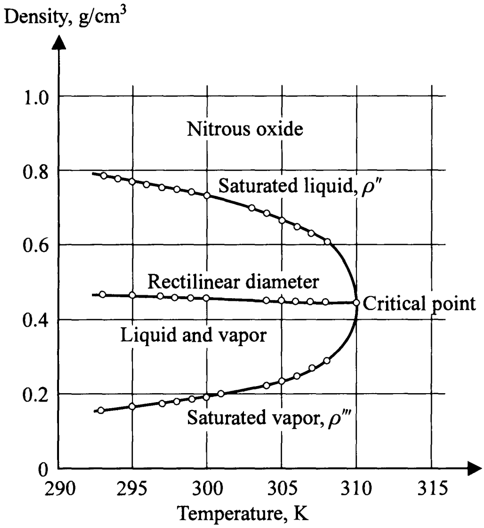

FIGURE 14-2
Measurements of liquid and vapor densities as a function of temperature for nitrous oxide, and extrapolation of mean density through the critical point. (D. Cook: *Transactions of the Faraday Society*, vol. 49, pp. 716–723, 1953.)

functions of the reduced temperature $\tilde{T} = T/T_C$. The former relationship is shown in Fig. 14-3 and the latter relationship is shown in Fig. 14-4. In the case of the density, it is customary to deal with the reduced order parameter $(\rho'' - \rho''')/\rho_C$, which is considered to be a function of the quantity ϵ, defined as

$$\epsilon \equiv \frac{T - T_C}{T_C}. \tag{14.1}$$

The dimensionless variable ϵ, which measures the reduced difference in temperature from the critical temperature, is also called the *expansion parameter.*

The reduced-order parameter is plotted as a function of ϵ on a log–log graph for carbon dioxide in Fig. 14-5. The resulting straight line means that the relationship between the order parameter and ϵ is

$$\rho'' - \rho''' \sim (-\epsilon)^{\beta}, \tag{14.2}$$

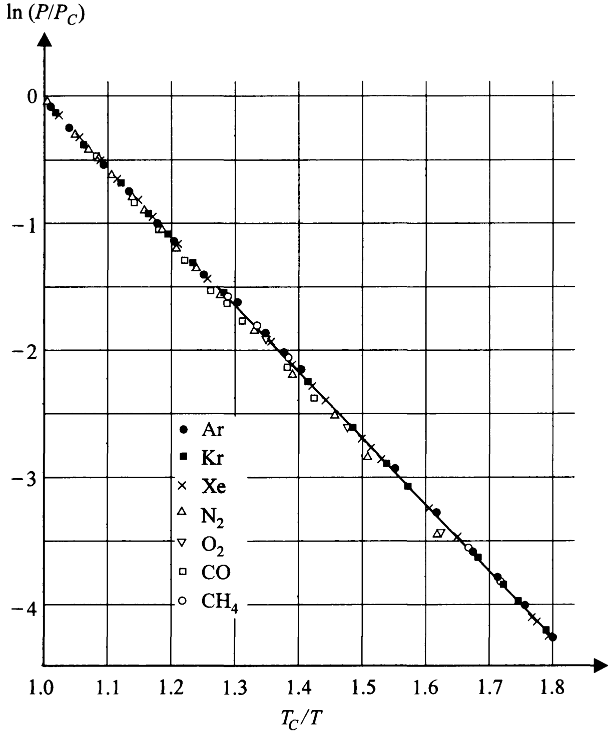

FIGURE 14-3
A principle of corresponding states for simple liquids over a wide temperature range. (E. A. Guggenheim: *Thermodynamics*, North-Holland, Amsterdam, 1967.)

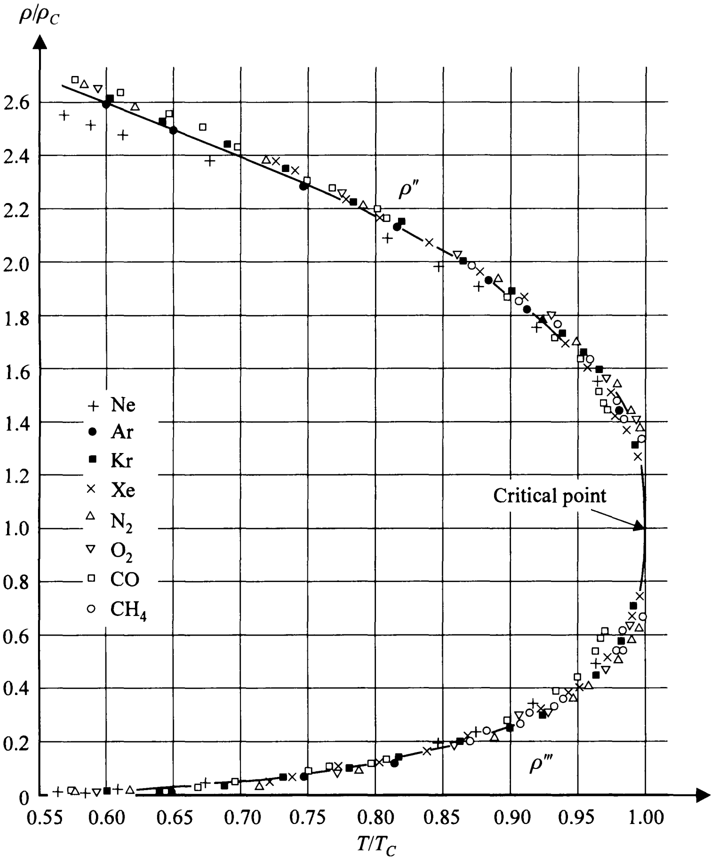

FIGURE 14-4

A principle of corresponding states for coexisting liquid and vapor phases: reduced density ρ/ρ_C vs. reduced temperature T/T_C. (E. A. Guggenheim: *Thermodynamics*, North-Holland, Amsterdam, 1967.)

where the slope β is known as a critical-point exponent, or simply, *critical exponent*. The order parameter vanishes at the critical point, but other thermodynamic variables have singularities at the critical point.

14.2
CRITICAL-POINT EXPONENTS OF A HYDROSTATIC SYSTEM

We mentioned in Sec. 14.1 that the isobaric molar heat capacity and isothermal compressibility are infinite at the critical point. There is, however, a more detailed mathematical statement about the precise functions that govern the

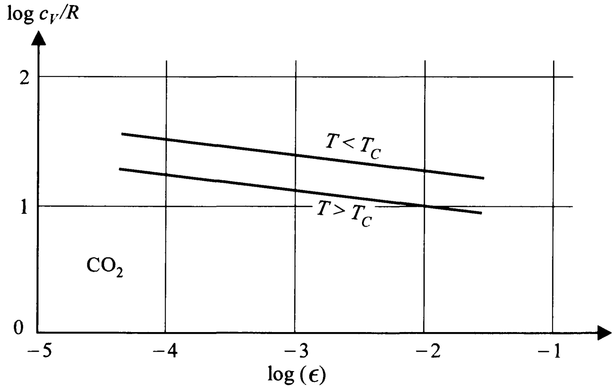

FIGURE 14-5
The logarithm of the isochoric molar specific heat c_V/R vs. log(ϵ) for CO_2. (J. A. Lipa, C. Edwards, and M. J. Buckingham: *Physical Review*, ser. A, vol. 15, pp. 778–789, 1977.)

behavior of various systems near the critical point. Therefore, we define six critical-point exponents, denoted by the Greek letters α, α', β, γ, γ', and δ, which are standard notation used in the description of asymptotic singular functions near the critical point.

The coefficient α characterizes the behavior of the molar specific heat capacity at constant volume (density) evaluated along the critical isochore:

$$c_{V=V_C} \sim \epsilon^{-\alpha}, \qquad \epsilon \to 0+, \tag{14.3}$$

where the quantity $\epsilon \to 0+$ symbolizes the fact that the temperature T approaches the critical temperature T_C from above. One may also introduce a similar coefficient α', which characterizes the specific heat at constant volume as the temperature approaches the critical point from below. Thus,

$$c_{V=V_C} \sim (-\epsilon)^{-\alpha'}, \qquad \epsilon \to 0-, \tag{14.4}$$

where α and α' are not necessarily equal.

The experimental values for the critical-point exponents α and α' may not be the same for a given simple system, as predicted by the principle of corresponding states. Kadanoff, in 1967, obtained $\alpha < 0.4$ and $\alpha' < 0.25$ for argon. Later results of Lipa, Edwards, and Buckingham, who obtained very precise values of c_V for CO_2, are shown in Fig. 14-5. An analysis of Fig. 14-5 by Heller† yields the values: $\alpha = 0.124 \pm 0.014$ and $\alpha' = 0.124 \pm 0.012$.

The critical-point exponent, β, used in Eq. (14.2) and shown to characterize the behavior of the order parameter, is the exponent in the following asymptotic function:

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† P. Heller: *Reports on Progress in Physics*, vol. 30, pt. II, pp. 731–826, 1967.

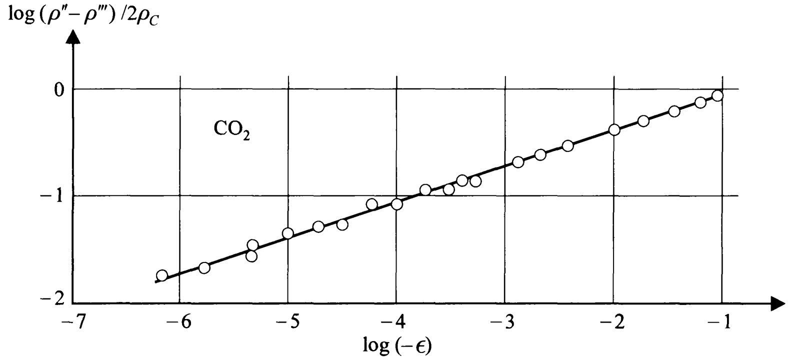


FIGURE 14-6

The logarithm of the reduced-order parameter $(\rho'' - \rho''')/2\rho_C$ vs. $\log(-\epsilon)$ from the coexistence curve data for CO_2. (P. Heller: *Reports on Progress in Physics*, vol. 30, pt. II, pp. 731–826, 1967.)

$$\rho'' - \rho''' \sim (-\epsilon)^{\beta}, \qquad \epsilon \to 0-, \tag{14.2}$$

where, of course, the function is meaningful only below the critical point in the region where $\rho'' - \rho'''$ is not zero. The data from the coexistence curve for CO_2 are shown in Fig. 14-6, using the results from five separate experiments. Heller calculates a value of $\beta = 0.34 \pm 0.015$ for CO_2.

The pair of coefficients γ and γ' characterize the behavior of the isothermal compressibility. Just as in the case of the isochoric specific heat, there is a difference in the functions describing κ as it approaches the critical temperature from above or below. In the former case,

$$\kappa \sim \epsilon^{-\gamma}, \qquad \epsilon \to 0+, \tag{14.5}$$

and, in the latter case,

$$\kappa \sim (-\epsilon)^{-\gamma'}, \qquad \epsilon \to 0-, \tag{14.6}$$

As before, these two critical exponents are not necessarily equal.

The isothermal compressibility data for carbon dioxide, normalized to κ_I of an ideal gas whose density and temperature are those of CO_2 at the critical point, are shown in Fig. 14-7. The slope of the straight line yields a value of the critical exponent $\gamma = 1.35 \pm 0.15$ for CO_2 above T_C. Below T_C, the isothermal compressibility can be determined for either the liquid or the vapor at densities on the coexistence curve. The analysis for data on CO_2 results in a value of $\gamma' = 1.1 \pm 0.4$. If subsequent experiments should show that the two values of gamma are indeed unequal, then the dependence of the isothermal compressibility as a function of reduced temperature would not be symmetric with respect to the critical temperature.

The last exponent δ describes the critical isotherm itself:

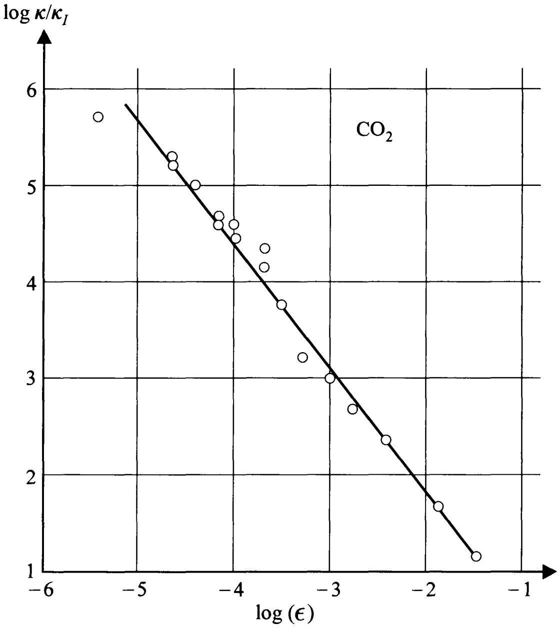


FIGURE 14-7
The logarithm of the reduced isothermal compressibility κ/κ_I above T_C vs. log (ϵ) for CO_2. The normalizing factor κ_I is the compressibility of an ideal gas whose density and temperature are those of CO_2 at the critical point. (P. Heller: *Reports on Progress in Physics*, vol. 30, pt. II, pp. 731–826, 1967.)

$$P - P_C \sim (\rho - \rho_C)^{\delta}, \qquad \rho \to \rho_C, \tag{14.7}$$

where the parameter $\epsilon = 0$ always. The critical exponent δ is a measure of the "flatness" of the critical isotherm at the critical point, as shown in Fig. 14-1. Because of the difficulty in obtaining accurate pressure and density measurements very close to the critical point along the coexistence curve, the shape of the coexistence curve is somewhat uncertain. Figure 14-8 shows the difference in pressures for carbon dioxide, normalized to the pressure of an ideal gas at the density and temperature of CO_2 at the critical point, as a function of the reduced density. Heller calculates the value of $\delta = 5.0 \pm 1$. For the xenon data shown in Fig. 14-1, the value of δ is 4.4 ± 0.4. Table 14.1 summarizes the definitions and conditions for the six critical-point exponents for a hydrostatic system and lists experimental values for the exponents in several systems.

The simplest rigorous relation among the critical-point exponents is an inequality known as the *Rushbrooke inequality*. Equation (10.38) can be written in terms of molar quantities as

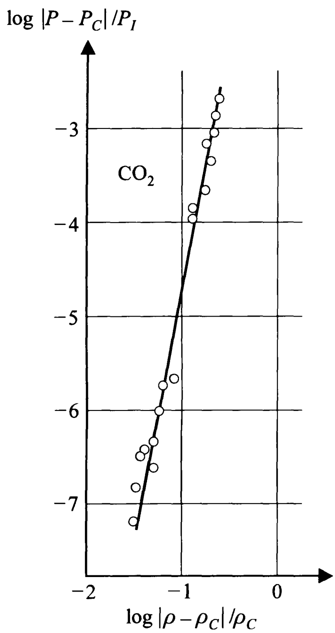


FIGURE 14-8
The logarithm of the reduced pressure difference $|P - P_C|/P_I$ vs. the logarithm of the reduced density $|\rho - \rho_C|/\rho_C$ for CO_2. The normalizing factor P_I is the pressure of an ideal gas at a critical density and temperature of CO_2. (P. Heller: *Reports on Progress in Physics*, vol. 30, pt. II, 731–826, 1967.)

$$c_P - c_V = -T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T,$$

or

$$= \frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_P^2 \kappa^{-1}.$$

In terms of asymptotic behavior, c_P, T, and v can be neglected, so

$$c_V \leq \left(\frac{\partial v}{\partial T}\right)_P^2 \kappa^{-1}. \tag{14.8}$$

TABLE 14.1
Summary of critical point exponents for hydrostatic systems

		Conditions							
Exponent	**Function**	ϵ	$P - P_C$	$\rho - \rho_C$	**Ar**	**Xe**	CO_2	^{3}He	^{4}He
α'	$c_{V=V} \sim (-\epsilon)^{-\alpha'}$	< 0	0	0	< 0.25	< 0.2	0.124	0.105	0.017
α	$c_{V=V} \sim \epsilon^{-\alpha}$	> 0	0	0	< 0.4	—	0.124	0.105	0.017
β	$\rho'' - \rho''' \sim (-\epsilon)^{\beta}$	< 0	0	$\neq 0$	0.362	0.35	0.34	0.361	0.354
γ'	$\kappa \sim (-\epsilon)^{-\gamma'}$	< 0	0	$\neq 0$	1.20	—	1.1	1.17	1.24
γ	$\kappa \sim \epsilon^{-\gamma}$	> 0	0	0	1.20	1.3	1.35	1.17	1.24
δ	$P - P_C \sim \lvert\rho'' - \rho'''\rvert^{\delta}$	0	$\neq 0$	$\neq 0$	—	4.4	5.0	4.21	4.0

Change variables from molar volume v to density ρ in the partial derivative to obtain

$$c_V \leq \left(\frac{\partial \rho}{\partial T}\right)_P^2 \kappa^{-1}. \tag{14.9}$$

The presence of the density has introduced the order parameter, so the results will apply only to temperatures less than T_C. From the asymptotic relations given in Eqs. (14.2), (14.4) and (14.6), Eq. (14.9) can be rewritten

$$\begin{aligned} (-\epsilon)^{-\alpha'} &\leq \left[\frac{\partial}{\partial T}(-\epsilon)^{\beta}_{P}\right]^2 \left[(-\epsilon)^{-\gamma'}\right]^{-1} \\ &\leq (-\epsilon)^{2\beta-2}(-\epsilon)^{\gamma'}; \end{aligned}$$

so

$$-\alpha' \leq 2\beta - 2 + \gamma',$$

or, rearranging terms,

$$\alpha' + 2\beta + \gamma' \geq 2. \tag{14.10}$$

It will be noticed from Table 14.1 that most of the substances either fulfill the Rushbrooke inequality, or come close to fulfilling it. Large uncertainties in some of the experimental data account for those substances that do not satisfy the inequality. There are additional inequalities, many of which involve critical-point exponents of singular functions not introduced here.

14.3
CRITICAL-POINT EXPONENTS OF A MAGNETIC SYSTEM

We have seen that the critical-point exponents describe the asymptotic behavior of singular functions near the critical point of a hydrostatic system. Another system that can be analyzed in terms of critical-point exponents is a ferromagnetic material. A ferromagnet is characterized by a permanent magnetization $\mathcal{M}$, which does not vanish when the magnetic intensity $\mathcal{H}$ is zero. When the temperature is raised to the Curie point (or critical temperature) T_C, the magnetization is directly proportional to the magnetic intensity; that is, the substance ceases to be ferromagnetic and becomes paramagnetic. In other words, the Curie point is the ferromagnetic critical point.

In the region above the Curie point, the temperature dependence of the ratio $\mathcal{M}/\mathcal{H}$ is described by the Curie-Weiss law, namely,

$$\frac{\mathcal{M}}{\mathcal{H}} = \frac{C_C}{T - T_C}, \qquad T > T_C, \tag{14.11}$$

which is a modification of the Curie law described in Sec. 2.9. The Curie constant C_C depends on the atomic properties of the substance and thus differs for each material. The Curie points of various ferromagnetic elements and compounds are listed in Table 14.2.

TABLE 14.2
Curie points of various ferromagnets

Substance	T_C, K
Co	1388
Fe	1042.5
$YFeO_3$	643
Ni	631.6
CrO_2	386.5
Gd	292.5
$CrBr_3$	32.56
EuS	16.50

The form of Eq (14.11) shows that, at the Curie point, one expects a singularity in the magnetic properties, namely, an infinite value of the ratio $\mathcal{M}/\mathcal{H}$. Since the maximum value of $\mathcal{M}$ is finite (being limited to the saturation magnetization obtained when all the microscopic magnetic dipoles of the substance are aligned parallel to one another), we must conclude that $\mathcal{H} = 0$. In other words, the substance is magnetized even in the absence of an external magnetic field. This "spontaneous magnetization," due to an internal field, is a characteristic of ferromagnets. The Curie point T_C is the boundary between paramagnetic behavior at $T > T_C$ and ferromagnetic behavior at $T < T_C$.

It is customary to compare the similarities between the hydrostatic and magnetic systems. The application of a pressure P to a fluid increases the density ρ, and the application of a magnetic intensity $\mathcal{H}$ to a magnet increases the total magnetization $\mathcal{M}$. Thus, $\mathcal{H}$ is analogous to P, and $\mathcal{M}$ is analogous to ρ.

Figure 14-9 shows an $\mathcal{H}\mathcal{M}T$ surface analogous to the surfaces of hydrostatic systems shown in Figs. 9-4 and 9-5. At temperatures very large compared with T_C, the Curie law is obeyed and the isotherm, therefore, is given by Eq. (2.20):

$$\frac{\mathcal{M}}{\mathcal{H}} = \frac{C_C}{T}. \tag{2.20}$$

As the temperature is decreased to near T_C, the Curie-Weiss law given by Eq. (14.11) describes the behavior of the isotherms. Below T_C, there is no simple analytic expression to describe temperature dependence of $\mathcal{M}/\mathcal{H}$. In fact, there are no stable states in the region shown as a flat plateau in Fig. 14-9. The projections of the $\mathcal{H}\mathcal{M}T$ surface on the $\mathcal{H}\mathcal{M}$, $\mathcal{H}T$, and $\mathcal{M}T$ planes are shown in Fig. 14-10.

For the hydrostatic system, the order parameter was defined as the difference in the densities of the liquid and vapor. For the magnetic system, the order parameter is the total magnetization $\mathcal{M}$. Similarly, the isothermal com-

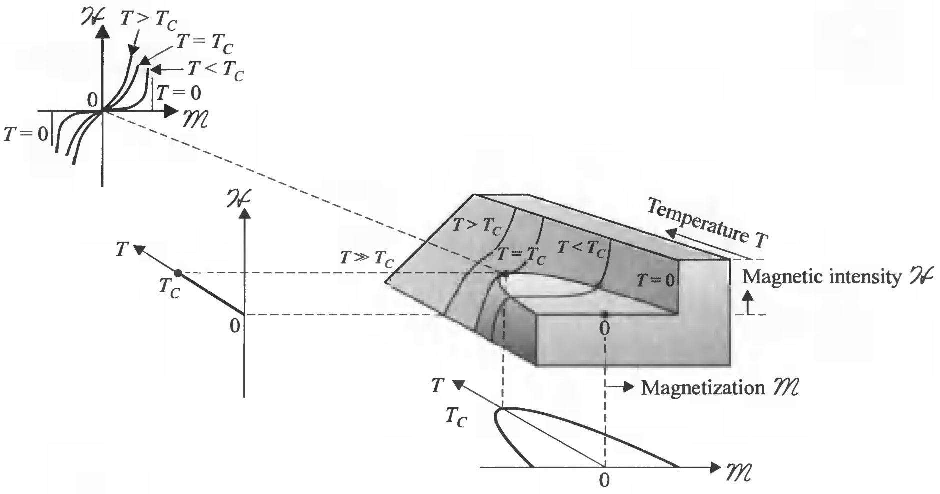


FIGURE 14-9
The $\mathcal{HMT}$ surface of a hypothetical ferromagnetic substance.

pressibility κ of the hydrostatic system finds its analog in the isothermal differential susceptibility χ', which is defined

$$\chi' = \left(\frac{\partial \mathcal{M}}{\partial \mathcal{H}}\right)_T. \tag{14.12}$$

Finally, the isochoric specific heat of the fluid system is replaced by the specific heat at constant magnetic intensity.

All three magnetic functions — specific heat, order parameter, and differential susceptibility — have singular behavior at the Curie (critical) temperature T_C and, correspondingly, six critical-point exponents that are,

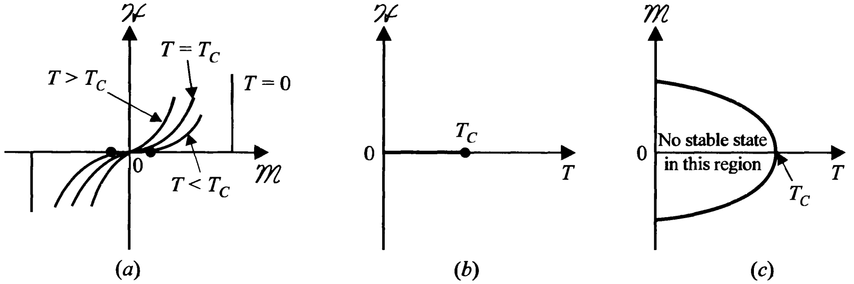


FIGURE 14-10
The projections of an $\mathcal{HMT}$ surface of a hypothetical ferromagnetic substance onto: (a) the $\mathcal{HM}$ plane; (b) the $\mathcal{H}T$ plane; and (c) the $\mathcal{M}T$ plane.

TABLE 14.3
Summary of critical point exponents for magnetic systems

		Conditions						
Exponent	**Function**	ϵ	$\mathcal{H}$	$\mathcal{M}$	**Fe**	**Ni**	**Gd**	**CrBr₃**
α'	$c_{\mathcal{H}=0} \sim (-\epsilon)^{-\alpha'}$	< 0	0	0	−0.12	−0.10	—	—
α	$c_{\mathcal{H}=0} \sim \epsilon^{-\alpha}$	> 0	0	0	−0.12	−0.10	—	—
β	$\mathcal{M} \sim (-\epsilon)^{\beta}$	< 0	0	$\neq 0$	0.34	0.33	—	0.365
γ'	$\chi' \sim (-\epsilon)^{-\gamma'}$	< 0	0	$\neq 0$	1.33	1.32	1.33	—
γ	$\chi \sim \epsilon^{-\gamma}$	> 0	0	0	1.33	1.32	1.33	1.215
δ	$\mathcal{H} \sim \lvert\mathcal{M}\rvert^{\delta}$	0	$\neq 0$	$\neq 0$	—	4.2	4.0	4.3

respectively, α, α', β, γ, γ', and δ. Table 14.3 provides a summary of the critical-point exponents for a magnetic system and lists experimental values for some ferromagnetic substances. Another example of a critical point, the lambda point of helium, will be presented in the next section.

The earliest attempts to understand critical phenomena were made for fluids, in 1873, by van der Waals and for ferromagnets, in 1907, by Weiss, both of whom proposed *mean field theories*, which erroneously assume that the interaction between molecules is infinite in range at all temperatures. The mean field theory was successful in predicting the power law dependence near the critical point, but unsuccessful in predicting the values of the critical-point exponents.

Two hypotheses were introduced to replace the mean field theories. The *scaling hypothesis* assumes that the long-range correlation of the order parameter, such as the density fluctuation in the fluid system near the critical point and the spin fluctuations in the ferromagnetic system near the Curie point, is responsible for all singularities in the thermodynamic properties. As a result, the Rushbrooke inequality and others, which are proven rigorously by thermodynamic arguments, become equalities in almost all real and theoretical critical systems. The *universality hypothesis,* which is independent of the details of any system, assumes that critical phenomena are determined entirely by the spatial dimensionality and spin dimensionality. For example, thin films of a ferromagnet have different critical-point exponents than the bulk crystal, because the film is two dimensional and the crystal is three dimensional.

The renormalization group method, originally used in quantum field theory, uses a set of symmetry operations to reformulate and simplify the ideas found in the scaling and universality hypotheses. Consequently, a fully operational formalism based on hypotheses beyond thermodynamics is able to calculate the critical exponents. Significant contributions were made by Kadanoff and Fisher, as well as Wilson who won the Nobel prize in 1982.

14.4
HIGHER-ORDER PHASE TRANSITIONS

The processes of sublimation, vaporization, and fusion were called phase transitions of the first order because the first-order derivatives of the molar Gibbs function g, namely, the molar entropy $s = -(\partial g/\partial T)_P$ and molar volume $v = (\partial g/\partial P)_T$, are discontinuous at the transition point; that is, s and v underwent finite changes during the transition. In contrast, there are phase transitions in which the molar entropy and the molar volume are the *same* at the end of the transition as they were in the beginning. In such phase changes, T, P, g, s, and v remain unchanged, and, therefore, U, H, and A also remain unchanged. If c_P, κ, and β experience *finite* changes in such a transition, then, since

$$\frac{c_P}{T} = \left(\frac{\partial s}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\left(-\frac{\partial g}{\partial T}\right)_P\right]_P = -\left(\frac{\partial^2 g}{\partial T^2}\right)_P, \tag{14.13}$$

$$\kappa v = -\left(\frac{\partial v}{\partial P}\right)_T = -\left[\frac{\partial}{\partial P}\left(\frac{\partial g}{\partial P}\right)_T\right]_T = -\left(\frac{\partial^2 g}{\partial P^2}\right)_T, \tag{14.14}$$

and

$$\beta v = \left(\frac{\partial v}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{\partial g}{\partial P}\right)_T\right]_P = \left(\frac{\partial^2 g}{\partial T \partial P}\right)_{T,P}, \tag{14.15}$$

there would be finite changes of the second-order derivatives of the Gibbs function. Such a transition is called a *second-order phase transition*, because the second derivative is the first discontinuous derivative. This scheme was first suggested by Ehrenfest, who derived two simple equations that expressed the constancy of s and v through the phase transition. The variations of the molar Gibbs function g and molar entropy s with temperature for a second-order phase transition are shown in Fig. 14-11. Notice that g and s are con-

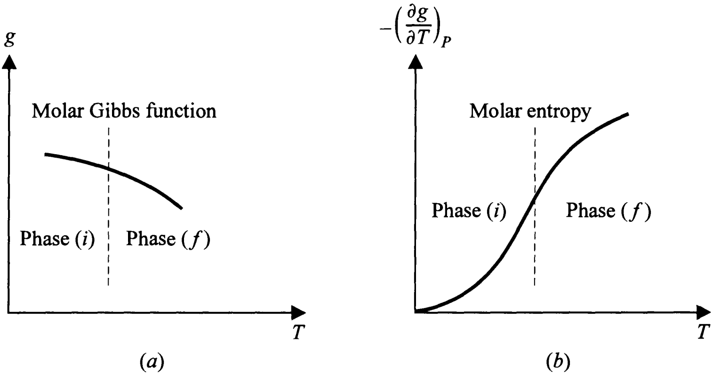


FIGURE 14-11
Characteristics of a continuous phase transition: (*a*) molar Gibbs function; (*b*) molar entropy. (Compare with Fig. 11-9.)

tinuous through the second-order phase transition, unlike a first-order transition as shown in Figs. 11-9, parts (*a*) and (*b*). Consequently, a second-order phase transition is an example of a *continuous transition.*

It was first thought that there were many examples of second-order transitions; but, as experimental measurements were made closer and closer to the transition temperature (sometimes to within 10^{-8} K!), neither c_P nor β was found to achieve the finite values expected at the beginning or at the end of a second-order phase transition. It may be that there is only one example of a second-order phase transition, namely, the change from superconductivity to normal conductivity in zero magnetic field.

The other example of a continuous phase transition is the very interesting *lambda transition*, characterized by the following behavior at the temperature of the phase transition:

1. T, P, and g are continuous.
2. s and v (also U, H, and A) are continuous.
3. c_P, κ, and β are infinite, contrary to the expectations of Eqs. (14.13), (14.14), and (14.15), respectively.

A graph of c_P against T serves to distinguish among the three types of phase transitions, as shown in Fig. 14-12. The name "lambda transition" is chosen because the shape of the c_P vs. T curve in the third graph resembles the Greek letter lambda. Among the many examples of λ-transitions are: (1) a fluid near its critical point; (2) the transition from ferromagnetism to paramagnetism at the Curie point; (3) the onset of ferroelectricity in certain crystals, such as Rochelle salt; (4) "order–disorder" transformations in alloys; (5) a change of orientation of an ion in a crystal lattice, such as the ammonium chloride transition; and, most interesting of all, (6) the transition of ^{4}He from normal

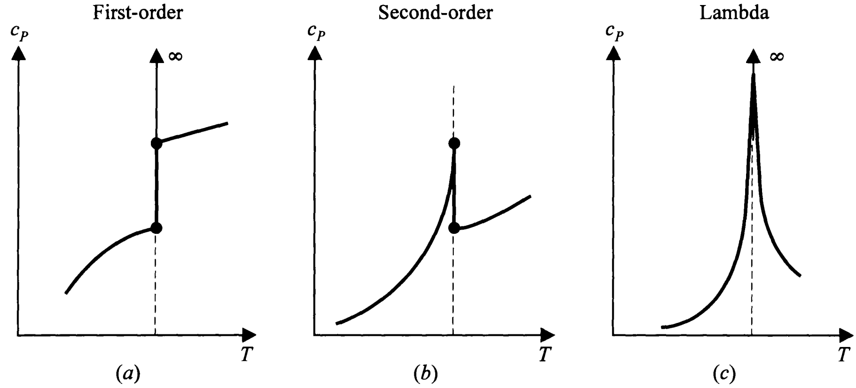


FIGURE 14-12
Distinguishing characteristics among the three types of phase transitions: (*a*) first-order; (*b*) second-order; (*c*) lambda.

liquid helium (liquid He I) to superfluid helium (liquid He II) at a temperature and corresponding pressure known as a *lambda point*. The lower-temperature liquid He II has zero viscosity, hence, it behaves as a *superfluid.*

It may be seen in Fig. 14-12(*a*) that, as a substance in any one phase approaches the temperature at which a first-order phase transition is to occur, its c_P remains finite up to the transition temperature. The isobaric molar heat capacity becomes infinite only when a small amount of the other phase is present, and its behavior *before* the transition occurs shows no evidence of the transition. In the case of a λ-transition, however, as is evident in Fig. 14-12(*c*), c_P starts to rise before the transition is reached, as though the substance, in the form of only one phase, "anticipated" the coming phase transition. The particles of substances undergoing λ-transitions interact strongly with one another, even at distances beyond those of their nearest neighbors. From either higher temperatures or lower temperatures, c_P asymptotically approaches the λ-point.

14.5

LAMBDA TRANSITIONS IN ^{4}He

In the treatment of phase transitions using the methods of renormalization group theory, the λ-transition is not a separate category of a continuous phase transition, but another example of a critical phenomenon. As a result, ^{4}He experiences two critical transitions: the transition of normal liquid to vapor at the fluid critical point with rising temperature and the transition from normal liquid to superfluid at the λ-point with falling temperature. Figure 14-13 shows the two different transitions on the molar heat capacity of ^{4}He.

The λ-transition of ^{4}He is particularly well suited for providing data showing asymptotic behavior. Near the λ-point, unlike the critical point in a hydrostatic fluid, variation of density due to the pressure of the fluid above the measuring device can be eliminated or calculated.

The temperatures and pressures at which the λ-transition takes place in ^{4}He constitute the λ-line, a portion of which is shown on the phase diagram of Fig. 14-14(*a*). Consider another curve parallel to the λ-line, but at a slightly higher temperature $T = T_\lambda + \Delta T$, shown by the dashed curve shifted a small temperature difference ΔT to the right of the λ-line. The slope of the λ-line at any point, $dP/dT (= P'_\lambda)$, will be the same at a corresponding point on the parallel curve where the temperature $T = T_\lambda + \Delta T$.

On the molar entropy curve of Fig. 14-14(*b*), the slope $ds/dT (= s'_\lambda)$ of the dashed curve marked T is the same as that of the λ-curve at a point at the same pressure, since ΔT is very small. The same is true on the molar volume diagram of Fig. 14-14(*c*). With these facts in mind, let us use the second $T\,dS$ equation to represent a small entropy change *on the dashed entropy curve* of Fig. 14-14(*b*), where $T = T_\lambda + \Delta T$. Using lower-case letters to indicate molar quantities,

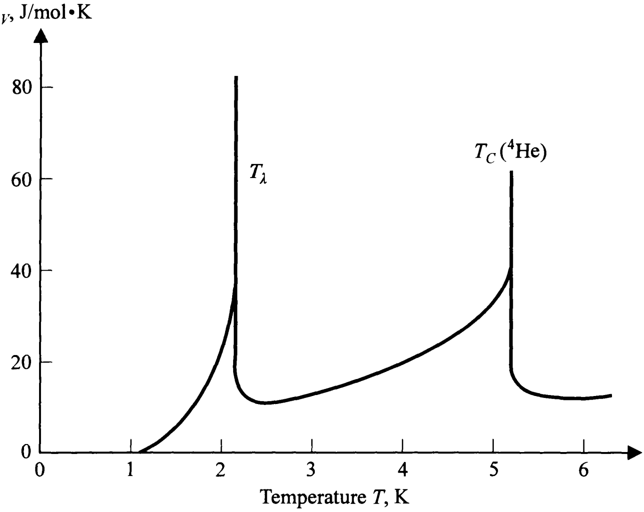


FIGURE 14-13
Molar specific heat at constant volume of ^{4}He as a function of temperature, showing the λ-transition and critical point. (M. R. Moldover and W. A. Little: *Physical Review Letters*, vol. 15, pp. 54–56, 1965.)

$$ds = \frac{c_P}{T}\,dT - v\beta\,dP,$$

or

$$\frac{c_P}{T} = \frac{ds}{dT} + v\beta\frac{dP}{dT}.$$

Since ds/dT and dP/dT are the same, respectively, as the slopes at the corresponding points on the curves where $T = T_\lambda$, we have

$$\frac{c_P}{T} = s'_\lambda + v\beta P'_\lambda. \tag{14.16}$$

This equation is true whether $T > T_\lambda$ or $T < T_\lambda$, and it shows that c_P/T should vary linearly with $v\beta$ as the transition is approached (either from above or below) with a slope equal to P'_λ. Using $T/T_\lambda - 1$ as a convenient parameter, experimental measurements of c_P and β, both as a function of $T/T_\lambda - 1$, when combined, should yield a linear relation between c_P/T and $v\beta$. Because it is not convenient to measure the c_P of liquid helium, the molar heat capacity at constant saturation vapor pressure c_{svp} is usually measured, and c_P is calculated from a simple relation that can be found in the problems at the end of this chapter. In the case of liquid helium, the correction is quite small.

The variation of c_{svp} (which is equivalent to c_P) of liquid helium II with $T/T_\lambda - 1$ is shown in Fig. 14-15, where the dependence on the logarithm of $T/T_\lambda - 1$, characteristic of λ-transitions, is displayed even down to $T/T_\lambda - 1 = 5 \times 10^{-8}$ K. The temperature dependence of the molar specific

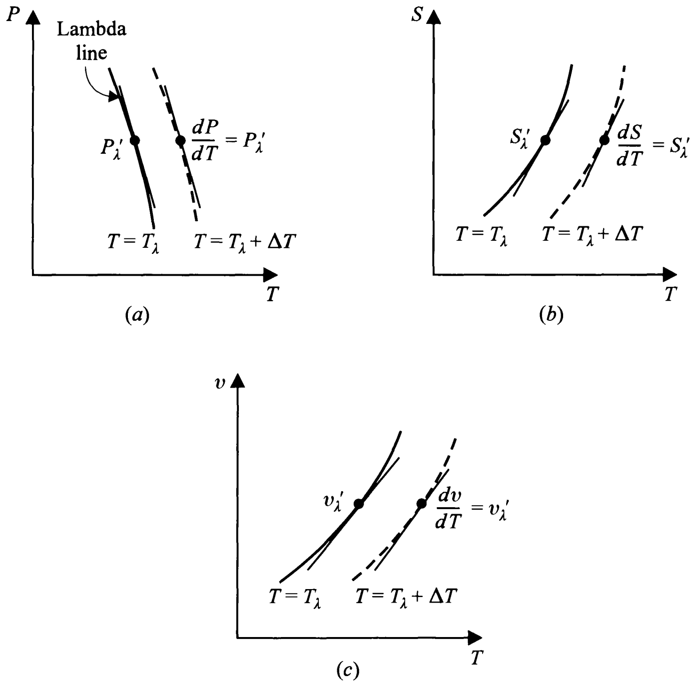


FIGURE 14-14
(*a*) A portion of the λ-line of ^{4}He on a phase diagram. (*b*) Molar entropy and (*c*) molar volume at points on the λ-line. The slope of a curve at a small temperature difference ΔT above (or below) the λ-line is the same as that at a corresponding point on the λ-line.

heat at saturated vapor pressure predicted by theory has the general form given by

$$c_P = B + (A/\alpha)\epsilon^{-\alpha}(1 - D\epsilon^{1/2}),$$

where $\epsilon = (T - T_\lambda)/T_\lambda$; α is the critical exponent for molar specific heat; and A, B, and D are constants. The constants can be evaluated from measurements in the range $10^{-8} \leq \epsilon \leq 10^{-3}$, which lead to the following:

$$c_P = 428.3 - 439.8\epsilon^{-0.014}(1 - 0.022\epsilon^{1/2})\ \mathrm{J/mol\cdot K}, \qquad \epsilon \to 0+; \qquad (14.17)$$

and

$$c_P = 427.7 - 415.6\epsilon^{-0.014}(1 - 0.020\epsilon^{1/2})\ \mathrm{J/mol\cdot K}, \qquad \epsilon \to 0- . \qquad (14.18)$$

Due to uncertainties in curve fitting, the initial constant B may be equal in the two equations.

At first sight, Eqs. (14.17) and (14.18) show no sign of the logarithmic behavior shown in Fig. 14-15, but, by expressing $\epsilon^{-\alpha}$ as $e^{(-\alpha \ln \epsilon)}$ and then expanding the function to first order, we obtain $\epsilon^{-\alpha} \approx 1 - \alpha \ln \epsilon$, provided that $|\alpha \ln \epsilon| \ll 1$. Since $\alpha = 0.014$, it follows that the approximation is valid

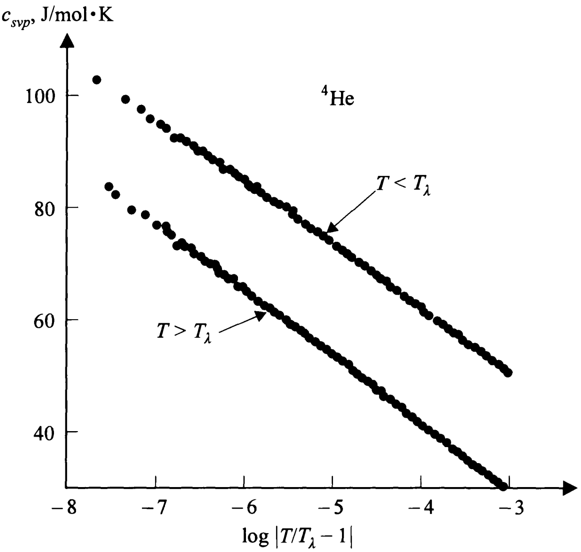


FIGURE 14-15
Molar specific heat at constant saturation vapor pressure c_{svp} of liquid He II vs. $\log|T/T_\lambda - 1|$. (J. A. Lipa and T. C. P. Chui: *Physical Review Letters*, vol. 51, pp. 2291–2294, 1983.)

over the temperature range shown in Fig. 14-15. The data approach to within 10^{-8} K of T_λ and still show logarithmic behavior. However, it is desirable to perform experiments in which an even closer approach in temperature to the λ-point occurs. In the approximation $c_P \approx 1 - \alpha \ln \epsilon$, $c_P \to \infty$ as $\epsilon \to 0$, while the slope $dc_P/d \log \epsilon$ remains finite. However, Eqs. (14.17) and (14.18) show that c_P has a finite maximum value of approximately 428 J/mol·K. In the temperature ranges thus far investigated, the experimental curves in Fig. 14-15 cannot be distinguished from logarithmic straight lines.

The logarithmic behavior for c_P is also seen in the volume expansivity β of liquid helium II as a function of $T/T_\lambda - 1$, as shown in Fig. 14-16, where the dependence on the logarithm of $T/T_\lambda - 1$, characteristic of λ-transitions, is displayed down to $T/T_\lambda - 1 = 10^{-4}$ K. The expected linear relation in Eq. (14-16) between c_P/T and $v\beta$ of liquid He II is shown in Fig. 14-17, even though c_P and β each display a logarithmic dependence on $T/T_\lambda - 1$. Some numerical values at three points on the λ-line are given in Table 14.4.

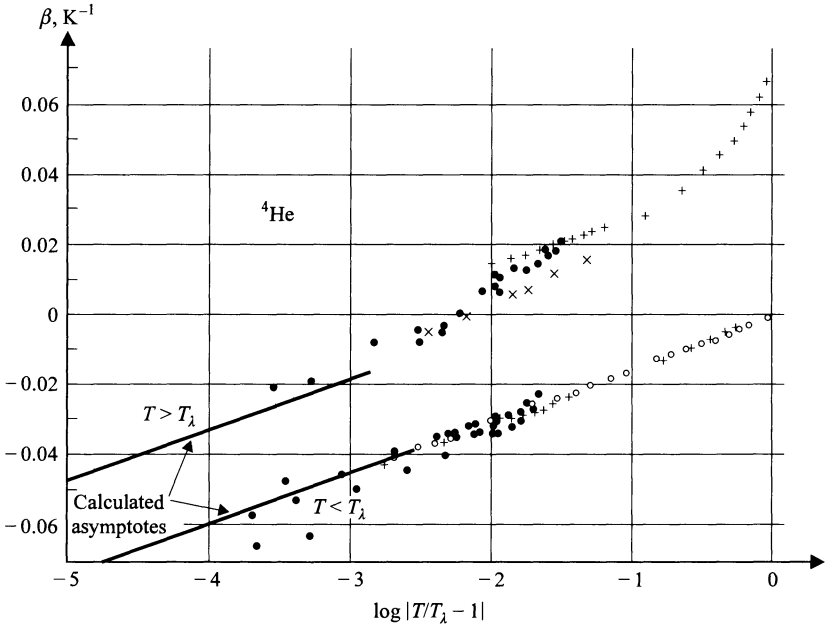


FIGURE 14-16

Volume expansivity β of liquid He II vs. $\log|T/T_\lambda - 1|$. (K. R. Atkins and M. H. Edwards: *Physical Review*, vol. 97, pp. 1429–1434, 1955; C. E. Chase, E. Maxwell, and W. E. Millett: *Physica*, vol. 27, pp. 1129–1145, 1961; E. C. Kerr and R. D. Taylor: *Annals of Physics*, vol. 26, pp. 292–306, 1964.)

14.6
LIQUID AND SOLID HELIUM

Any state in which the temperature and pressure of three phases of the same substance may coexist in equilibrium is a triple point. Water and many other substances have several triple points, but only one triple point refers to the equilibrium of solid, liquid, and vapor phases. Every material that has been studied has such a triple point, with the exception of helium. As the vapor of liquid ^{4}He is pumped away, the temperature of the remaining liquid decreases; and, at the λ-point, liquid helium II forms, so that the λ-point may be regarded as a triple point for liquid I, liquid II, and vapor, as shown on the phase diagram in Fig. 14-18.

The zero-point energy of liquid helium is about 210 J/mol, or about three times as large as the enthalpy of vaporization. If a crystal were to form, it would be unstable under its own vapor pressure; therefore, as the vapor above liquid helium is pumped away, helium remains a liquid down to the lowest temperatures yet achieved ($\sim 10^{-7}$ K). To produce solid helium, it is necessary to bring the helium atoms closer together, to the point where attractive forces

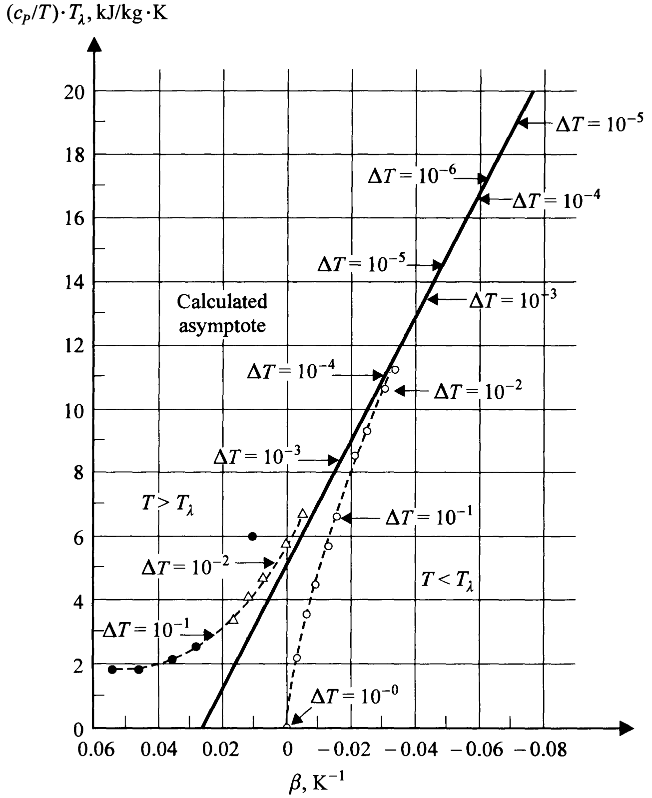


FIGURE 14-17
Straight-line relation between c_P/T and β of liquid He II; the molar volume v is essentially constant throughout the experiment.

TABLE 14.4
Quantities at three points on the λ-line of ^{4}He

P_λ, kPa	T_λ, K	ρ_λ, kg/m^3	$(dP/dT)_\lambda$, MPa/K	$(\partial v/\partial T)_\lambda$, 10^{-3}/mol·K	$(\partial s/\partial T)_\lambda$, kJ/mol·K
5.035	2.177	146.2	−11.25	51.5	10.9
1487	2.00	167	−7.1	11.0	3.8
3013	1.763	180.4	−5.58	5.3	2.7

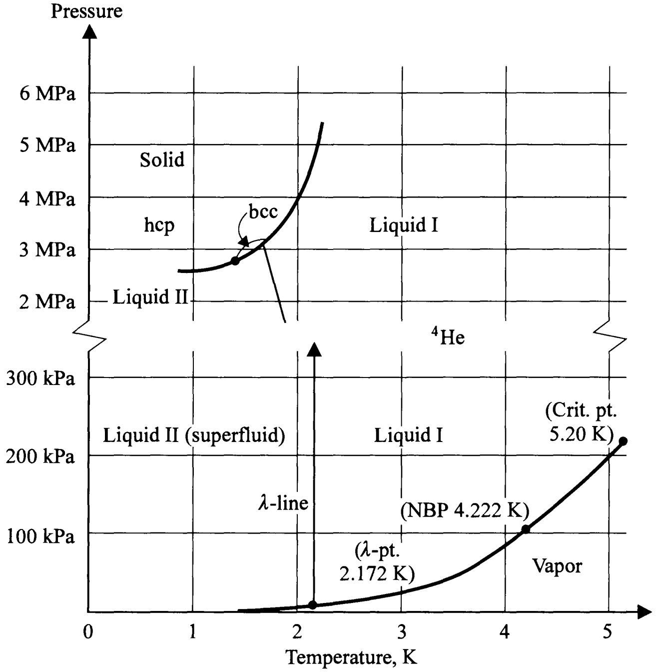


FIGURE 14-18
Phase diagram of ^{4}He.

may produce cohesion. This requires an increase of pressure above 25 atm, so that there is an *upper triple point* where two liquids and a solid may coexist in equilibrium. As a matter of fact, the phase diagram of Fig. 14-18 shows the presence of two different crystal structures for solid ^{4}He: hexagonal close-packed (abbreviated hcp) and body-centered cubic (abbreviated bcc).

About one part in a million of ^{4}He is the light isotope ^{3}He, the phase diagram of which is shown in Fig. 14-19. Three features are quite striking about Fig. 14-19(*a*):

1. The normal boiling point of ^{3}He (at which the vapor pressure is 101 kPa) is 3.2 K, so that by pumping the ^{3}He vapor away, temperatures may be produced that are lower than those obtainable with ^{4}He. Thus, by lowering the vapor pressure of ^{3}He to 3.2 Pa, a temperature of 0.4 K can be reached. To reach the same temperature with ^{4}He would require lowering the vapor pressure to 3.6×10^{-5} Pa, which is very difficult.
2. It *appears* that ^{3}He has no triple points at all, at least at temperatures above 0.1 K.
3. The melting curve, which is the locus of points representing temperatures and pressures at which solid and liquid ^{3}He are in equilibrium, *shows a minimum* at about 0.32 K.

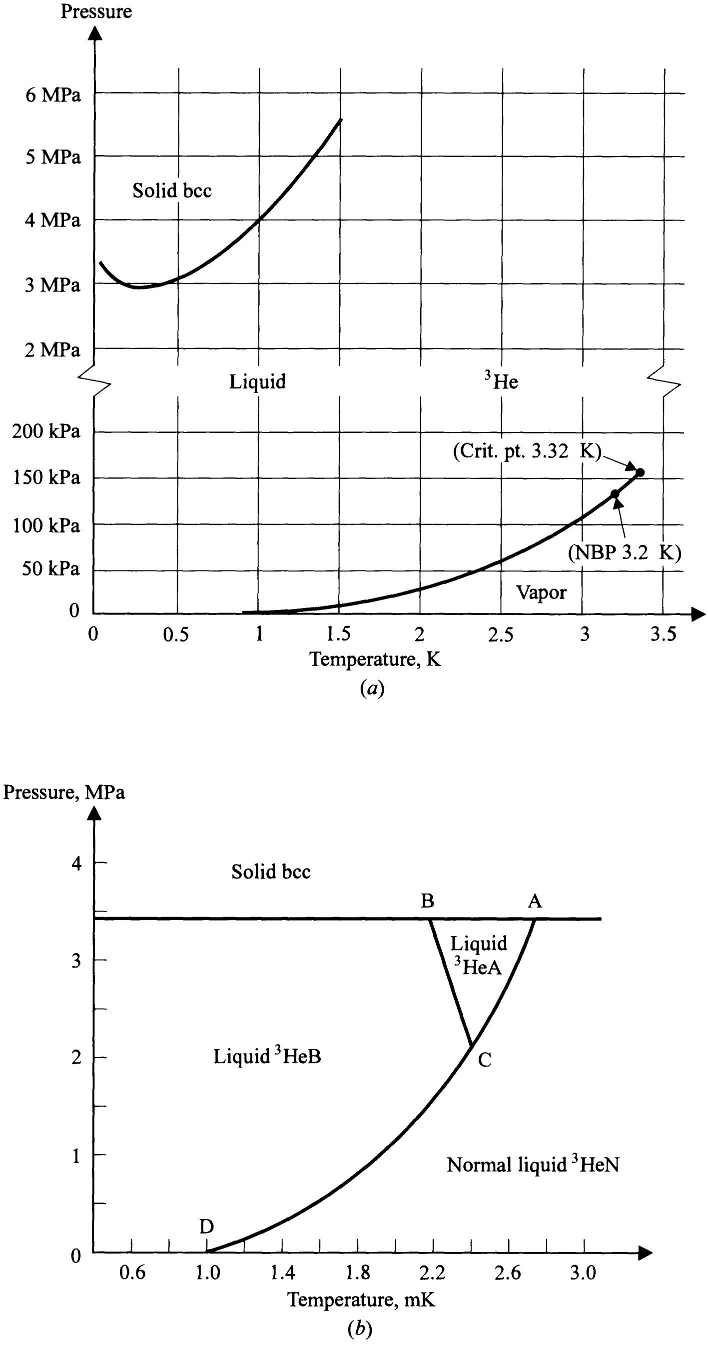


FIGURE 14-19

Phase diagram of ^{3}He in zero magnetic field: (*a*) high-temperature region showing fluid critical point and all three normal phases; (*b*) low-temperature region showing normal and superfluid phases.

Figure 14-19(*b*) shows the phase diagram of ^{3}He below 0.003 K in zero magnetic field, where two new liquid phases appear. The fusion curve of Fig. 14-19(*a*), which has a negative slope near absolute zero, appears to be isobaric at 3.44 MPa in Fig. 14-19(*b*). The points labeled A, B, C, and D identify curves separating phases of ^{3}He; in fact, A, B, and C are triple points. The curve ACD separates normal liquid ^{3}He at higher temperatures from superfluid liquid ^{3}He at lower temperatures. Curve ACD is analogous to the λ-line for ^{4}He shown in Fig. 14-18. In the case of ^{3}He, however, there are *two* superfluid phases, known as HeA and HeB. The curve BC separates HeA from HeB. The normal liquid phase of ^{3}He is written as HeN, while the normal liquid phase of ^{4}He is He I.

In the region of high pressures, from 10 to 500 MPa, other crystal structures form in both ^{4}He and ^{3}He, as shown in Fig. 14-20, where a face-centered cubic structure is abbreviated fcc. The molar heat capacity of these solids has been measured and found to obey Debye's T^3-law, with a Debye Θ depending both on T and on the molar volume v. The temperature dependence is such as to enable an extrapolation to be made to zero temperature, so that the volume

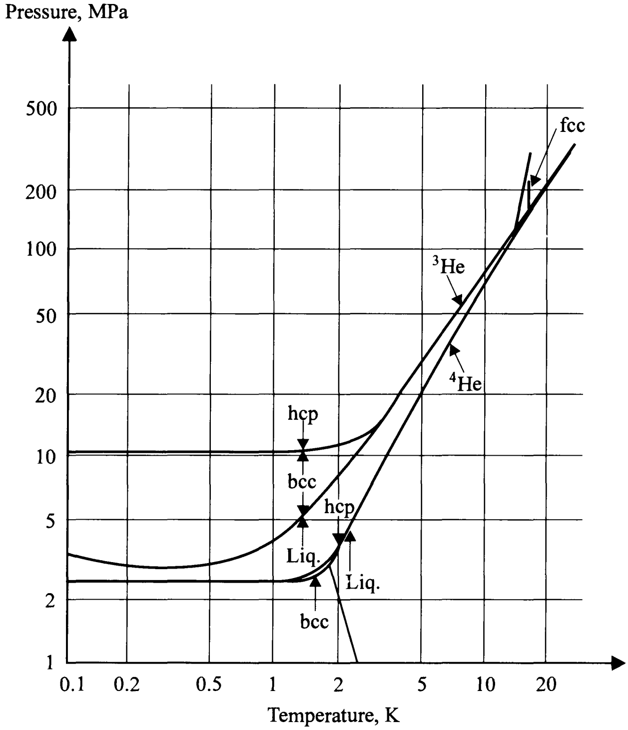


FIGURE 14-20
Phase diagrams for ^{4}He and ^{3}He at high pressures. (D. A. Young: *Phase Diagrams of the Elements*, University of California Press, Berkeley, Calif., 1991.)

dependence of Θ_0 can be studied. This is shown in Fig. 14-21, and the curves have a twofold purpose:

1. By using the result of Prob. 13.2, namely, that the zero-point energy of a crystal is $\frac{9}{8}R\Theta_0$, one can calculate the zero-point energy of solid helium and compare it with that of liquid helium. At $\Theta_0 = 30\,\mathrm{K}$, $\frac{9}{8}R\Theta_0 \approx 270\,\mathrm{J/mol}$; and at $\Theta_0 = 110\,\mathrm{K}$, $\frac{9}{8}R\Theta_0 \approx 1000\,\mathrm{J/mol}$. Both of these extreme values *exceed* the zero-point energy of the liquid.
2. By using the result of Prob. 13.5, namely, that the Grüneisen Γ is given by

$$\Gamma = -\frac{d\ln\Theta_0}{d\ln v}$$

in conjunction with the curves in Fig. 14-21, the result is obtained that $\Gamma \sim 2.5$.

The transition between the solid and liquid phases of ^{4}He and of ^{3}He is particularly interesting. The enthalpy of fusion $h'' - h'$ (latent heat l_F) may be calculated from experimental values of $v'' - v'$ and of dP/dT, using the Clausius-Clapeyron equation. The results of such calculations by Simon and Swenson on ^{4}He and by Dugdale and Simon on ^{3}He are shown in Fig. 14-22. Notice that, in both cases, the latent heat becomes practically zero at low

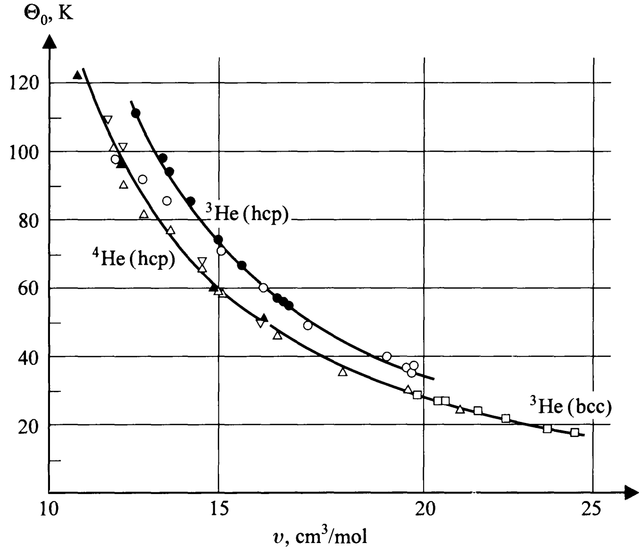


FIGURE 14-21
Debye Θ_0 as a function of molar volume for solid ^{4}He and ^{3}He. (E. C. Heltemes and C. A. Swenson: *Physical Review*, vol. 128, pp. 1512–1519, 1962; J. S. Dugdale and J. P. Franck: *Philosophical Transactions of the Royal Society*, vol. 257, pp. 1–29, 1965.)

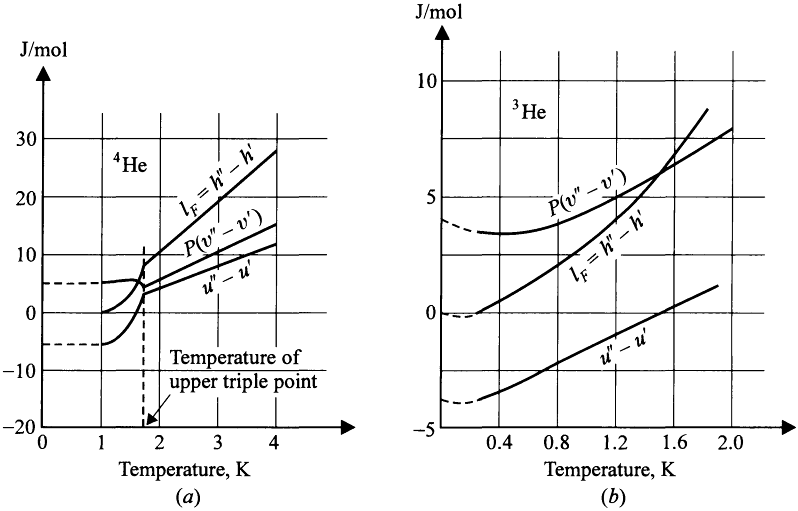


FIGURE 14-22
Energy relations for liquid and solid helium calculated with the aid of the Clausius-Clapeyron equation and the first law of thermodynamics: (*a*) ^{4}He. (F. E. Simon and C. A. Swenson: *Nature*, vol. 165, pp. 829–831, 1950.) (*b*) ^{3}He. (J. S. Dugdale and F. E. Simon: *Proceedings of the Royal Society (London)*, ser. A, vol. 218, pp. 291–310, 1953.)

temperatures, whereas $P(v'' - v')$ does not. As a result, the energy difference $u'' - u' = (h'' - h') - P(v'' - v')$ becomes negative, indicating that *the energy of solid helium is greater than that of liquid helium* at the same temperature. The melting of solid helium at such temperatures is a purely mechanical process, since there is practically no latent heat in this temperature region. An isothermal reduction in pressure produces melting; conversely, an isothermal increase of pressure produces solidification. Another interesting characteristic of solid helium is that its compressibility is greater than that of liquid helium.

PROBLEMS

14.1. A substance experiences a phase transition at the temperatures and pressures indicated by the points on the curves in Fig. 14-14, parts (*a*), (*b*), and (*c*). Choose any point where the slope is $(dP/dT)_\lambda$ in part (*a*), $(ds/dT)_\lambda$ in part (*b*), and $(dv/dT)_\lambda$ in part (*c*). *Near* this point, where $T = T_\lambda + \Delta T$, show that:

$$\frac{c_V}{T} = \left(\frac{ds}{dT}\right)_\lambda - \frac{\beta}{\kappa}\left(\frac{dv}{dT}\right)_\lambda,$$

and

$$\beta = \frac{1}{v}\left(\frac{dv}{dT}\right)_\lambda - \kappa\left(\frac{dP}{dT}\right)_\lambda.$$

14.2. In a second-order phase transition, $s^{(i)} = s^{(f)}$ at (T, P), and $s^{(i)} + ds^{(i)} = s^{(f)} + ds^{(f)}$ at $(T + dT, P + dP)$.

(*a*) Prove that

$$\frac{dP}{dT} = \frac{1}{Tv}\frac{c_P^{(f)} - c_P^{(i)}}{\beta^{(f)} - \beta^{(i)}}$$

In a second-order phase transition, $v^{(i)} = v^{(f)}$ at (T, P), and $v^{(i)} + dv^{(i)} = v^{(f)} + dv^{(f)}$ at $(T + dT, P + dP)$.

(*b*) Prove that

$$\frac{dP}{dT} = \frac{\beta^{(f)} - \beta^{(i)}}{\kappa^{(f)} - \beta^{(i)}}.$$

(*Note*: These are *Ehrenfest's equations.*)

14.3. For a two-phase system in equilibrium, P is a function of T only; therefore,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_S = \frac{dP}{dT}.$$

For such a system show that

$$\frac{C_V}{\kappa_S} = TV\left(\frac{dP}{dT}\right)^2,$$

regardless of the type of transition between the phases.

14.4. Using the van der Waals equation of state expressed in "reduced variables," namely,

$$\left(P_R + \frac{3}{v_R^2}\right)\left(v_R - \frac{1}{3}\right) = \tfrac{8}{3}T_R,$$

where $P_R = P/P_C$, $v_R = v/v_C$, and $T_R = T/T_C$, calculate values for the following critical-point exponents: (*a*) δ; (*b*) γ. From the molar internal energy for the van der Waals gas, given by

$$u = cT - \frac{a}{V},$$

(*c*) calculate the critical-point exponent α.

CHAPTER 15

Chemical Equilibrium

15.1
DALTON'S LAW

Imagine a homogeneous mixture of inert ideal gases at a temperature T, a pressure P, and a volume V. Suppose that there are c chemical constituents: n_1 moles of gas B_1, n_2 moles of gas $B_2, \cdots$, up to n_c moles of gas B_c. Since there is no chemical reaction, the mixture is in a state of equilibrium with the equation of state

$$PV = (n_1 + n_2 + \cdots + n_c)RT,$$

or

$$P = \frac{n_1}{V}RT + \frac{n_2}{V}RT + \cdots + \frac{n_c}{V}RT.$$

It is clear that the expression

$$\frac{n_j}{V}RT$$

represents the pressure that the jth constituent of the mixture of gases would exert if it occupied the volume V alone. This is called the *partial pressure* of the jth gas and is denoted by p_j. Thus,

$$p_1 = \frac{n_1}{V}RT, \qquad p_2 = \frac{n_2}{V}RT, \qquad \cdots, \qquad p_c = \frac{n_c}{V}RT,$$

and

$$P = p_1 + p_2 + \cdots + p_c. \tag{15.1}$$

Equation (15.1) expresses the fact that the total pressure of a mixture of inert ideal gases is equal to the sum of the partial pressures. This is *Dalton's law.*

Now,
$$V = (n_1 + n_2 + \cdots + n_c)\frac{RT}{P}$$
$$= \sum n_j \frac{RT}{P},$$

and the partial pressure of the *j*th gas is

$$p_j = \frac{n_j}{V} RT.$$

Substituting the value for V, we get

$$p_j = \frac{n_j}{\sum n_j} P.$$

The ratio $n_j / \sum n_j$ is called the *mole fraction* of the *j*th gas and is denoted by x_j. Thus,

$$x_1 = \frac{n_1}{\sum n_j}, \qquad x_2 = \frac{n_2}{\sum n_j}, \qquad \cdots, \qquad x_c = \frac{n_c}{\sum n_j},$$

and
$$p_1 = x_1 P, \qquad p_2 = x_2 P, \qquad \cdots, \qquad p_c = x_c P.$$

The mole fractions are convenient dimensionless quantities with which to express the composition of a mixture. It is clear that

$$x_1 + x_2 + \cdots + x_c = \frac{n_1}{\sum n_j} + \frac{n_2}{\sum n_j} + \cdots + \frac{n_c}{\sum n_j}$$
$$= 1.$$

Hence, if all but one mole fraction is determined, then the last mole fraction can be calculated from the preceding equation.

15.2
SEMIPERMEABLE MEMBRANE

When a narrow tube of palladium is closed at one end and the open end is sealed into a glass tube, as shown in Fig. 15-1, the system may be pumped to a very low pressure. While the palladium remains at room temperature, the pressure can be maintained indefinitely. If, however, an ordinary bunsen burner is placed so that the blue cone surrounds part of the tube, with the rest of the flame causing the palladium tube to become red-hot, then hydrogen gas present in the blue cone will pass through the tube, but other gases will not. Red-hot palladium is said to be a *semipermeable membrane*, permeable to hydrogen only. This is the simplest laboratory method of obtaining pure dry hydrogen.

Experiment shows that hydrogen continues to flow through the red-hot palladium until the pressure of hydrogen in the vessel reaches a value equal to the partial pressure of the hydrogen in the flame. When the flow stops, *membrane equilibrium* is said to exist. Membrane equilibrium is achieved when the

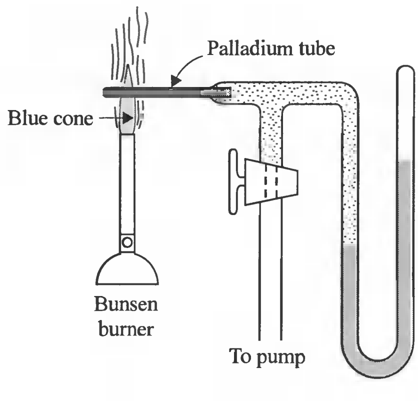


FIGURE 15-1
Palladium tube permeable to hydrogen.

partial pressure of the gas to which the membrane is permeable is the same on both sides of the membrane. We shall suppose that there exists a special membrane permeable to each gas with which we have to deal. Whether this is actually so is not important. We shall make use of the principle of the semipermeable membrane as an ideal device for theoretical purposes.

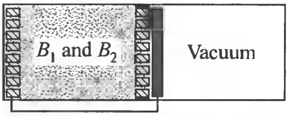
15.3
GIBBS' THEOREM

With the aid of a device equipped with two semipermeable membranes, it is possible to conceive of separating, in a reversible manner, a mixture of two inert ideal gases. The vessel depicted in Fig. 15-2 is divided into two equal compartments by a rigid wall, which is a membrane permeable only to the gas B_1. Two pistons coupled so that they move together at a constant distance apart are constructed of materials such that the right-hand piston is impermeable to all gases, and the left-hand piston is permeable only to the gas B_2. The initial state is depicted in Fig. 15-2(*a*). A mixture of B_1 and B_2 is in the left-hand chamber, and the right-hand chamber is evacuated.

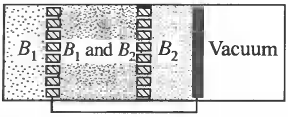
Now, imagine pushing the coupled pistons to the right in such a manner that the following conditions are satisfied:

1. The motion is infinitely slow, so that membrane equilibrium exists at all times.
2. There is no friction.
3. The whole system is kept at constant temperature.

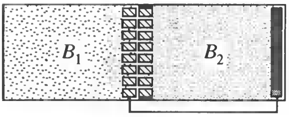
These conditions define a *reversible isothermal process*. Consider the system at any intermediate state such as that depicted in Fig. 15-2(*b*). If p_1 and p_2 are the partial pressures, respectively, of B_1 and B_2 in the mixture, P_1 is the pressure of B_1 alone, and P_2 is the pressure of B_2 alone, then the forces acting on the coupled pistons are the following:



(*a*) Initial equilibrium state (designated *i*)



(*b*) Intermediate equilibrium state



(*c*) Final equilibrium state (designated *f*)

FIGURE 15-2
Reversible isothermal separation of two inert ideal gases.

$$\text{Force to the left} = (p_1 + p_2) \times \text{area of piston},$$

and $$\text{Sum of the forces to the right} = (P_1 + P_2) \times \text{area of piston}.$$

Since membrane equilibrium exists, $p_1 = P_1$ and $p_2 = P_2$; hence, the resultant force acting on the coupled pistons is zero. After the pistons have moved all the way to the right, the gases are completely separated as shown in Fig. 15-2(*c*).

Since the resultant force was infinitesimal in the beginning and zero throughout the remainder of the process, $W = 0$. Also, since the process was isothermal and the internal energy of an ideal gas is a function of T only, $U_f = U_i$. Finally, since the process was both reversible and isothermal, the heat transferred Q is equal to $T(S_f - S_i)$. We have, therefore, the result that

$$T(S_f - S_i) = 0,$$

and, since T is not zero,

$$S_i = S_f.$$

Now, S_i is the entropy of the mixture at the temperature T and the volume V, while S_f is the sum of the entropies of the two gases, each at the same temperature and each occupying the volume V alone. If we define the *partial entropy* of one of the gases of a mixture as the entropy that the gas would have if it occupied the whole volume alone at the same temperature, then we obtain the result that the *entropy of a mixture of ideal gases is the sum of the partial entropies*. This is known as *Gibbs' theorem*. The generalization for any number of gases is obvious.

15.4
ENTROPY OF A MIXTURE OF INERT IDEAL GASES

Imagine a number of inert ideal gases separated from one another by suitable partitions, all the gases being at the same temperature T and pressure P. Suppose, again, that there are c chemical constituents: n_1 moles of gas B_1, n_2 moles of gas $B_2, \cdots$, up to n_c moles of gas B_c. Before the partitions are removed, the entropy of the whole system S_i is the sum of the separate entropies. The entropy of 1 mol of the jth constituent of the mixture of gases at temperature T and pressure P is

$$s_j = \int c_{P_j} \frac{dT}{T} + s_{0_j} - R \ln P;$$

therefore,

$$S_i = \sum n_j \left(\int c_{P_j} \frac{dT}{T} + s_{0_j} - R \ln P \right)$$

$$= R \sum n_j \left(\frac{1}{R} \int c_{P_j} \frac{dT}{T} + \frac{s_{0_j}}{R} - \ln P \right).$$

It is convenient to represent the first two terms within the parentheses by σ, thus:

$$\sigma_j = \frac{1}{R} \int c_{P_j} \frac{dT}{T} + \frac{s_{0_j}}{R}. \tag{15.2}$$

Then,

$$S_i = R \sum n_j (\sigma_j - \ln P). \tag{15.3}$$

After the partitions are removed, the temperature and pressure remain the same because there is no chemical reaction, but the gases diffuse and, by Gibbs' theorem, the entropy of the mixture is the sum of the partial entropies. The partial entropy of the jth gas is the entropy that the jth gas would have if it occupied the whole volume alone at the same temperature, in which case it would exert a pressure equal to the partial pressure p_j. Therefore, the total entropy of the mixture is

$$S_f = R \sum n_j (\sigma_j - \ln p_j).$$

Since $p_j = x_j P$,

$$S_f = R \sum n_j (\sigma_j - \ln P - \ln x_j); \tag{15.4}$$

therefore, the change of entropy due to the diffusion of any number of inert gases is equal to

$$\boxed{S_f - S_i = -R \sum n_j \ln x_j.} \tag{15.5}$$

Each of the mole fractions is a number less than unity with a negative logarithm. Therefore, the whole expression is positive, as it should be. Since

$$x_j = \frac{n_j}{\sum n_j} = \frac{n_j RT}{\sum n_j RT} = \frac{n_j P v}{PV} = \frac{n_j v}{V},$$

we may write

$$S_f - S_i = n_1 R \ln \frac{V}{n_1 v} + n_2 R \ln \frac{V}{n_2 v} + \cdots.$$

The foregoing result shows that the entropy change due to the diffusion of any number of ideal gases is the same as that which would take place if each gas were caused to undergo a free expansion from the volume that it occupies alone at T and P to the volume of the mixture at the same T and P. The validity of this result was assumed in Chap. 8 in order to calculate the entropy change of the universe when two ideal gases diffuse. The assumption is, therefore, seen to be justified.

As an example, consider the diffusion of 1 mol of helium and 1 mol of neon. Then, from Eq. (15.5)

$$\begin{aligned} S_f - S_i &= -R(1 \ln \tfrac{1}{2} + 1 \ln \tfrac{1}{2}) \\ &= 2R \ln 2. \end{aligned}$$

In this expression, there are no quantities such as heat capacities or entropy constants that distinguish one gas from another. The result is the same for the diffusion of any two inert ideal gases, no matter how similar or dissimilar they are. If the two gases are identical, however, then the concept of diffusion has no meaning, and there is no change of entropy. From the microscopic point of view, this result means that the diffusion of any two dissimilar gases brings about the same degree of disorder, whereas the diffusion of two identical gases introduces no element of disorder.

The application of mathematics to the macroscopic processes of nature usually gives rise to continuous results. Our experience suggests that, as the two diffusing gases become more and more alike, the entropy change due to diffusion should get smaller and smaller, approaching zero as the gases become identical. The fact that this is not the case is known as *Gibbs' paradox.* The paradox has been resolved by P. W. Bridgman in the following way. To recognize that two gases are dissimilar requires a set of experimental operations. These operations become more and more difficult as the gases become more and more alike; but, at least in principle, the operations are possible. In the limit, when the gases become identical, there is a discontinuity in the instrumental operations inasmuch as no instrumental operation exists by which the gases may be distinguished. Hence, a discontinuity in a function, such as that of an entropy change, is to be expected.

15.5
GIBBS FUNCTION OF A MIXTURE OF INERT IDEAL GASES

The enthalpy and the entropy of 1 mol of an ideal gas at temperature T and pressure P are, respectively,

$$h = h_0 + \int c_P \, dT,$$

and

$$s = \int c_P \frac{dT}{T} + s_0 - R \ln P;$$

therefore, the molar Gibbs function $g = h - Ts$ is equal to

$$g = h_0 + \int c_P \, dT - T \int c_P \frac{dT}{T} - Ts_0 + RT \ln P.$$

Applying the formula for integration by parts,

$$\int c_P \, dT - T \int c_P \frac{dT}{T} = -T \int \frac{\int c_P \, dT}{T^2} dT,$$

we get

$$\begin{aligned} g &= h_0 - T \int \frac{\int c_P \, dT}{T^2} dT - Ts_0 + RT \ln P \\ &= RT\left(\frac{h_0}{RT} - \frac{1}{R}\int \frac{\int c_P \, dT}{T^2} dT - \frac{s_0}{R} + \ln P\right). \end{aligned}$$

It is convenient to denote the first three terms within the parentheses by ϕ, thus:

$$\phi = \frac{h_0}{RT} - \frac{1}{R}\int \frac{\int c_P \, dT}{T^2} dT - \frac{s_0}{R}. \tag{15.6}$$

The molar Gibbs function of an ideal gas may, therefore, be written as

$$\boxed{g = RT(\phi + \ln P),} \tag{15.7}$$

where ϕ is a function of T only.

Consider a number of inert ideal gases separated from one another, all at the same T and P. Suppose, again, that there are c chemical constituents: n_1 moles of gas B_1, n_2 moles of gas $B_2, \cdots$, up to n_c moles of gas B_c. Before the gases are mixed, the Gibbs function of the system G is the sum of the separate Gibbs functions, or the initial Gibbs function G_i is

$$\begin{aligned} G_i &= \sum n_j g_j \\ &= RT \sum n_j(\phi_j + \ln P), \end{aligned}$$

where the summation extends from $j = 1$ to $j = c$. To express the Gibbs function after mixing G_f, it is necessary merely to replace the total pressure P by the partial pressure p_j, because all the gases are at the same pressure before and after mixing. Thus,

$$\begin{aligned} G_f &= RT\sum n_j(\phi_j + \ln p_j) \\ &= RT\sum n_j(\phi_j + \ln P + \ln x_j). \end{aligned}$$

Therefore,

$$G_f - G_i = RT\sum n_j \ln x_j,$$

where the expression on the right is a negative quantity. It is seen, therefore, that the Gibbs function after diffusion is less than the Gibbs function before diffusion. This will be shown later to be an expression of a general law that holds for all irreversible processes which take place at constant T and P.

We have shown that the Gibbs function of a mixture of inert ideal gases at temperature T and pressure P is

$$\boxed{G = RT\sum n_j(\phi_j + \ln P + \ln x_j),} \tag{15.8}$$

where ϕ_j is given by Eq. (15.6).

15.6
CHEMICAL EQUILIBRIUM

Consider a homogeneous mixture of 1 mol of hydrogen and 1 mol of oxygen at room temperature and at atmospheric pressure. It is a well-known fact that this mixture will remain indefinitely at the same temperature, pressure, and composition. The most careful measurements over a long period of time will disclose no appreciable spontaneous change of state. One might be inclined to deduce from this that such a mixture represents a system in a state of thermodynamic equilibrium. However, this is not the case. If a small piece of platinum-coated asbestos is introduced or if an electric spark is created across two electrodes, then an explosion takes place involving a sudden change in the temperature, the pressure, and the composition. If, at the end of the explosion, the system is brought back to the same temperature and pressure, then it will be found that the composition is now $\frac{1}{2}$ mol of oxygen, no measurable amount of hydrogen, and 1 mol of water vapor.

The piece of material, such as platinum-coated asbestos, by whose agency a chemical reaction is started, is known as a *catalyst*. If chemical combination is started in a mixture of 1 mol of hydrogen and 1 mol of oxygen with different amounts and different kinds of catalysts, and if the final composition of the mixture is measured in each case, then it is found that: (1) the final composition does not depend on the amount of catalyst used; (2) the final composition does not depend on the kind of catalyst used; and (3) the catalyst itself is the same at the end of the reaction as at the beginning. These results lead us to the following conclusions:

1. The initial state of the mixture is a state of mechanical and thermal equilibrium, but not of chemical equilibrium.
2. The final state is a state of thermodynamic equilibrium.
3. The transition from the initial nonequilibrium state to the final equilibrium state is accompanied by a chemical reaction that is too slow to be measured when it takes place spontaneously. Through the agency of the catalyst, the reaction is caused to take place more rapidly.

Imagine a vessel divided into two compartments by a removable partition, as shown in Fig. 15-3(*a*). Suppose that one compartment contains a dilute solution of sodium chloride and water maintained at standard atmospheric pressure and at a temperature of 298 K — the mole fraction of the salt being, say, 0.01. Under these conditions, the solution is in thermodynamic equilibrium. Suppose that the other compartment contains solid salt in equilibrium, also at standard atmospheric pressure and a temperature of 298 K. Now, imagine that the partition is removed, as shown in Fig. 15-3(*b*), and that the pressure and temperature of the whole system are kept constant at the original values. Experiment shows that some solid salt dissolves; that is, the mole fraction of the salt in the solution increases spontaneously at constant pressure and temperature. After a while, the change ceases and the mole fraction is found to be about 0.1.

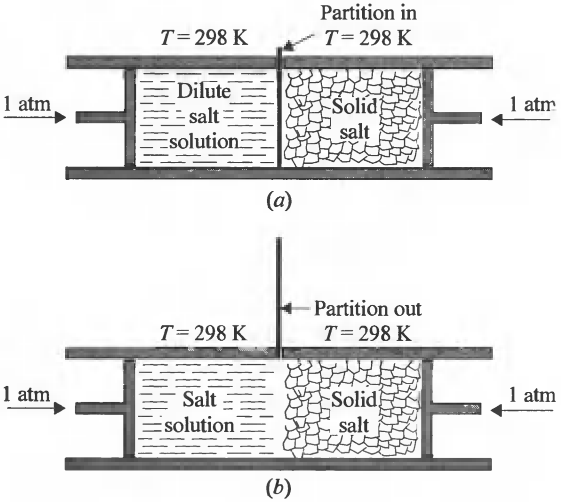


FIGURE 15-3
Transport of matter across the boundary between two phases.

Focusing our attention on the solution from the moment it was put in contact with the solid salt, we are led to the following conclusions:

1. The initial state of the solution (at the moment it was put in contact with the solid salt) is one of mechanical and thermal equilibrium, but not of chemical equilibrium.
2. The final state of the solution is a state of thermodynamic equilibrium.
3. The transition from the initial nonequilibrium state to the final equilibrium state is accompanied by a transport of a chemical constituent into the solution.

15.7

THERMODYNAMIC DESCRIPTION OF NONEQUILIBRIUM STATES

A *phase* is defined as a system or a portion of a system composed of any number of chemical constituents satisfying the requirements: (1) that it is homogeneous and (2) that it has a definite boundary. The hydrogen–oxygen mixture described in Sec. 15.6 is a gaseous phase of two chemical constituents and of constant mass. The salt solution is a liquid phase of two chemical constituents whose mass, when in contact with the solid-salt phase, is variable. Although the initial states of both these phases are nonequilibrium states, it is possible to describe them in terms of thermodynamic coordinates. Since each phase is in mechanical and thermal equilibrium, a definite P and T may be assigned to each; since each has a definite boundary, each has a definite volume; and, since each is homogeneous, the composition of each phase may be described by specifying the number of moles of each constituent. In general, a phase consisting of c chemical constituents in mechanical and thermal equilibrium may be described with the aid of the thermodynamic coordinates P, V, T, n_1, n_2, $\cdots$, n_c.

Under a given set of conditions, a phase may undergo a change of state in which some or all of these coordinates change. While this change is occurring, the phase passes through states not in thermodynamic equilibrium, but in mechanical and thermal equilibrium only. These states are connected by an equation of state that is a relation among P, V, T, and the n_j's. Whether a phase is in chemical equilibrium or not, it has a definite energy. Since we wish to restrict ourselves to an energy formulation with P, V, T, and n_j as the independent, easily measured, thermodynamic variables, it is appropriate to consider either the Helmholtz function $A(V, T, n)$ or Gibbs function $G(P, T, n)$, given in differential form in Eqs. (11.23) and (11.24), respectively, for a single substance.

During a change of state, the n_j's, which determine the composition of the phase, change either because of a chemical reaction or because of a transport of matter across the boundaries between phases, or both.[†] In general, under given conditions, there is a set of values of the n_j's for which the phase is in chemical and, therefore, thermodynamic equilibrium. The functions that express the properties of a phase when it is not in chemical equilibrium must obviously reduce to those for thermodynamic equilibrium when the equilibrium values of the n_j's are substituted. We are, therefore, led to assume that *any property of a phase in mechanical and thermal equilibrium can be represented by a function of any two of P, V, T, and the* n_j*'s of the same form as that used to denote the same property when the phase is in thermodynamic equilibrium.*

Consider, for example, a phase consisting of a mixture of ideal gases. When the gases are inert, the equation of state is

$$PV = \sum n_j RT,$$

the entropy is

$$S = R \sum n_j (\sigma_j - \ln P - \ln x_j),$$

and the Gibbs function is

$$G = RT \sum n_j (\phi_j + \ln P + \ln x_j).$$

According to the assumption just made, these same equations may be used in connection with an ideal-gas phase in mechanical and thermal equilibrium when the gases are chemically active, when the phase is in contact with other phases, or under both conditions, whether chemical equilibrium exists or not. Under these conditions, the n_j's and x_j's are variables. Whether the n_j's and x_j's are all independent variables or not is a question that cannot be answered until the conditions under which a change of state takes place are specified. It is clear that, if the mass of the phase remains constant and the gases are inert, then the n_j's and x_j's are constants. If the mass of the phase remains constant and the gases are chemically active, then it will be shown that each n_j (and, therefore, each x_j) is a function of only one independent variable, the degree of reaction. If the mass of the phase is variable, then the number of n_j's that are independent depends on the number of other phases in contact with the original phase and on the chemical constituents of these other phases.

A system composed of two or more phases is called a *heterogeneous system.* Any extensive property, such as V, U, S, H, A, or G of any one of the phases, may be expressed as a function of thermodynamic coordinates, say, T, P, and the n's of that phase. Thus, for the Gibbs function of the first phase,

---

[†] During a chemical reaction, the system is no longer closed, but *open* to a change in the number of moles of each constituent. Sections 11.6 and 11.7 considered a change of state due to transport of matter, rather than a chemical reaction.

$$G^{(1)} = \text{function of } (T, P, n_1^{(1)}, n_2^{(1)}, \cdots);$$

for the second phase,

$$G^{(2)} = \text{function of } (T, P, n_1^{(2)}, n_2^{(2)}, \cdots);$$

and so on. The Gibbs function of the whole heterogeneous system $\boldsymbol{G}$ is, therefore,

$$\boldsymbol{G} = G^{(1)} + G^{(2)} + \cdots.$$

This result holds for any extensive property of a heterogeneous system.

15.8
CONDITIONS FOR CHEMICAL EQUILIBRIUM

Consider any hydrostatic system of constant mass, either homogeneous or heterogeneous, in mechanical and thermal equilibrium, but not in chemical equilibrium. Suppose that the system is in contact with a reservoir at temperature T and undergoes an infinitesimal irreversible process involving an exchange of heat $đQ$ from the reservoir. The process may involve a chemical reaction or a transport of matter between phases, or both. Let dS denote the entropy change of the system and dS_0 the entropy change of the reservoir. The total entropy change of the universe is, therefore, $dS_0 + dS$; and, since the performance of an irreversible process is attended by an increase in the entropy of the universe, we may write

$$dS_0 + dS > 0.$$

Since $$dS_0 = -\frac{đQ}{T},$$

we have $$-\frac{đQ}{T} + dS > 0,$$

or $$đQ - T\,dS < 0.$$

During the infinitesimal irreversible process, the internal energy of the system changes by an amount dU, and an amount of work $P\,dV$ is performed. The first law for a hydrostatic system can, therefore, be written in its usual form,

$$đQ = dU + P\,dV,$$

and the inequality becomes

$$\boxed{dU + P\,dV - T\,dS < 0.} \tag{15.9}$$

This inequality holds during any infinitesimal portion and, therefore, during all infinitesimal portions of the irreversible process. According to the assumption made in the preceding section, U, V, and S may all be regarded as functions of thermodynamic coordinates.

During the irreversible process for which the inequality in Eq. (15.9) holds, some, or all, of the coordinates may change. If we restrict the irreversible process by imposing the condition that two of the thermodynamic coordinates remain constant, then the inequality can be reduced to a simpler form. Suppose, for example, that the internal energy and the volume remain constant. Then, the inequality reduces to $dS > 0$, which means that the entropy of a system at constant U and V increases during an irreversible process, approaching a maximum at the final state of equilibrium. This result, however, is obvious from the second law, since a system at constant U and V is isolated and is, therefore, so to speak, its own universe. The two most important sets of conditions for chemical equilibrium are the following:

1. *If T and V are constant*, then the inequality reduces to

$$d(U - TS) < 0,$$

or

$$dA < 0, \tag{15.10}$$

expressing the result that *the Helmholtz function A of a system at constant T and V decreases during an irreversible process* and becomes a minimum at the final equilibrium state.

2. *If T and P are constant*, then the inequality reduces to

$$d(U + PV - TS) < 0,$$

or

$$dG < 0, \tag{15.11}$$

expressing the result that *the Gibbs function G of a system at constant T and P decreases during an irreversible process* and becomes a minimum at the final equilibrium state.

The student will recall that the condition for equilibrium of a conservative mechanical system is that the potential energy shall be a minimum. The Helmholtz and Gibbs functions, therefore, are seen to play a similar role in thermodynamics. For this reason, J. W. Gibbs called the function A the *thermodynamic potential at constant volume* and the function G the *thermodynamic potential at constant pressure.*

15.9
CONDITION FOR MECHANICAL STABILITY

In discussing the important equation

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

in Sec. 10.8, the remark was made that $(\partial P/\partial V)_T$ is always negative. This will now be proved for any system of constant mass. Consider the system depicted symbolically in Fig. 15-4. At first, each half of the system is in equilibrium as well as the entire system. Suppose, now, that the left half is compressed by an amount δV and the right half is expanded by the same amount, with each half remaining at constant temperature and the *total* volume remaining constant.

The Helmholtz function A_L of the left half may now be expanded in a Taylor series about its equilibrium value $A_{\min}/2$ as follows:

$$A_L = \frac{A_{\min}}{2} - \left(\frac{\partial A_L}{\partial V}\right)_T \delta V + \tfrac{1}{2}\left(\frac{\partial^2 A_L}{\partial V^2}\right)_T (\delta V)^2 - \cdots,$$

which may be terminated after the squared term if δV is small enough. But, there is no difference between the behavior of half the system and that of the whole system, that is

$$\left(\frac{\partial A_L}{\partial V}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T.$$

Hence,
$$A_L = \frac{A_{\min}}{2} - \left(\frac{\partial A}{\partial V}\right)_T \delta V + \tfrac{1}{2}\left(\frac{\partial^2 A}{\partial V^2}\right)_T (\delta V)^2.$$

Similarly, for the right half,

$$A_R = \frac{A_{\min}}{2} + \left(\frac{\partial A}{\partial V}\right)_T \delta V + \tfrac{1}{2}\left(\frac{\partial^2 A}{\partial V^2}\right)_T (\delta V)^2.$$

Adding these two equations, the total Helmholtz function of the system *in the nonequilibrium state* is

$$A_L + A_R = A_{\min} + \left(\frac{\partial^2 A}{\partial V^2}\right)_T (\partial V)^2,$$

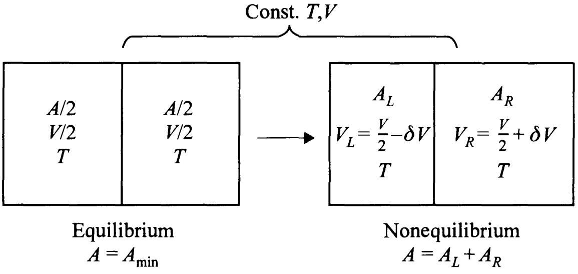


FIGURE 15-4
Transition from a state of thermodynamic equilibrium to a state characterized by a lack of mechanical equilibrium.

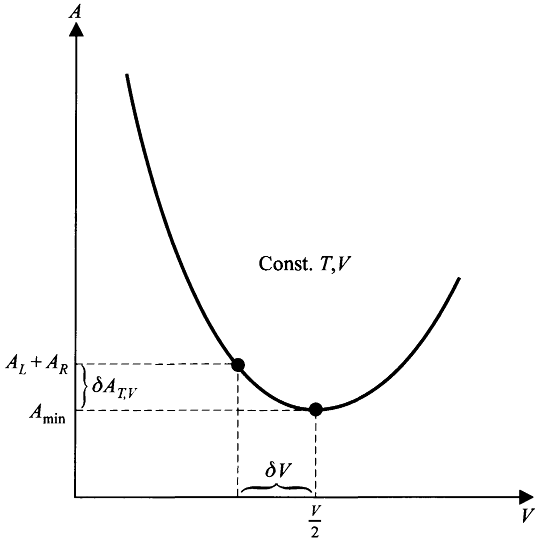


FIGURE 15-5
Dependence of the Helmholtz function of the entire system on the volume of half of it, when the total volume and the temperature are constant.

or

$$A_L + A_R - A_{\min} = \delta A_{T,V} = \left(\frac{\partial^2 A}{\partial V^2}\right)_T (\delta V)^2.$$

The relation between A and the volume V of either half of the system at constant T and V is shown in Fig. 15-5. Since $\delta A_{T,V}$ is positive, it follows that

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T > 0.$$

But

$$\left(\frac{\partial A}{\partial V}\right)_T = -P,$$

and hence, finally,

$$\left(\frac{\partial P}{\partial V}\right)_T < 0.$$

This is *the condition for mechanical stability.*

15.10
THERMODYNAMIC EQUATIONS FOR A PHASE

Consider a phase composed of c chemical constituents, of which there are n_1 moles of substance B_1, n_2 moles of $B_2, \cdots, n_c$ moles of B_c; the phase is in thermal equilibrium at temperature T and in mechanical equilibrium at pressure P. The Gibbs function of the phase, which is open to changes in n_j, can be written as follows:

$$G = \text{function of } (T, P, n_1, n_2, \cdots, n_c).$$

If the constituents are inert, then the phase is in chemical and, therefore, thermodynamic equilibrium. Imagine the performance of an infinitesimal *reversible* process in which the temperature and pressure are changed by dT and dP, respectively, and the numbers of moles of the various constituents are altered by the amounts dn_1, $dn_2, \cdots, dn_c$. Since we have assumed that the constituents are inert, the changes in the n's are to be regarded as accomplished by the reversible addition or withdrawal of the constituents with the aid of suitable semipermeable membranes. The resulting change in the Gibbs function of the phase is given by

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP + \frac{\partial G}{\partial n_1} dn_1 + \frac{\partial G}{\partial n_2} dn_2 + \cdots + \frac{\partial G}{\partial n_c} dn_c,$$

where it is understood that G is a function of T, P, and the n's, and that each partial derivative implies that all variables other than the one indicated are to be kept constant.

As a special case, consider an infinitesimal reversible process in which all the dn's are zero. Under these conditions, the composition and the mass of the phase remain constant, and the equation becomes

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP \qquad \text{(for constant composition and mass).}$$

But, for this case, it has already been shown in Chap. 10 that

$$dG = -S\,dT + V\,dP.$$

It follows, therefore, that

$$\frac{\partial G}{\partial T} = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\cdots,n_c} = -S, \tag{15.12}$$

$$\frac{\partial G}{\partial P} = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\cdots,n_c} = V, \tag{15.13}$$

and $$dG = -S\,dT + V\,dP + \frac{\partial G}{\partial n_1} dn_1 + \frac{\partial G}{\partial n_2} dn_2 + \cdots + \frac{\partial G}{\partial n_c} dn_c.$$

Now, consider the effect upon the Gibbs function when a small amount of one of the constituents (say, the jth constituent, B_j) is introduced into the phase, T, P, and the other n_j's remain constant. If dn_j moles of B_j are introduced into the system, then the effect on the Gibbs function is expressed by the partial derivative

$$\mu_j = \frac{\partial G}{\partial n_j}, \tag{15.14}$$

where μ_j is the *chemical potential* of the jth constituent of the phase in question, as discussed also in Eq. (11.14). A chemical potential of one constituent is a function of T, P, and *all* the n_j's. If a substance is not present in a phase, then it does not follow that its chemical potential is zero. The chemical potential is a measure of the effect on the Gibbs function when a substance *is* introduced. Even though the substance is not present in the phase, there is always the possibility of introducing it, in which case the Gibbs function would be altered and the value of μ_j would be finite. We may now write

$$dG = -S\,dT + V\,dP + \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_c\,dn_c$$

for an infinitesimal change in the Gibbs function of any phase consisting of inert constituents.

Suppose, now, that the constituents are chemically active. Changes in the n_j's may then take place because of a chemical reaction. Although the phase is always considered to be in thermal and mechanical equilibrium, an infinitesimal process involving a change in T, P, and the n_j's will, in general, be irreversible, since chemical equilibrium may not exist. According to our previous assumption as to the form of the expressions denoting properties of a phase in thermal and mechanical equilibrium but not in chemical equilibrium, *we shall assume that the equation*

$$\boxed{dG = -S\,dT + V\,dP + \sum \mu_j\,dn_j} \tag{15.15}$$

correctly expresses the change in the Gibbs function for ***any*** *infinitesimal process in which the n_j's may be caused to change, either by the transfer of constituents to or from the phase or by the agency of a chemical reaction, or both.* Equation (15.15) is the same as Eq. (11.13), except that the present application is a chemical reaction. The third term is the reversible chemical work $đW_C$ introduced in Eq. (11.10).

Imagine a phase at constant T and P in which all constituents are increased in the same proportion. Since the Gibbs function is an extensive quantity, it also will be increased in the same proportion. Infinitesimal changes in the mole numbers in the same proportion are represented by

$$dn_1 = n_1\,d\lambda, \qquad dn_2 = n_2\,d\lambda, \qquad \ldots, \qquad dn_c = n_c\,d\lambda,$$

and the corresponding change in G is

$$dG = G\,d\lambda,$$

where $d\lambda$ is the proportionality factor. Since

$$dG_{T,P} = \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_c\,dn_c,$$

we have

$$G\,d\lambda = \mu_1 n_1\,d\lambda + \mu_2 n_2\,d\lambda + \cdots + \mu_c n_c\,d\lambda,$$

or

$$\boxed{\begin{aligned} G &= \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_c n_c \\ &= \sum \mu_j n_j. \end{aligned}} \tag{15.16}$$

Equation (15.16) shows that *the chemical potentials are intensive quantities*, because, if all the n's are increased in the same proportion at constant T and

P, then the μ's must remain constant in order that G increase in the same proportion.

15.11
CHEMICAL POTENTIALS

The chemical potentials play a fundamental role in chemical thermodynamics. The chemical potential of the jth constituent of a phase was defined in Eq. (11.14) as

$$\mu_j = \frac{\partial G}{\partial n_j},$$

and is a function of T, P, and all the n_j's. In order that μ_j may be an intensive quantity, it is clear that the n_j's must be combined in such a way that, when all of them are multiplied by the same factor, the value of μ_j remains the same. The mole fraction of the jth constituent,

$$x_j = \frac{n_j}{\sum n_j},$$

satisfies that requirement; hence, it is to be expected that μ_j is a function of T, P, and x_j. The actual form of the function depends, of course, on the nature of the phase. Consider the following phases:

1. *Phase consisting of only one constituent.* In this simple, but not trivial case,

   $$G = \mu n$$

   and
   $$\mu = \frac{G}{n} = g; \tag{15.17}$$

   that is, the chemical potential μ is the molar Gibbs function g and is a function of T and P only.
2. *Phase consisting of a mixure of ideal gases.* In this case, we have, from Sec. 15.5,

   $$G = RT \sum n_j(\phi_j + \ln P + \ln x_j),$$

   which, when compared with the general equation

   $$G = \sum n_j \mu_j,$$

   shows that the chemical potential of one ideal gas in a mixture of ideal gases is

   $$\mu = RT(\phi + \ln P + \ln x), \tag{15.18}$$

   which may be written in the two alternative forms

   $$\mu = RT(\phi + \ln p),$$

and
$$\mu = g + RT \ln x. \tag{15.19}$$

3. *Phase consisting of an ideal solution.* An ideal solution is defined as one in which the chemical potential of each constituent has the form

$$\mu_j = g_j + RT \ln x_j, \tag{15.20}$$

where g_j is the Gibbs function of 1 mol of the jth constituent in the pure state, expressed as a function of T and P.

4. *Phase consisting of a dilute solution.* In the case of a dilute solution in which the mole fraction of the solvent x_0 is very much larger than each of the mole fractions of the solutes $x_1, x_2, \ldots$, it can be shown that, for the solvent,

$$\mu_0 = g_0 + RT \ln x_0, \tag{15.21}$$

where g_0 is the molar Gibbs function of the solvent in the pure state, expressed as a function of T and P. For any one of the solutes,

$$\mu_j = g_{0j} + RT \ln x_j, \tag{15.22}$$

where g_{0j} is a function of T and P only, but depends upon the nature of the solvent as well as upon the solute.

5. *Other phases.* By defining functions known as *fugacity* and *activity coefficients*, it is possible to express the chemical potentials of constituents of a mixture of real gases and also of concentrated solutions. This is beyond the scope of this book.

We shall assume that it is always possible to express the chemical potential of any constituent of any phase as a function of T, P, and the x_j of that constituent. It will be a surprise to the student to discover how much valuable information can be obtained with the aid of this assumption, without knowing the exact expressions for the chemical potentials of the constituents of a phase.

15.12
DEGREE OF REACTION

If we introduce into a vessel a mixture of any arbitrary number of moles of water vapor, hydrogen, and oxygen, the chemical reaction capable of taking place is indicated by the notation

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2,$$

where the quantity on the left is called an *initial constituent* and those on the right are *final constituents.* The numbers which precede the chemical symbols and which "balance" the equation (it is understood that both H_2O and H_2 are preceded by unity) are called the *stoichiometric coefficients* and are proportional to the number of moles of the constituents that *change* during the reaction. Thus, if the reaction proceeds to the right to the extent that 1 mol of water vapor dissociates, then 1 mol of hydrogen and $\frac{1}{2}$ mol of oxygen are formed; or if 0.1 mol of water vapor dissociates, then 0.1 mol of hydrogen and 0.05 mol of oxygen are formed; or, if n_0 moles of water vapor dissociate (n_0 being any number whatever), then n_0 moles of hydrogen and $n_0/2$ moles of oxygen are formed. Similarly, if the reaction proceeds to the left to the extent that n_0' moles of hydrogen combine with $n_0'/2$ moles of oxygen, then n_0' moles of water vapor are formed.

In general, suppose that we have a mixture of four substances whose chemical symbols are B_1, B_2, B_3, and B_4. Let B_1 and B_2 be the initial constituents (reactants) and B_3 and B_4 the final constituents (products), with the reaction being represented by

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4.$$

We have chosen four substances only for convenience. The equations to be developed have such a character that they can be applied to reactions in which any number of substances participate. The ν_j's are the stoichiometric coefficients, which are always positive integers or fractions.

Let us start with arbitrary amounts of *both* initial and final constituents. If we imagine the reaction to proceed completely to the right, then at least one of the initial constituents (say, B_1) will completely disappear. Next, it is possible to find a positive number n_0 such that the original number of moles of each of the initial constituents is expressed in the form:

$$n_1(\text{original}) = n_0\,\nu_1,$$

and

$$n_2(\text{original}) = n_0\,\nu_2 + N_2,$$

where N_2 is a constant representing the number of moles of B_2 that cannot combine. If we imagine the reaction to proceed completely to the left, then at least one of the final constituents (say, B_3) will completely disappear. In this event, another positive number n_0' may be found such that the original number of moles of each final constituent is expressed in the form:

$$n_3(\text{original}) = n_0'\nu_3,$$

and

$$n_4(\text{original}) = n_0'\nu_4 + N_4.$$

If the reaction is imagined to proceed completely to the *left*, then there is the maximum amount possible of each initial constituent and the minimum amount of each final constituent:

$$\begin{aligned} n_1(\text{max}) &= (n_0 + n_0')\nu_1, & n_3(\text{min}) &= 0,\\ n_2(\text{max}) &= (n_0 + n_0')\nu_2 + N_2, & n_4(\text{min}) &= N_4, \end{aligned}$$

If the reaction is imagined to proceed completely to the *right*, then there is the minimum amount possible of each initial constituent and the maximum amount of each final constituent:

$$\begin{aligned} n_1(\text{min}) &= 0, & n_3(\text{max}) &= (n_0 + n_0')\nu_3,\\ n_2(\text{min}) &= N_2, & n_4(\text{max}) &= (n_0 + n_0')\nu_4 + N_4. \end{aligned}$$

Suppose that the reaction proceeds partially either to the right or to the left to such an extent that there are n_1 moles of B_1, n_2 moles of B_2, n_3 moles of B_3, and n_4 moles of B_4 present at a given moment. We define the *degree of reaction* ϵ in terms of any one of the initial constituents (say, B_1) as the fraction,

$$\boxed{\epsilon = \frac{n_1(\max) - n_1}{n_1(\max) - n_1(\min)}.} \tag{15.23}$$

It follows from this definition that $\epsilon = 0$ when the reaction is completely to the left, and $\epsilon = 1$ when the reaction is completely to the right. When the reaction consists in the dissociation of one initial constituent, ϵ is called the *degree of dissociation*; when the reaction consists in the ionization of one initial constituent, ϵ is called the *degree of ionization.* Expressing $n_1(\max)$ and $n_1(\min)$ in terms of the constants that express the original amounts of the constituents, we get

$$\epsilon = \frac{(n_0 + n_0')\nu_1 - n_1}{(n_0 + n_0')\nu_1};$$

and, solving for n_1,

$$n_1 = (n_0 + n_0')\nu_1(1 - \epsilon).$$

The number of moles of each of the constituents is, therefore, given by the following expressions:

$$\begin{aligned} n_1 &= (n_0 + n_0')\nu_1(1 - \epsilon), & n_3 &= (n_0 + n_0')\nu_3\,\epsilon, \\ n_2 &= (n_0 + n_0')\nu_2(1 - \epsilon) + N_2, & n_4 &= (n_0 + n_0')\nu_4\,\epsilon + N_4. \end{aligned} \tag{15.24}$$

When a chemical reaction takes place, all the n_j's change, but not independently. The restrictions imposed on the n_j's are given by the relations in Eq. (15.24). These equations, therefore, are examples of *equations of constraint.*

The equations of constraint are equally valid whether the system is heterogeneous or homogeneous. If each constituent is present in, say, φ different phases, with $n_1^{(1)}$ moles of constituent B_1 in phase 1 and $n_1^{(2)}$ moles of the same constituent in phase 2, etc., then the total number of moles of constituent B_1 is

$$n_1 = n_1^{(1)} + n_1^{(2)} + \cdots + n_1^{(\varphi)} = (n_0 + n_0')\nu_1(1 - \epsilon),$$

and similarly for the other constituents. For the present, however, we shall limit ourselves to homogeneous systems, reserving heterogeneous systems for Chap. 17.

Since all the n_j's are functions of ϵ only, it follows that in a homogeneous system all the mole fractions are functions of ϵ only. An example will show how simple these expressions are when the starting conditions are simple. Consider a vessel containing n_0 moles of water vapor only, with no hydrogen or oxygen present. If dissociation occurs until the degree of dissociation is ϵ, then the n_j's and x_j's are shown as functions of ϵ in Table 15.1. Since the

TABLE 15.1
$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$

B	ν	n	x
$B_1 = H_2O$	$\nu_1 = 1$	$n_1 = n_0(1-\epsilon)$	$x_1 = \dfrac{1-\epsilon}{1+\epsilon/2}$
$B_3 = H_2$	$\nu_3 = 1$	$n_3 = n_0\epsilon$	$x_3 = \dfrac{\epsilon}{1+\epsilon/2}$
$B_4 = O_2$	$\nu_4 = \frac{1}{2}$	$n_4 = \dfrac{n_0\epsilon}{2}$ $\sum n = n_0(1+\epsilon/2)$	$x_4 = \dfrac{\epsilon/2}{1+\epsilon/2}$

chemical potential of each gas in the mixture is a function of T, P, and x_j, it follows that every chemical potential is a function of T, P, and ϵ.

If the reaction is imagined to proceed to an infinitesimal extent, the degree of reaction changing from ϵ to $\epsilon + d\epsilon$, the various n_j's will change by the following amounts:

$$\begin{aligned} dn_1 &= -(n_0 + n_0')\nu_1\, d\epsilon, & dn_3 &= (n_0 + n_0')\nu_3\, d\epsilon, \\ dn_2 &= -(n_0 + n_0')\nu_2\, d\epsilon, & dn_4 &= (n_0 + n_0')\nu_4\, d\epsilon. \end{aligned}$$

These equations show that the changes in the n_j's are proportional to the ν_j's, with the factor of proportionality being, for the initial constituents, $-(n_0 + n_0')d\epsilon$, and, for the final constituents, $+(n_0 + n_0')d\epsilon$. Another way of writing these changes is as follows:

$$\frac{dn_1}{-\nu_1} = \frac{dn_2}{-\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = (n_0 + n_0')\, d\epsilon, \tag{15.25}$$

which shows perhaps more clearly that the dn_j's are proportional to the ν_j's.

15.13
EQUATION OF REACTION EQUILIBRIUM

Consider a homogeneous phase consisting of arbitrary amounts of the four constituents B_1, B_2, B_3, and B_4, and represent the reaction as follows:

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4.$$

Suppose that the phase is at uniform temperature T and pressure P. If n_1, n_2, n_3, and n_4 denote the numbers of moles of each constituent that are present at any moment and μ_1, μ_2, μ_3, and μ_4 are the respective chemical potentials, then the Gibbs function of the mixture is

$$G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \mu_4 n_4.$$

The n_j's are given by the equations of constraint:

$$n_1 = (n_0 + n_0')\nu_1(1-\epsilon), \qquad n_3 = (n_0 + n_0')\nu_3\,\epsilon,$$
$$n_2 = (n_0 + n_0')\nu_2(1-\epsilon) + N_2, \qquad n_4 = (n_0 + n_0')\nu_4\,\epsilon + N_4.$$

The μ_j's are functions of T, P, and ϵ. Therefore, it follows that G is a function of T, P, and ϵ.

Let us imagine that the reaction is allowed to take place at constant T and P. Under these conditions, the Gibbs function decreases; that is, during an infinitesimal change in ϵ from ϵ to $\epsilon + d\epsilon$,

$$dG_{T,P} < 0.$$

We have shown that, for any infinitesimal change to which a phase in thermal and mechanical equilibrium is subjected,

$$dG = -S\,dT + V\,dP + \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots.$$

Therefore, for this mixture of four constituents,

$$dG_{T,P} = \mu_1\,dn_1 + \mu_2\,dn_2 + \mu_3\,dn_3 + \mu_4\,dn_4,$$

with the equations of constraint in differential form:

$$dn_1 = -(n_0 + n_0')\nu_1\,d\epsilon, \qquad dn_3 = (n_0 + n_0')\nu_3\,d\epsilon,$$
$$dn_2 = -(n_0 + n_0')\nu_2\,d\epsilon, \qquad dn_4 = (n_0 + n_0')\nu_4\,d\epsilon.$$

Substituting, we obtain a general expression for an infinitesimal change of the Gibbs function at constant T and P. Thus,

$$dG_{T,P} = (n_0 + n_0')(-\nu_1\,\mu_1 - \nu_2\,\mu_2 + \nu_3\,\mu_3 + \nu_4\,\mu_4)\,d\epsilon. \tag{15.26}$$

It follows from this equation that when the reaction proceeds spontaneously to the right, so that $d\epsilon$ is positive, then, in order that $dG_{T,P} < 0$,

$$\nu_1\,\mu_1 + \nu_2\,\mu_2 > \nu_3\,\mu_3 + \nu_4\,\mu_4 \qquad \text{(reaction to right)}.$$

Conversely, if the reaction proceeds spontaneously to the left,

$$\nu_1\,\mu_1 + \nu_2\,\mu_2 < \nu_3\,\mu_3 + \nu_4\,\mu_4 \qquad \text{(reaction to left)}.$$

The mixture will be in equilibrium at the given T and P when the Gibbs function is a minimum at which an infinitesimal change in ϵ will produce no change in the Gibbs function. Therefore, for $dG_{T,P} = 0$ at equilibrium, we have

$$\boxed{\nu_1\,\mu_1 + \nu_2\,\mu_2 = \nu_3\,\mu_3 + \nu_4\,\mu_4} \qquad \text{(at equilibrium)}, \tag{15.27}$$

which is called the *equation of reaction equilibrium*. It should be noted that this equation contains only intensive variables. Evidently, to determine the composition of a homogeneous mixture after the reaction has come to equilibrium, it is necessary merely to substitute the appropriate expressions for the chemical potentials into the equation of reaction equilibrium. This will be done in the case of ideal gases in the next chapter.

PROBLEMS

15.1. Prove Gibbs' theorem by using the apparatus depicted in Fig. 15-2 in such a way that the gases are separated reversibly and adiabatically.

15.2. What is the minimum amount of work required to separate 1 mol of air at 27°C and 1 atm pressure (assumed to be composed of $\frac{1}{5}$ O_2 and $\frac{4}{5}$ N_2) into O_2 and N_2, each at 27°C and 1 atm pressure?

15.3. Calculate the entropy change of the universe due to the diffusion of two ideal gases (1 mol of each) at the same temperature and pressure, by calculating $\int đQ/T$ over a series of reversible processes involving the use of the apparatus depicted in Fig. 15-2.

15.4. There are n_1 moles of an ideal monatomic gas at temperature T_1 and pressure P in one compartment of an insulated container. In an adjoining compartment separated by an insulating partition are n_2 moles of another ideal monatomic gas at temperature T_2 and pressure P. When the partition is removed:

(*a*) Show that the final pressure of the mixture is P.
(*b*) Calculate the entropy change when the gases are identical.
(*c*) Calculate the entropy change when the gases are different.

15.5. There are n_1 moles of an ideal gas at pressure P_1 and temperature T in one compartment of an insulated container. In an adjoining compartment separated by a partition are n_2 moles of an ideal gas at pressure P_2 and temperature T. When the partition is removed:

(*a*) Calculate the final pressure of the mixture.
(*b*) Calculate the entropy change when the gases are identical.
(*c*) Calculate the entropy change when the gases are different.
(*d*) Prove that the entropy change in part (*c*) is the same as that which would be produced by two independent free expansions.

15.6. Suppose that we have 1 mol of a monatomic gas B_1, whose nuclei are in their lowest energy state, and 1 mol of a monatomic gas B_2 consisting of exactly the same atoms as B_1, except that the nuclei are in an excited state whose energy ϵ is much larger than kT and whose lifetime is much larger than the time for diffusion to occur. Both gases are at the same pressure and are maintained at the same temperature T by a heat reservoir.

(*a*) Immediately after the nuclei of gas B_2 have been excited, diffusion takes place. Calculate the entropy change of the universe.
(*b*) After the nuclei of gas B_2 have been excited, a time much larger than the lifetime of the excited state is allowed to elapse, and then diffusion takes place. Calculate the entropy change of the universe.
(*c*) Show that the answer to part (*b*) is larger than that to part (*a*). (This problem is due to M. J. Klein.)

15.7. Consider the system depicted in Fig. P15-1, where the whole system and also each half are in equilibrium. Consider a process to take place in which each half of the system remains at the constant volume $V/2$, but a small amount of heat δU (at

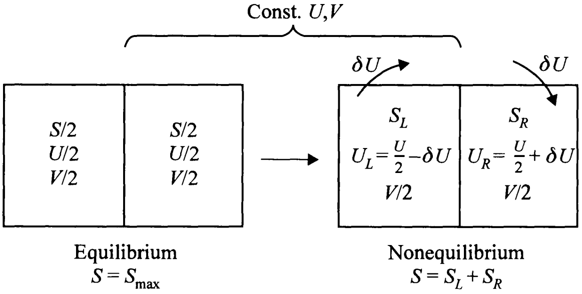


FIGURE P15-1

constant volume, $đQ = dU$) is extracted from the left half and transferred to the right half, as shown in Fig. P15-1. Realizing that

$$\left(\frac{\partial S_L}{\partial U}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V$$

(*a*) Expand the entropy S_L of the left half by means of a Taylor series about the equilibrium value $S_{\max}/2$, terminating the series after the squared term. Do the same for S_R.

(*b*) Show that

$$\delta S_{U,V} = S_L + S_R - S_{\max} = \left(\frac{\partial^2 S}{\partial U^2}\right)_V (\delta U)^2.$$

(*c*) Show that $C_V > 0$, which is the *condition for thermal stability.*

15.8. (*a*) Show that the molar Helmholtz function a of an ideal gas is

$$a = u_0 - T\int \frac{\int c_V\, dT}{T^2}\, dT - Ts_0 - RT \ln v.$$

(*b*) Show that the Helmholtz function of a mixture of inert ideal gases is

$$A = \sum n_j(a_j + RT \ln x_j).$$

(*c*) Show that the change in the Helmholtz function due to diffusion is

$$A_f - A_i = RT \sum n_j \ln x_j.$$

15.9. Consider a hydrostatic system of constant mass maintained in thermal and mechanical equilibrium. It is not in chemical equilibrium, however, because of chemical reactions and transport of matter between phases. Under these circumstances, the system undergoes an irreversible cycle. Prove that

$$\oint_I \frac{đQ}{T} < 0.$$

15.10. By means of the equations $dG = -S\,dT + V\,dP + \sum \mu_j\, dn_j$ and $G = \sum \mu_j n_j$, prove that:

(*a*) $-S\,dT + V\,dP = \sum n_j\,d\mu_j$.
(*b*) $-s\,dT + v\,dP = \sum x_j\,d\mu_j$.

15.11. Show that, if the internal energy of a phase is expressed as a function of S, V, n_1, $n_2, \ldots, n_c$, then:
(*a*) $dU = T\,dS - P\,dV + \sum \mu_j\,dn_j$, where $\mu_j = (\partial U/\partial n_j)_{S,V,\,\text{other } n\text{'s}}$.
(*b*) $U = TS - PV + \sum \mu_j n_j$.
(*c*) $-S\,dT + V\,dP = \sum n_j\,d\mu_j$.

15.12. Show that, if the Helmholtz function of a phase is expressed as a function of $T, V, n_1, n_2, \ldots, n_c$, then:
(*a*) $dA = -S\,dT - P\,dV + \sum \mu_j\,dn_j$, where $\mu_j = (\partial A/\partial n_j)_{T,V,\,\text{other } n\text{'s}}$.
(*b*) $A = -PV + \sum \mu_j n_j$.
(*c*) $-S\,dT + V\,dP = \sum n_j\,d\mu_j$.

15.13. Prove that:

(*a*) $$Td\left(\frac{A}{T}\right) = -\frac{U}{T}dT - P\,dV + \sum \mu_j\,dn_j.$$

(*b*) $$d(PV) = S\,dT + V\,dP + \sum n_j\,d\mu_j.$$

15.14. Show that, for an ideal gas in a mixture of ideal gases,

$$d\mu_j = \frac{\mu_j - h_j}{T}dT + v_j\,dP + RT\,d\ln x_j.$$

15.15. Consider a uniform substance of variable mass. Suppose that, at any moment, there are n moles of substance and that the system undergoes an infinitesimal reversible process in which n changes by dn. For any 1 mol of substance,

$$đq = T\,ds = du + P\,dv,$$

and the total heat transfer $đQ = n\,đq = nT\,ds$.
(*a*) Prove that

$$đQ = dU + P\,dV - h\,dn,$$

where U and V refer to the entire system, but h is the molar enthalpy.
(*b*) From Prob. 15.11(*a*) show that

$$T\,dS = dU + P\,dV - g\,dn.$$

(*c*) How does $T\,dS$ differ from $đQ$?
(*d*) Show that, if T and P remain constant, then $đQ = 0$ but $T\,dS$ does not.

15.16. Starting with n_0 moles of CO and n_0 moles of H_2O capable of undergoing the reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

in the gaseous phase, set up a table of values of A, v, n, and x, similar to that of Table 15.1.

15.17. Starting with n_0 moles of H_2S and $2n_0$ moles of H_2O, capable of undergoing the reaction

$$H_2S + 2H_2O \rightleftharpoons 3H_2 + SO_2$$

in the gaseous phase, set up a table of values of A, v, n, and x, similar to that of Table 15.1.

CHAPTER 16

Ideal-Gas Reactions

16.1
LAW OF MASS ACTION

It has been shown that when four substances, which are capable of undergoing the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4,$$

and which form a homogeneous phase at constant temperature and pressure, come to equilibrium, the equation of reaction equilibrium

$$\nu_1 \mu_1 + \nu_2 \mu_2 = \nu_3 \mu_3 + \nu_4 \mu_4$$

must be satisfied. If the constituents are ideal gases, then the chemical potentials are given by expressions of the type

$$\mu_j = RT(\phi_j + \ln P + \ln x_j),$$

where the ϕ_j's are functions of the temperature only. Substituting in the equation of reaction equilibrium, we get

$$\begin{aligned} &\nu_1(\phi_1 + \ln P + \ln x_1) + \nu_2(\phi_2 + \ln P + \ln x_2) \\ &\qquad = \nu_3(\phi_3 + \ln P + \ln x_3) + \nu_4(\phi_4 + \ln P + \ln x_4). \end{aligned}$$

Rearranging terms yields

$$\begin{aligned} &\nu_3 \ln x_3 + \nu_4 \ln x_4 - \nu_1 \ln x_1 - \nu_2 \ln x_2 + (\nu_3 + \nu_4 - \nu_1 - \nu_2) \ln P \\ &\qquad = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2), \end{aligned}$$

or $$\ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}} P^{\nu_3+\nu_4-\nu_1-\nu_2} = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2).$$

The right-hand term is a quantity whose value depends only on the temperature. Denoting it by $\ln K$, where K is known as the *equilibrium constant*,

$$\ln K = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2), \tag{16.1}$$

we get, finally,

$$\boxed{\left(\frac{x_3^{\nu_3}x_4^{\nu_4}}{x_1^{\nu_1}x_2^{\nu_2}}\right)_{\epsilon=\epsilon_e} P^{\nu_3+\nu_4-\nu_1-\nu_2} = K.} \tag{16.2}$$

This form of the equation of reaction equilibrium was first presented by two Norwegian chemists, Guldberg and Waage, in 1863. For some unknown reason, it is called the *law of mass action*, a misnomer that is harmless. The fraction involving the equilibrium values of the x_j's is a function of the equilibrium value of the degree of reaction ϵ — that is, of ϵ_e — and hence the law of mass action is seen to be a relation among ϵ_e, P, and T.

It is obvious that, if there are more than two initial constituents and two final constituents, then the law of mass action becomes

$$\left(\frac{x_3^{\nu_3}x_4^{\nu_4}\cdots}{x_1^{\nu_1}x_2^{\nu_2}\cdots}\right)_{\epsilon=\epsilon_e} P^{\nu_3+\nu_4+\,\cdots\,-\nu_1-\nu_2-\,\cdots} = K,$$

where K is given by

$$\ln K = -(\nu_3\phi_3 + \nu_4\phi_4 + \cdots - \nu_1\phi_1 - \nu_2\phi_2 - \cdots).$$

16.2
EXPERIMENTAL DETERMINATION OF EQUILIBRIUM CONSTANTS

It has been pointed out that a mixture of hydrogen and oxygen will remain indefinitely, without reacting, at atmospheric pressure and at room temperature. If the temperature is raised considerably, however, then water vapor forms and equilibrium takes place quickly. If the mixture is then cooled very suddenly so as not to disturb the equilibrium, then an analysis of the composition of the mixture yields the values of the mole fractions corresponding to equilibrium at the high temperature. The equilibrium has, so to speak, been "frozen." Sometimes a flow method is used. The reacting gases are mixed in known proportions at a low temperature, and the mixture is caused to flow slowly through a long reacting tube at a desired temperature. The gases remain at this temperature a sufficient time for equilibrium to take place. The mixture is then allowed to flow through a capillary, where it is suddenly cooled. The equilibrium values of the mole fractions are then measured by the methods of chemical analysis.

It is a consequence of the law of mass action that the equilibrium constant corresponding to a given temperature is independent of the amounts of products that are originally mixed. For example, in the case of the "water-gas" reaction,

$$CO_2 + H_2 \rightleftharpoons CO + H_2O,$$

the law of mass action requires that, at equilibrium,

$$\frac{x_{CO}x_{H_2O}}{x_{CO_2}x_{H_2}}P^{1+1-1-1} = K,$$

or

$$\frac{x_{CO}x_{H_2O}}{x_{CO_2}x_{H_2}} = \text{const.}$$

at a constant temperature, independent of the starting conditions. For conditions that involve starting with arbitrary amounts of CO_2 and H_2 and maintaining the temperature constant at 1259 K, the equilibrium values of the mole fractions are given in Table 16.1, where it may be seen that K is quite constant.

The water-gas reaction is an example of a reaction that does not involve a change in the total number of moles. If such a reaction were to take place at constant temperature and pressure, then there would be no change in volume. There are, however, many reactions in which the total number of moles varies. In such cases, it is possible to measure the value of the degree of reaction at equilibrium by merely measuring the volume (or the density) of the mixture at equilibrium. If ϵ_e is known, then the equilibrium constant can be calculated. As an example of this procedure, consider the dissociation of nitrogen tetroxide, according to the equation

$$N_2O_4 \rightleftharpoons 2NO_2.$$

If we start with n_0 moles of N_2O_4 at temperature T and pressure P, then the initial volume is expressed as

$$V_0 = n_0\frac{RT}{P}.$$

TABLE 16.1

Equilibrium data for the water-gas reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ at 1259 K

Original mixture		Equilibrium mixture			$K = \frac{x_{CO}x_{H_2O}}{x_{CO_2}x_{H_2}}$
x_{CO_2}	x_{H_2}	x_{CO_2}	$x_{CO} = x_{H_2O}$	x_{H_2}	
0.101	0.899	0.0069	0.094	0.805	1.591
0.310	0.699	0.0715	0.2296	0.4693	1.571
0.491	0.509	0.2122	0.2790	0.2295	1.598
0.609	0.391	0.3443	0.2645	0.1267	1.604
0.703	0.297	0.4750	0.2282	0.0685	1.600

If V_e denotes the volume at equilibrium, with the temperature and pressure remaining the same, then

$$V_e = [n_0(1-\epsilon_e) + 2n_0\epsilon_e]\frac{RT}{P},$$

where ϵ_e is the value of the degree of dissociation at equilibrium. This can be written as

$$V_e = (1+\epsilon_e)V_0,$$

or

$$\epsilon_e = \frac{V_e}{V_0} - 1.$$

Since the density ρ is inversely proportional to the volume, we get, finally,

$$\epsilon_e = \frac{\rho_0}{\rho_e} - 1.$$

Now, at equilibrium,

$$x_{N_2O_4} = \frac{n_0(1-\epsilon_e)}{n_0(1+\epsilon_e)} \quad \text{and} \quad x_{NO_2} = \frac{2n_0\epsilon_e}{n_0(1+\epsilon_e)};$$

therefore, the law of mass action becomes

$$\frac{[2\epsilon_e/(1+\epsilon_e)]^2}{(1-\epsilon_e)/(1+\epsilon_e)}P = K,$$

or

$$\frac{4\epsilon_e^2}{1-\epsilon_e^2}P = K.$$

The pressure is, by custom, measured in atmospheres, even though the "atmosphere" is not an SI unit. Numerical data for this reaction are given in Table 16.2, where it is seen that, at the constant temperature of 323 K, the equilibrium constant remains fairly constant for three different values of the pressure.

There are many other methods of measuring equilibrium constants. For a complete account of this important branch of physical chemistry, the student is referred to an advanced treatise.

TABLE 16.2
$N_2O_4 \rightleftharpoons 2NO_2$

Temp., K	P, atm	ρ_0, kg/m^3	ρ_e, kg/m^3	$\epsilon_e = \frac{\rho_0}{\rho_e} - 1$	$K = \frac{4\epsilon^2}{1-\epsilon^2}P$, atm
323	0.124	1.093	0.615	0.777	0.756
323	0.241	1.093	0.651	0.679	0.825
323	0.655	1.093	0.737	0.483	0.797

16.3
HEAT OF REACTION

The equilibrium constant is defined by the equation

$$\ln K = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2).$$

Differentiating ln K with respect to T, we get

$$\frac{d}{dT}\ln K = -\left(\nu_3\frac{d\phi_3}{dT} + \nu_4\frac{d\phi_4}{dT} - \nu_1\frac{d\phi_1}{dT} - \nu_2\frac{d\phi_2}{dT}\right).$$

Since

$$\phi_j = \frac{h_{0j}}{RT} - \frac{1}{R}\int\frac{\int c_{Pj}\,dT}{T^2}dT - \frac{s_{0j}}{R},$$

we have

$$\begin{aligned}\frac{d\phi_j}{dT} &= -\frac{h_{0j}}{RT^2} - \frac{\int c_{Pj}\,dT}{RT^2}\\ &= -\frac{1}{RT^2}\left(h_{0j} + \int c_{Pj}\,dT\right),\end{aligned}$$

and

$$\frac{d\phi_j}{dT} = -\frac{h_j}{RT^2}. \tag{16.3}$$

Therefore,

$$\frac{d}{dT}\ln K = \frac{1}{RT^2}(\nu_3h_3 + \nu_4h_4 - \nu_1h_1 - \nu_2h_2),$$

where all the h_j's refer to the same temperature T and the same pressure P. The right-hand term has a simple interpretation. If ν_1 moles of B_1 and ν_2 moles of B_2 are converted at constant temperature and pressure into ν_3 moles of B_3 and ν_4 moles of B_4, the heat transferred will be equal to the final enthalpy $\nu_3h_3 + \nu_4h_4$ minus the initial enthalpy $\nu_1h_1 + \nu_2h_2$. Calling this heat the *heat of reaction* and denoting it by ΔH, we have

$$\Delta H = \nu_3h_3 + \nu_4h_4 - \nu_1h_1 - \nu_2h_2, \tag{16.4}$$

and

$$\boxed{\frac{d}{dT}\ln K = \frac{\Delta H}{RT^2}.} \tag{16.5}$$

The preceding equation, called the *van't Hoff isobar*, is one of the most important equations in chemical thermodynamics.

Rewriting the equation as

$$\frac{d\ln K}{dT/T^2} = \frac{\Delta H}{R},$$

or

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H}{R},$$

we get

$$\Delta H = -2.30R\,\frac{d\log K}{d(1/T)}. \tag{16.6}$$

The van't Hoff isobar enables one to calculate the heat of reaction at any desired temperature or within any desired temperature range, once the temperature variation of the equilibrium constant is known. The slope of the curve obtained by plotting log K against $1/T$, multiplied by $2.30R$, is the heat of reaction at the temperature corresponding to the point chosen. As a rule, log K can be measured only within a small temperature range, in which case the curve is usually a straight line.

As an example of this procedure, consider the dissociation of water vapor according to the reaction

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2.$$

Starting with n_0 moles of water vapor and no hydrogen or oxygen, the mole fractions corresponding to any value ϵ of the degree of dissociation are shown in Table 15.1. At equilibrium,

$$\left(\frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1}}\right)_{\epsilon=\epsilon_e} P^{\nu_3+\nu_4-\nu_1} = K,$$

or

$$\frac{\dfrac{\epsilon_e}{1+\epsilon_e/2}\left(\dfrac{\epsilon_e/2}{1+\epsilon_e/2}\right)^{1/2}}{\dfrac{1-\epsilon_e}{1+\epsilon_e/2}} P^{1/2} = K,$$

or

$$\frac{\epsilon_e^{3/2}}{(2+\epsilon_e)^{1/2}(1-\epsilon_e)} P^{1/2} = K.$$

When the equilibrium value of the degree of reaction ϵ_e is very much smaller than unity, this equation reduces to

$$K = \sqrt{\frac{\epsilon_e^3 P}{2}}.$$

In Table 16.3, experimental values of ϵ_e are given at a number of temperatures and at constant atmospheric pressure, along with the corresponding

TABLE 16.3

$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$ ($P = 1$ atm)

Temp., K	ϵ_e (measured)	$K = \dfrac{\epsilon^{3/2} P^{1/2}}{(2+\epsilon_e)^{1/2}(1-\epsilon_e)}$, (atm)$^{1/2}$	Log K	$\dfrac{1}{T}$
1500	1.97×10^{-4}	1.95×10^{-6}	-5.71	6.67×10^{-4}
1561	3.4×10^{-4}	4.48×10^{-5}	-5.36	6.41×10^{-4}
1705	1.2×10^{-3}	2.95×10^{-5}	-4.53	5.87×10^{-4}
2155	1.2×10^{-2}	9.0×10^{-4}	-3.05	4.64×10^{-4}
2257	1.77×10^{-2}	1.67×10^{-3}	-2.78	4.43×10^{-4}
2300	2.6×10^{-2}	2.95×10^{-3}	-2.53	4.35×10^{-4}

values of K, $\log K$, and $1/T$. The graph of $\log K$ against $1/T$ is shown in Fig. 16-1, where it is seen that the points lie on a straight line with a slope equal to $-13{,}100\,\mathrm{K}$. It follows, therefore, that the heat of dissociation at the average temperature of about 1900 K is equal to

$$\begin{aligned}\Delta H &= -2.30R \times -13{,}100\,\mathrm{K}\\ &= 251\,\mathrm{kJ/mol}.\end{aligned}$$

It is rather difficult to measure the heat of reaction accurately by a direct calorimetric method. Most heats of reaction are obtained either with the aid of the van't Hoff isobar or by means of an electrochemical cell. In a few cases in which it is possible to measure the equilibrium constant over a very wide temperature range, the graph of $\log K$ against $1/T$ is found to have a variable slope, indicating that the heat of reaction depends on the temperature. Such a graph is impossible to obtain in most cases, however, since at low temperatures a reaction either does not proceed or, if it does, then the equilibrium value of the degree of reaction is too small to measure. Thus, in the case of the dissociation of water vapor, the degree of dissociation at room temperature and atmospheric pressure is about 10^{-27}, which means that, under these conditions, not even one molecule of H_2O dissociates.

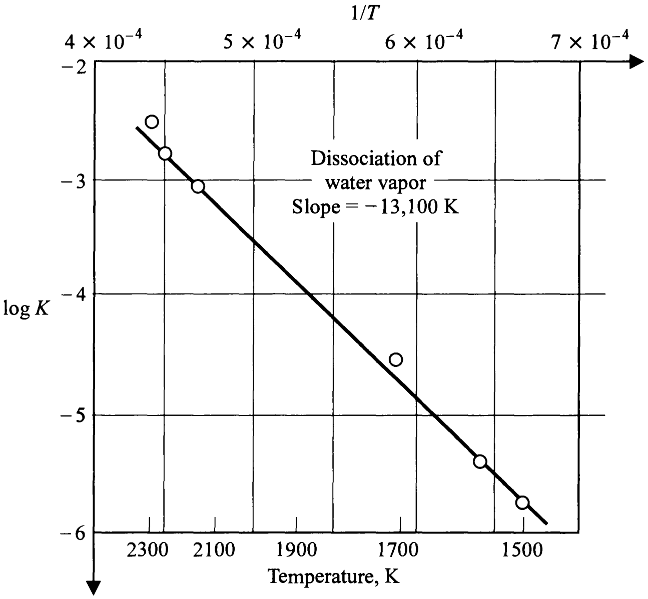


FIGURE 16-1
Graph of $\log K$ against $1/T$ for dissociation of water vapor.

To obtain the heat of reaction at any desired temperature, it is necessary to know the temperature dependence of the specific heats of all the reacting gases. Since

$$\Delta H = \nu_3 h_3 + \nu_4 h_4 - \nu_1 h_1 - \nu_2 h_2$$

and

$$h_j = h_{0j} + \int c_{Pj}\, dT,$$

then

$$\Delta H = \nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02} + \int (\nu_3 c_{P3} + \nu_4 c_{P4} - \nu_1 c_{P1} - \nu_2 c_{P2})\, dT.$$

Denoting the constant part by ΔH_0, thus:

$$\Delta H_0 = \nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02}, \tag{16.7}$$

and defining

$$\Delta C_P = \nu_3 c_{P3} + \nu_4 c_{P4} - \nu_1 c_{P1} - \nu_2 c_{P2}, \tag{16.8}$$

we get

$$\boxed{\Delta H = \Delta H_0 + \int \Delta C_P\, dT.} \tag{16.9}$$

The integral can be determined by substituting for the c_{Pj}'s the empirical equations expressing their temperature dependence. If ΔH is known at one temperature, therefore, ΔH_0 can be calculated and the equation may be used to provide ΔH at any temperature.

16.4
NERNST'S EQUATION

The equilibrium constant is defined by the equation

$$\ln K = -(\nu_3 \phi_3 + \nu_4 \phi_4 - \nu_1 \phi_1 - \nu_2 \phi_2),$$

where

$$\phi_j = \frac{h_{0j}}{RT} - \frac{1}{R} \int \frac{\int c_{Pj}\, dT}{T^2}\, dT - \frac{s_{0j}}{R}.$$

We have, therefore,

$$\begin{aligned}\ln K = & -\frac{1}{RT}(\nu_3 h_{03} + \nu_4 h_{04} - \nu_1 h_{01} - \nu_2 h_{02}) \\ & + \frac{1}{R} \int \frac{\int (\nu_3 c_{P3} + \nu_4 c_{P4} - \nu_1 c_{P1} - \nu_2 c_{P2})\, dT}{T^2}\, dT \\ & + \frac{1}{R}(\nu_3 s_{03} + \nu_4 s_{04} - \nu_1 s_{01} - \nu_2 s_{02}).\end{aligned}$$

Defining

$$\Delta S_0 = \nu_3 s_{03} + \nu_4 s_{04} - \nu_1 s_{01} - \nu_2 s_{02},$$

the equation becomes

$$\boxed{\ln K = -\frac{\Delta H_0}{RT} + \frac{1}{R}\int \frac{\int \Delta C_P \, dT}{T^2} \, dT + \frac{\Delta S_0}{R},} \tag{16.10}$$

which is known as *Nernst's equation.*

An interesting application of Nernst's equation was made by Megh Nad Saha to the thermal ionization of a monatomic gas. If a monatomic gas is heated to a high enough temperature, then some ionization occurs and the atoms, ions, and electrons may be regarded as a mixture of three ideal monatomic gases undergoing the reaction

$$B \rightleftharpoons B^+ + e.$$

Starting with n_0 moles of atoms alone, the state of affairs at equilibrium is shown in Table 16.4. For this reaction,

$$\ln K = \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1}} P^{\nu_3+\nu_4-\nu_1}$$

$$= \ln \frac{[\epsilon_e/(1+\epsilon_e)][\epsilon_e/(1+\epsilon_e)]}{(1-\epsilon_e)/(1+\epsilon_e)} P,$$

or

$$\ln K = \ln \frac{\epsilon_e^2}{1-\epsilon_e^2} P.$$

ΔH_0 is the amount of energy necessary to ionize 1 mol of atoms. If we denote the *ionization potential* of the atom in volts by E, then $\Delta H_0 = FE$, where F is Faraday's constant. Since the three gases are monatomic, each c_{Pj} is equal to $\frac{5}{2}R$. Therefore, $\Delta C_P = \frac{5}{2}R$, and

$$\frac{1}{R}\int \frac{\int \Delta C_P \, dT}{T^2} \, dT = \tfrac{5}{2} \ln T.$$

Let us put

$$\frac{\Delta S_0}{R} = \ln D.$$

TABLE 16.4
$B \rightleftharpoons B^+ + e$

B	ν	***n***	***x***
$B_1 = B$	$\nu_1 = 1$	$n_1 = n_0(1-\epsilon_e)$	$x_1 = \dfrac{1-\epsilon_e}{1+\epsilon_e}$
$B_3 = B^+$	$\nu_3 = 1$	$n_3 = n_0\epsilon_e$	$x_3 = \dfrac{\epsilon_e}{1+\epsilon_e}$
$B_4 = e$	$\nu_4 = 1$	$n_4 = n_0\epsilon_e$	$x_4 = \dfrac{\epsilon_e}{1+\epsilon_e}$
	$\nu_3 + \nu_4 - \nu_1 = 1$	$\sum n_j = n_0(1+\epsilon_e)$	

Introducing these results into Nernst's equation, we get

$$\ln \frac{\epsilon_e^2}{1-\epsilon_e^2} P = -\frac{FE}{RT} + \tfrac{5}{2} \ln T + \ln D.$$

Expressing P in atmospheres, changing to common logarithms, and introducing the value of D from statistical mechanics, Saha finally obtained the formula

$$\log \frac{\epsilon_e^2}{1-\epsilon_e^2} P(\text{atm}) = -(5050\,\text{K/V}) \frac{E}{T} + \tfrac{5}{2} \log T + \log \frac{\omega_\text{i} \omega_\text{e}}{\omega_\text{a}} - 6.491, \qquad (16.11)$$

where ω_i, ω_e, and ω_a are constants that refer, respectively, to the ion, the electron, and the atom.

In order to apply Saha's equation to a specific problem, it is necessary to know the ionization potential and the ω_j's. A complete discussion of these quantities is beyond the scope of this book. Values of these constants for a few elements are listed in Table 16.5. The constant ω_e for an electron is 2.

Saha applied his equation to the determination of the temperature of a stellar atmosphere. The spectrum of a star contains lines which originate from atoms (*arc lines*) and also those which originate from ions (*spark lines*). A comparison of the intensity of a spark line with that of an arc line, both referring to the same element, gives rise to a value of the degree of ionization ϵ_e. When a star is treated as a sphere of ideal gas, it is possible to obtain an estimate of the pressure of a stellar atmosphere. Since all the other quantities are known, the temperature can be calculated.

TABLE 16.5
Values of E and ω

Element	E, V	ω_a	ω_i
Na	5.139	2	1
Cs	3.894	2	1
Ca	6.113	1	2
Cd	8.993	1	2
Zn	9.394	1	2
Tl	6.108	2	1

16.5
AFFINITY

It was shown in Sec. 15.5 that the molar Gibbs function of an ideal gas at temperature T and pressure P is equal to

$$g = RT(\phi + \ln P).$$

If we have four gases that can engage in the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4,$$

then we define the change of Gibbs function of the reaction by the expression

$$\Delta G = \nu_3 g_3 + \nu_4 g_4 - \nu_1 g_1 - \nu_2 g_2, \tag{16.12}$$

where the g_j's refer to the gases completely separated at T, P. It should be emphasized that ΔG is defined in terms of the separate Gibbs functions of the gases, not in terms of the mixture. Among American chemists, ΔG is known as the *free-energy change*. The connection between ΔG and the behavior of the gases when mixed is shown by introducing the values of the g_j's. Thus,

$$\Delta G = RT(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2) + RT \ln P^{\nu_3+\nu_4-\nu_1-\nu_2}.$$

But,

$$\ln K = -(\nu_3\phi_3 + \nu_4\phi_4 - \nu_1\phi_1 - \nu_2\phi_2);$$

therefore,

$$\Delta G = -RT \ln K + RT \ln P^{\nu_3+\nu_4-\nu_1-\nu_2}. \tag{16.13}$$

Recall that K also contains the pressure P raised to the $(\nu_3 + \nu_4 - \nu_1 - \nu_2)$th power. It follows, therefore, that the above equation will be satisfied when both P's are measured in the same units, whatever the units are. If we express P in atmospheres, as usual, and calculate ΔG when each gas is at a pressure of 1 atm, then the second term on the right drops out. Under these conditions, ΔG is known as the *standard Gibbs function change*, and is denoted by ΔG°. Therefore,

$$\boxed{\Delta G^\circ = -RT \ln K.} \tag{16.14}$$

Let us imagine that ν_1 moles of gas B_1 and ν_2 moles of gas B_2 are mixed at uniform temperature T and pressure P and that a chemical reaction occurs, thereby forming constituents B_3 and B_4. At any moment when the degree of reaction is ϵ, the Gibbs function of the mixture is

$$G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \mu_4 n_4,$$

where

$$n_1 = \nu_1(1-\epsilon), \qquad n_3 = \nu_3\,\epsilon,$$
$$n_2 = \nu_2(1-\epsilon), \qquad n_4 = \nu_4\,\epsilon,$$

and each chemical potential is a function of T, P, and ϵ. It follows that G is a function of T, P, and ϵ; therefore, at constant T and P, G is a function of ϵ only. The graph of G against ϵ has somewhat the form shown in Fig. 16-2.

At the equilibrium point where $\epsilon = \epsilon_e$, the curve has a minimum at which

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = 0 \qquad (\text{at } \epsilon = \epsilon_e).$$

The slopes of the curve at the points $\epsilon = 0$ and $\epsilon = 1$ may be calculated from Eq. (15.26), namely,

$$dG_{T,P} = (n_0 + n_0')(\nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2)\,d\epsilon,$$

which, in this case, becomes

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = \nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2. \tag{16.15}$$

Since $\mu_j = RT(\phi_j + \ln P + \ln x_j)$

and $g_j = RT(\phi_j + \ln P)$,

the chemical potential may be written in convenient form:

$$\mu_j = g_j + RT \ln x_j.$$

Therefore,

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = \nu_3 g_3 + \nu_4 g_4 - \nu_1 g_1 - \nu_2 g_2 + RT(\nu_3 \ln x_3 + \nu_4 \ln x_4 - \nu_1 \ln x_1 - \nu_2 \ln x_2),$$

or

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = \Delta G + RT \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}}. \tag{16.16}$$

It should be borne in mind that the x_j's in this equation are not equilibrium values, but correspond to *any* value of ϵ. Now, when $\epsilon = 0$, there are no final constituents (products of the reaction) and, therefore, both x_3 and x_4 are zero. Hence,

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = -\infty \qquad (\text{at } \epsilon = 0).$$

On the other hand, when $\epsilon = 1$, there are no initial constituents (reactants) and, therefore, x_1 and x_2 are zero. Hence,

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = +\infty \qquad (\text{at } \epsilon = 1).$$

The graph in Fig. 16-2 has these properties.

Consider the point $\epsilon = \frac{1}{2}$ at which there are $\nu_1/2$ moles of gas B_1, $\nu_2/2$ moles of gas B_2, $\nu_3/2$ moles of gas B_3, and $\nu_4/2$ moles of gas B_4. At this point, the constituents are present in proportion to their stoichiometric coefficients ν, and the mole fractions are

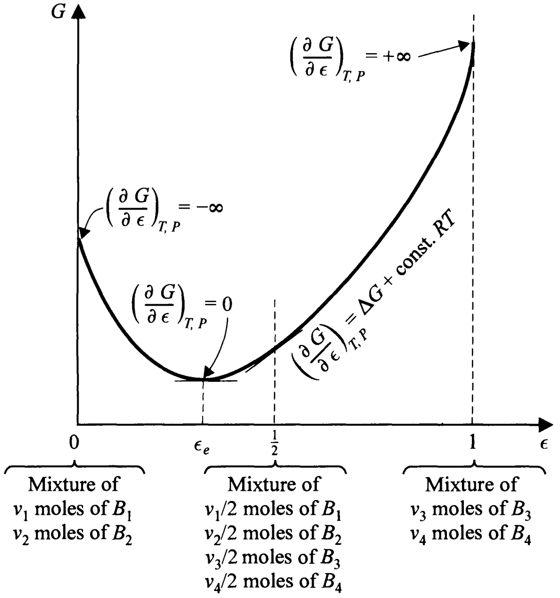


FIGURE 16-2
Graph of G against ϵ at constant T and P.

$$x_1 = \frac{\nu_1}{\sum \nu_j}, \qquad x_3 = \frac{\nu_3}{\sum \nu_j},$$

$$x_2 = \frac{\nu_2}{\sum \nu_j}, \qquad x_4 = \frac{\nu_4}{\sum \nu_j}.$$

The slope of the curve at this point indicates whether such a mixture is in equilibrium or not. If this slope is positive, then the equilibrium point is to the left; that is, when both the initial and final constituents are mixed, there will be a tendency for the reaction to proceed to the left, causing initial constituents to be formed. Conversely, if the slope of the curve at $\epsilon = \frac{1}{2}$ is negative, then the equilibrium point is to the right; or when both initial and final constituents are mixed, there will be a tendency for the reaction to proceed to the right, causing final constituents to be formed. Finally, if this slope is zero, a mixture of both initial and final constituents is in equilibrium, and there is no tendency for the reaction to proceed at all.

It is seen, therefore, that the *sign* of the slope of the $G\epsilon$-curve at $\epsilon = \frac{1}{2}$ is an indication of the behavior of a system composed of initial and final constituents mixed in proportion to their stoichiometric coefficients. Furthermore, it is obvious from the curve that the *magnitude* of this slope is a measure of the departure from, or nearness to, equilibrium of such a mixture. We shall call the slope of the $G\epsilon$-curve at the point $\epsilon = \frac{1}{2}$ the *affinity* of the reaction, which is equal to

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P}(\epsilon = \tfrac{1}{2}) = \Delta G + RT \ln \frac{(\nu_3/\sum \nu)^{\nu_3}(\nu_4/\sum \nu)^{\nu_4}}{(\nu_1/\sum \nu)^{\nu_1}(\nu_2/\sum \nu)^{\nu_2}}. \tag{16.17}$$

This equation is true at all temperatures and pressures. Let us choose $T = 298\,\mathrm{K}$ and $P = 1\,\mathrm{atm}$. The last term on the right is a constant for each reaction. When all the stoichiometric coefficients ν_j are unity, this term is zero. In general, its value is much less than ΔG°_{298}. Consequently, ΔG°_{298} has more effect on the quantity $(\partial G/\partial \epsilon)_{T,P}$ than the other term. We may write, therefore,

$$\boxed{\frac{\partial G}{\partial \epsilon}\begin{bmatrix} \epsilon = \frac{1}{2} \\ T = 298\,\mathrm{K} \\ P = 1\,\mathrm{atm} \end{bmatrix} \sim \sum \Delta G^\circ_{298}.} \tag{16.18}$$

Therefore, *the standard Gibbs function change at 298 K is an indication of the direction and amount to which a reaction will proceed at this temperature.* For example ΔG°_{298} for the water-vapor reaction is a large positive number, meaning that the equilibrium point is far to the left of $\epsilon = \frac{1}{2}$; therefore, ϵ_e is very small. Again, ΔG°_{298} is a large negative number for the reaction $NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2$; therefore, the equilibrium point is far to the right of $\epsilon = \frac{1}{2}$, and ϵ_e is almost unity.

16.6
DISPLACEMENT OF EQUILIBRIUM

The equilibrium value of the degree of reaction was obtained by setting $(\partial G/\partial \epsilon)_{T,P}$ equal to zero. This condition, however, is also the condition that G be a maximum as well as a minimum. In order to verify that G is a minimum, it is necessary to show that $(\partial^2 G/\partial \epsilon^2)_{T,P}$ is positive at the equilibrium point. For a mixture of arbitrary amounts of four chemically active ideal gases, we have

$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = (n_0 + n_0')\left(\Delta G + RT \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}}\right)$$

for all values of ϵ. Therefore, since ΔG is a function of T and P only,

$$\left(\frac{\partial^2 G}{\partial \epsilon^2}\right)_{T,P} = (n_0 + n_0')RT \frac{d}{d\epsilon} \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}}. \tag{16.19}$$

The right-hand member of this equation can be easily evaluated for any value of ϵ (the details of this calculation are found in Prob. 16.14), and is found to be

$$\frac{d}{d\epsilon} \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}} = \frac{n_0 + n_0'}{\sum n_j}\left[\frac{\nu_1^2}{x_1} + \frac{\nu_2^2}{x_2} + \frac{\nu_3^2}{x_3} + \frac{\nu_4^2}{x_4} - (\Delta \nu)^2\right], \tag{16.20}$$

where $\Delta \nu = \nu_3 + \nu_4 - \nu_1 - \nu_2$. It may be proved rigorously that the expression in brackets is positive for all values of the ν_j's and x_j's. The proof, however, is rather lengthy. If we do not insist on complete generality but choose as starting conditions $n_0\nu_1$ moles of B_1 and $n_0\nu_2$ moles of B_2, with no amount of B_3 and B_4, then the preceding equation reduces to the following simple form (also found in Prob. 16.14):

$$\frac{d}{d\epsilon}\ln\frac{x_3^{\nu_3}x_4^{\nu_4}}{x_1^{\nu_1}x_2^{\nu_2}} = \frac{n_0}{\sum n_j}\,\frac{(\nu_1+\nu_2)(\nu_3+\nu_4)}{\epsilon(1-\epsilon)}. \tag{16.21}$$

Since the right-hand term of this equation is always positive for all ν_j's and all values of ϵ, it follows that $(\partial^2 G/\partial\epsilon^2)_{T,P}$ is always positive; hence, when $\epsilon = \epsilon_e$, G is a minimum and not a maximum. It will be seen that this result plays an important role in determining the displacement of equilibrium when the temperature or the pressure is changed.

Let us consider, first, the effect on the equilibrium value of the degree of reaction of a change of temperature at constant pressure. We know that, at equilibrium, the law of mass action provides us with a relation among T, ϵ_e, and P, which may be written in the form

$$\ln K = \ln\left(\frac{x_3^{\nu_3}x_4^{\nu_4}}{x_1^{\nu_1}x_2^{\nu_2}}\right)_{\epsilon=\epsilon_0} + (\nu_3+\nu_4-\nu_1-\nu_2)\ln P,$$

where $\ln K$ is a function of T only, and the first term on the right is a function of ϵ_e only. Now,

$$\begin{aligned}\left(\frac{\partial\epsilon_e}{\partial T}\right)_P &= \left(\frac{\partial\epsilon_e}{\partial\ln K}\right)_P\left(\frac{\partial\ln K}{\partial T}\right)_P\\ &= \frac{(d\ln K)/dT}{(\partial\ln K/\partial\epsilon_e)_P}.\end{aligned}$$

Using the van't Hoff isobar to evaluate the numerator, and the law of mass action to evaluate the denominator, we get

$$\boxed{\left(\frac{\partial\epsilon_e}{\partial T}\right)_P = \frac{\Delta H}{RT^2\,d[\ln(x_3^{\nu_3}x_4^{\nu_4}/x_1^{\nu_1}x_2^{\nu_2})]/d\epsilon_e.}} \tag{16.22}$$

Since we have already mentioned that the denominator on the right is positive, it follows that the sign of $(\partial\epsilon_e/\partial T)_P$ is determined by the sign of ΔH. Therefore, *an increase of temperature at constant pressure causes a displacement in the equilibrium value of the degree of reaction in the direction in which the heat of reaction is absorbed.*

To determine the effect of a change of pressure at constant temperature, we write

$$\begin{aligned}\left(\frac{\partial\epsilon_e}{\partial P}\right)_T &= -\left(\frac{\partial\epsilon_e}{\partial\ln K}\right)_P\left(\frac{\partial\ln K}{\partial P}\right)_{\epsilon_e}\\ &= -\frac{(\partial\ln K/\partial P)_{\epsilon_e}}{(\partial\ln K/\partial\epsilon_e)_P}.\end{aligned}$$

Using the law of mass action to evaluate both numerator and denominator, we get

$$\boxed{\left(\frac{\partial \epsilon_e}{\partial P}\right)_T = -\frac{\nu_3 + \nu_4 - \nu_1 - \nu_2}{P\, d[\ln(x_3^{\nu_3} x_4^{\nu_4}/x_1^{\nu_1} x_2^{\nu_2})]/d\epsilon_e}.} \tag{16.23}$$

The numerator on the right is proportional to the change in the number of moles of the constituents as the reaction proceeds to the right. If the numerator is positive, then the volume increases at constant T and P. Therefore, *an increase of pressure at constant temperature causes a displacement in the equilibrium value of the degree of reaction in the direction in which a decrease of volume takes place.*

16.7
HEAT CAPACITY OF REACTING GASES IN EQUILIBRIUM

Let us consider, as usual, a mixture of arbitrary amounts of four ideal gases capable of undergoing the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4.$$

At equilibrium, the enthalpy of the mixture is

$$H = \sum n_j h_j,$$

where

$$n_1 = (n_0 + n_0')\nu_1(1 - \epsilon_e), \qquad n_3 = (n_0 + n_0')\nu_3 \epsilon_e,$$
$$n_2 = (n_0 + n_0')\nu_2(1 - \epsilon_e) + N_2, \qquad n_4 = (n_0 + n_0')\nu_4 \epsilon_e + N_4,$$

and ϵ_e is the equilibrium value of the degree of reaction. Suppose that an infinitesimal change of temperature occurs *at constant pressure* in such a way that equilibrium is maintained. Then, ϵ_e will change to the value $\epsilon_e + d\epsilon_e$ and the enthalpy will change by the amount

$$dH_P = \sum n_j\, dh_j + \sum h_j\, dn_j.$$

Since $dh_j = c_{Pj}\, dT$ and $dn_j = \pm(n_0 + n_0')\nu_j\, d\epsilon_e$,

$$dH_P = \sum n_j c_{Pj}\, dT + (n_0 + n_0')(\nu_3 h_3 + \nu_4 h_4 - \nu_1 h_1 - \nu_2 h_2)\, d\epsilon_e,$$

and the heat capacity of the reacting gas mixture is

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \sum n_j c_{Pj} + (n_0 + n_0')\Delta H \left(\frac{\partial \epsilon_e}{\partial T}\right)_P.$$

From the preceding section,

$$\left(\frac{\partial \epsilon_e}{\partial T}\right)_P = \frac{\Delta H}{RT^2\, d[\ln(x_3^{\nu_3} x_4^{\nu_4}/x_1^{\nu_1} x_2^{\nu_2})]/d\epsilon_e};$$

consequently,

$$\boxed{C_P = \sum n_j c_{Pj} + (n_0 + n_0') \frac{(\Delta H)^2}{RT^2\, d[\ln(x_3^{\nu_3} x_4^{\nu_4}/x_1^{\nu_1} x_2^{\nu_2})]/d\epsilon_e}.} \tag{16.24}$$

As an example, consider the equilibrium mixture of H_2O vapor, H_2, and O_2 caused by the dissociation of 1 mol of H_2O at 1 atm and 1900 K. We have $n_0 = 1$, $n_0' = 0$, $\Delta H = 250\,\text{kJ/mol}$, $R = 8.31\,\text{J/mol}\cdot\text{K}$, $\epsilon_e = 3.2 \times 10^{-3}$, $\sum n_j = n_0(1 + \epsilon_e/2)$, $\nu_1 = 1$, $\nu_2 = 0$, $\nu_3 = 1$, $\nu_4 = \frac{1}{2}$, and

$$\frac{d}{d\epsilon_e} \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}} = \frac{n_0}{\sum n_j} \frac{(\nu_1 + \nu_2)(\nu_3 + \nu_4)}{\epsilon_e(1 - \epsilon_e)}.$$

Hence,
$$\begin{aligned} C_P - \sum n_j c_{Pj} &= \frac{(\Delta H)^2 (1 + \epsilon_e/2)\epsilon_e(1 - \epsilon_e)}{RT^2(\nu_1 + \nu_2)(\nu_3 + \nu_4)} \\ &= \frac{(250{,}000)^2 \times 3.2 \times 10^{-3}}{8.31 \times (1900)^2 \times \frac{3}{2}} \\ &= 4.32\,\text{J/K}. \end{aligned}$$

PROBLEMS

16.1. Show that the law of mass action may be written

$$\frac{p_3^{\nu_3} p_4^{\nu_4}}{p_1^{\nu_1} p_2^{\nu_2}} = K,$$

where the p's are the equilibrium values of the partial pressures.

16.2. If we start with n_0 moles of NH_3, which dissociates according to the equation $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$, show that, at equilibrium,

$$K = \frac{\sqrt{27}}{4} \frac{\epsilon_e^2}{1 - \epsilon_e^2} P.$$

16.3. Starting with n_0 moles of CO and $3n_0$ moles of H_2, which react according to the equation $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$, show that, at equilibrium,

$$K = \frac{4\epsilon_e^2(2 - \epsilon_e)^2}{27(1 - \epsilon_e)^4 P^2}.$$

16.4. A mixture of $n_0\,\nu_1$ moles of B_1 and $n_0\,\nu_2$ moles of B_2 at temperature T and pressure P occupies a volume V_0. When the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4$$

has come to equilibrium at the same T and P, the volume is V_e. Show that

$$\epsilon_e = \frac{V_e - V_0}{V_0} \frac{\nu_1 + \nu_2}{\nu_3 + \nu_4 - \nu_1 - \nu_2}.$$

16.5. At 35°C and 1 atm, the degree of dissociation of N_2O_4 at equilibrium is 0.27.

(*a*) Calculate K.

(*b*) Calculate ϵ_e at the same temperature when the pressure is 100 mm Hg.

(*c*) The equilibrium constant for the dissociation of N_2O_4 has the values 0.664 and 0.141 at the temperatures 318 K and 298 K, respectively. Calculate the average heat of reaction within this temperature range.

16.6 The equilibrium constant of reaction $SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$ has the following values:

Kelvin temperature	800	900	1000	1105
Equilibrium constant	0.0319	0.153	0.540	1.59

Determine the average heat of dissociation graphically.

16.7. Calculate the degree of ionization of cesium vapor at 10^{-6} atm at the two temperatures 2260 K and 2520 K.

16.8. Calculate the degree of ionization of calcium vapor in the sun's chromosphere. The temperature and pressure of the sun's chromosphere are approximately 6000 K and 10^{-10} atm, respectively.

16.9. (*a*) Show that

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P.$$

(*b*) Show that

$$\Delta G = -RT \ln \frac{x_3^{\nu_3} x_4^{\nu_4}}{x_1^{\nu_1} x_2^{\nu_2}},$$

where the x's are equilibrium values.

16.10. Calculate the heat capacity of the equilibrium mixture of Prob. 16.7 at the temperature of 2260 K.

16.11. When 1 mol of HI dissociates according to the reaction

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

at $T = 675$ K, $K = 0.132$ and $\Delta H = 2950$ J/mol. Calculate $(\partial \epsilon_e / \partial T)_P$ at this temperature.

16.12. Starting with ν_1 moles of B_1 and ν_2 moles of B_2, show that:

(*a*) At any value of ϵ,

$$G = \epsilon(\nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2) + \nu_1\mu_1 + \nu_2\mu_2.$$

(*b*) At equilibrium,

$$G(\min) = \nu_1\mu_{1_e} + \nu_2\mu_{2_e},$$

where the subscript e denotes an equilibrium value.

(*c*)
$$\frac{G - G(\min)}{RT} = \epsilon\left(\ln\frac{x_3^{\nu_3}x_4^{\nu_4}}{x_1^{\nu_1}x_2^{\nu_2}} - \ln\frac{x_{3e}^{\nu_3}x_{4e}^{\nu_4}}{x_{1e}^{\nu_1}x_{2e}^{\nu_2}}\right) + \ln x_1^{\nu_1}x_2^{\nu_2} - \ln x_{1e}^{\nu_1}x_{2e}^{\nu_2}.$$

(*d*) At $\epsilon = 0$,

$$\frac{G_0 - G(\min)}{RT} = \ln\left(\frac{\nu_1}{\nu_1+\nu_2}\right)^{\nu_1}\left(\frac{\nu_2}{\nu_1+\nu_2}\right)^{\nu_2} - \ln x_{1e}^{\nu_1}x_{2e}^{\nu_2}.$$

(*e*) At $\epsilon = 1$,

$$\frac{G_1 - G(\min)}{RT} = \ln\left(\frac{\nu_3}{\nu_3+\nu_4}\right)^{\nu_3}\left(\frac{\nu_4}{\nu_3+\nu_4}\right)^{\nu_4} - \ln x_{3e}^{\nu_3}x_{4e}^{\nu_4}.$$

16.13. In the case of the ionization of a monatomic gas, show that:

(*a*)
$$\frac{G - G(\min)}{RT} = \epsilon\left(\ln\frac{\epsilon^2}{1-\epsilon^2} - \ln\frac{\epsilon_e^2}{1-\epsilon_e^2}\right) + \ln\frac{1-\epsilon}{1+\epsilon} - \ln\frac{1-\epsilon_e}{1+\epsilon_e}.$$

(*b*) At $\epsilon = 0$,

$$\frac{G_0 - G(\min)}{RT} = -\ln\frac{1-\epsilon_e}{1+\epsilon_e}.$$

(*c*) At $\epsilon = 1$,

$$\frac{G_1 - G(\min)}{RT} = \ln\tfrac{1}{4} - \ln\frac{\epsilon_e^2}{(1+\epsilon_e)^2}.$$

(*d*) Plot $[G - G(\min)]/2.30RT$ against ϵ for the ionization of cesium vapor at 2260 K and 10^{-6} atm, using the result of Prob. 16.7.

16.14. (*a*) Prove that, for a mixture of reacting ideal gases,

$$\frac{d}{d\epsilon}\ln\frac{x_3^{\nu_3}x_4^{\nu_4}}{x_1^{\nu_1}x_2^{\nu_2}} = \frac{n_0 + n_0'}{\sum n_j}\,\frac{1}{\psi},$$

where $\displaystyle \frac{1}{\psi} = \frac{\nu_1^2}{x_1} + \frac{\nu_2^2}{x_2} + \frac{\nu_3^2}{x_3} + \frac{\nu_4^2}{x_4} - (\Delta\nu)^2,$

and $\Delta\nu = \nu_3 + \nu_4 - \nu_1 - \nu_2.$

(*b*) If we start with $n_0\nu_1$ moles of B_1 and $n_0\nu_2$ moles of B_2, and no B_3 or B_4, show that

$$\psi = \frac{\epsilon(1-\epsilon)}{(\nu_1+\nu_2)(\nu_3+\nu_4)}.$$

16.15. Prove that, for a mixture of reacting ideal gases *in equilibrium*,

(*a*)
$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{P} - \frac{(n_0 + n_0')RT(\Delta\nu)^2}{P^2(d/d\epsilon_e)\ln(x_3^{\nu_3}x_4^{\nu_4}/x_1^{\nu_1}x_2^{\nu_2})}.$$

(*b*)
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} + \frac{(n_0 + n_0')\Delta\nu\,\Delta H}{PT(d/d\epsilon_e)\ln(x_3^{\nu_3}x_4^{\nu_4}/x_1^{\nu_1}x_2^{\nu_2})}.$$

(*c*)
$$\left(\frac{\partial P}{\partial T}\right)_{\epsilon_e} = -\frac{P\,\Delta H}{RT^2\,\Delta\nu}.$$

16.16. Prove that, for a mixture of reacting ideal gases *in equilibrium*,

$$dS = \sum n_j\left[\sum x_j c_{Pj} + \frac{\psi(\Delta H)^2}{RT^2}\right]\frac{dT}{T} - R\sum n_j\left[1 + \frac{\psi\,\Delta H\,\Delta\nu}{RT}\right]\frac{dP}{P},$$

where ψ is given in Prob. 16.14.

CHAPTER 17

Heterogeneous Systems

17.1
THERMODYNAMIC EQUATIONS FOR A HETEROGENEOUS SYSTEM

It was shown in Eq. (15.16) that the Gibbs function of any homogeneous phase, consisting of c constituents and in thermal and mechanical equilibrium at temperature T and pressure P, is equal to

$$G = \sum \mu_j n_j,$$

where each chemical potential is a function of T, P, and the mole fraction of the respective constituent, and the summation is taken over all the constituents. Furthermore, if the phase undergoes an infinitesimal process involving a change of temperature dT, a change of pressure dP, and changes in each of the n_j's, the accompanying change in the Gibbs function is equal to

$$dG = -S\,dT + V\,dP + \sum \mu_j\,dn_j.$$

Suppose that we have a heterogeneous system of φ phases, all homogeneous and all at the uniform temperature T and pressure P. As usual, let us denote constituents by subscripts and phases by superscripts. The total Gibbs function of the heterogeneous system $\mathbf{G}$ is the sum of the Gibbs function of all the phases; that is,

$$\begin{aligned}\mathbf{G} = {} & \sum \mu_j^{(1)} n_j^{(1)} \text{ over all the constituents of the 1st phase} \\ & + \sum \mu_j^{(2)} n_j^{(2)} \text{ over all the constituents of the 2nd phase} \\ & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ & + \sum \mu_j^{(\varphi)} n_j^{(\varphi)} \text{ over all the constituents of the } \varphi\text{th phase.} \qquad (17.1)\end{aligned}$$

If an infinitesimal process takes place in which *all* the phases undergo a change in temperature dT and a change in pressure dP, then the change in the Gibbs function is

$$\begin{aligned} dG = & -S^{(1)}dT + V^{(1)}dP + \sum \mu_j^{(1)}\, dn_j^{(1)} && \text{(for 1st phase)} \\ & -S^{(2)}dT + V^{(2)}dP + \sum \mu_j^{(2)}\, dn_j^{(2)} && \text{(for 2nd phase)} \\ & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots && \\ & -S^{(\varphi)}dT + V^{(\varphi)}dP + \sum \mu_j^{(\varphi)}\, dn_j^{(\varphi)} && \text{(for } \varphi\text{th phase).} \end{aligned}$$

This equation evidently reduces to

$$dG = -S\,dT + V\,dP + \sum \mu_j^{(1)} dn_j^{(1)} + \sum \mu_j^{(2)} dn_j^{(2)} + \cdots + \sum \mu_j^{(\varphi)} dn_j^{(\varphi)}, \tag{17.2}$$

where S and V are the entropy and volume, respectively, of the whole heterogeneous system.

The problem of the equilibrium of a heterogeneous system is to obtain an equation or a set of equations among the μ_j's that are applicable when all the phases are in chemical equilibrium. If the system is assumed to approach equilibrium at constant T and P, then G is a minimum at equilibrium, and the problem can be stated thus: *To render G a minimum at constant T and P, subject to whatever conditions are imposed on the n_j's by virtue of the constraints of the system.* The mathematical condition that G be a minimum at constant T and P is that

$$dG_{T,P} = 0.$$

Hence, the equation that must be satisfied at equilibrium is

$$dG_{T,P} = \sum \mu_j^{(1)} dn_j^{(1)} + \sum \mu_j^{(2)} dn_j^{(2)} + \cdots + \sum \mu_j^{(\varphi)} dn_j^{(\varphi)} = 0, \tag{17.3}$$

where the dn_j's are not all independent, but are connected by equations of constraint.

To return for a moment to the system treated in Chap. 15 — namely, one phase consisting of a mixture of chemically active substances — we found that the equations of constraint were of such a simple form that, by direct substitution, G could be expressed as a function of T, P, and only one other independent variable ϵ and that $dG_{T,P}$ could be expressed in terms of only one differential, $d\epsilon$. Thus:

$$dG_{T,P} = (n_0 + n_0')(\nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2)\, d\epsilon. \tag{15.26}$$

At equilibrium, when $dG_{T,P} = 0$, only one equation, the equation of reaction equilibrium, was obtained.

In the case of a heterogeneous system, however, the situation is more complicated. In the first place, there is generally more than one independent variable besides T and P. In the second place, the equations of constraint are usually of such a nature that it is either impossible or exceedingly cumbersome to attempt, by direct substitution, to express G in terms of the independent variables only, and dG in terms of differentials of these independent variables. Finally, instead of only one equation of equilibrium, there may be several, depending on the type of heterogeneous system.

We are, therefore, confronted with a type of problem that requires the use of the method of Lagrangian multipliers, as shown in Appendix B.

17.2
PHASE RULE WITHOUT CHEMICAL REACTION

Consider a heterogeneous system of c chemical constituents that do not combine chemically with one another. Suppose that there are φ phases, each of which is in contact with every other phase in such a way that there are no impediments to the transport of any constituent from one phase to another. Let us assume temporarily that every constituent is present in every phase. As usual, constituents will be denoted by subscripts and phases by superscripts. As we have shown previously, the Gibbs function of the whole heterogeneous system is

$$G = \sum_{j=1}^{c} n_j^{(1)} \mu_j^{(1)} + \sum_{j=1}^{c} n_j^{(2)} \mu_j^{(2)} + \cdots + \sum_{j=1}^{c} n_j^{(\varphi)} \mu_j^{(\varphi)},$$

where all the summations extend from $j = 1$ to $j = c$, since all the constituents are present in all the phases. G is a function of T, P, and the n_j's, of which there are $c\varphi$ in number. Not all these n_j's, however, are independent. Since there are no chemical reactions, the only way in which the n_j's may change is by the transport of constituents from one phase to another, in which case the total number of moles of each constituent remains constant. We have as our equations of constraint, therefore,

$$\begin{array}{c}
n_1^{(1)} + n_1^{(2)} + \cdots + n_1^{(\varphi)} = \text{const.} \\
n_2^{(1)} + n_2^{(2)} + \cdots + n_2^{(\varphi)} = \text{const.} \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
n_c^{(1)} + n_c^{(2)} + \cdots + n_c^{(\varphi)} = \text{const.}
\end{array}$$

In order to find the equations of chemical equilibrium, it is necessary to render G a minimum at constant T and P, subject to these equations of constraint. Applying the method of Lagrangian multipliers, we have

$$\begin{array}{llllll}
dG = \mu_1^{(1)}dn_1^{(1)} + \cdots + \mu_c^{(1)}dn_c^{(1)} & + \cdots + & \mu_1^{(\varphi)}dn_1^{(\varphi)} + \cdots + \mu_c^{(\varphi)}dn_c^{(\varphi)} & = 0 \\
\lambda_1 \; dn_1^{(1)} & + \cdots + & \lambda_1 \; dn_1^{(\varphi)} & = 0 \\
\quad \ddots & & \quad \ddots & \vdots \\
\qquad \lambda_c dn_c^{(1)} + \cdots & & \qquad + \lambda_c dn_c^{(\varphi)} & = 0,
\end{array}$$

where there are c Lagrangian multipliers λ_c, one for each equation of constraint. Adding and equating each coefficient of each dn_j to zero, we get

$$\begin{array}{llll}
\mu_1^{(1)} = -\lambda_1, & \mu_1^{(2)} = -\lambda_1, & \ldots, & \mu_1^{(\varphi)} = -\lambda_1 \\
\mu_2^{(1)} = -\lambda_2, & \mu_2^{(2)} = -\lambda_2, & \ldots, & \mu_2^{(\varphi)} = -\lambda_2 \\
\cdots\cdots & \cdots\cdots & \cdots & \cdots\cdots \\
\mu_c^{(1)} = -\lambda_c, & \mu_c^{(2)} = -\lambda_c, & \ldots, & \mu_c^{(\varphi)} = -\lambda_c,
\end{array}$$

or

$$\boxed{\begin{array}{l}
\mu_1^{(1)} = \mu_1^{(2)} = \cdots = \mu_1^{(\varphi)} \\
\mu_2^{(1)} = \mu_2^{(2)} = \cdots = \mu_2^{(\varphi)} \\
\cdots\cdots\cdots\cdots\cdots\cdots \\
\mu_c^{(1)} = \mu_c^{(2)} = \cdots = \mu_c^{(\varphi)}.
\end{array}} \tag{17.4}$$

These are the *equations of phase equilibrium*, which express the important fact that, at equilibrium, the chemical potential of a constituent in one phase must be equal to the chemical potentail of the same constituent in every other phase.

As a simple example, suppose that we have only one constituent present in two phases. Then,

$$dG_{T,P} = \mu_1^{(1)}dn_1^{(1)} + \mu_1^{(2)}dn_1^{(2)};$$

and, since $dn_1^{(2)} = -dn_1^{(1)}$,

$$dG_{T,P} = (\mu_1^{(1)} - \mu_1^{(2)})\, dn_1^{(1)}.$$

Now, before equilibrium is reached, suppose there is a flow of matter from phase 1 to phase 2. Then, $dn_1^{(1)}$ is negative; and, since this flow is irreversible, $dG_{T,P}$ must be negative. Therefore, *while the flow is taking place,*

$$\mu_1^{(1)} > \mu_1^{(2)} \qquad \text{(flow of matter from phase 1 to phase 2),}$$

as mentioned after Eq. (11.20). Obviously, the transfer of matter ceases when the two chemical potentials become equal. The chemical potentials of a constituent in two neighboring phases may be compared with the temperatures and pressures of these phases, thus:

1. If the temperature of phase 1 is greater than that of phase 2, there is a flow of heat that ceases when the temperatures are equal, that is, when thermal equilibrium is established.
2. If the pressure of phase 1 is greater than that of phase 2, there is a "flow" of work that ceases when the pressures are equal, that is, when mechanical equilibrium is established.
3. If the chemical potential of a constituent of phase 1 is greater than that of phase 2, there is a flow of that constituent, which ceases when the chemical potentials are equal, that is, when chemical equilibrium is established.

The equations of phase equilibrium expressing the equality of the chemical potentials of any one constituent in all the φ phases are obviously $\varphi - 1$ in number. Therefore, for c constituents, there are a total of $c(\varphi - 1)$ equations among the μ_j's.

Using the method of Lagrangian multipliers, we should complete our solution of the problem by solving the $c(\varphi - 1)$ equations of phase equilibrium and the c equations of constraint for the $c\varphi$ values of the n_j's that make G a minimum. These values should, of course, be functions of the parameters T and P. We find, however, that the equations do not contain the n_j's in such fashion as to determine their values, because the equations of phase equilibrium are equations among the chemical potentials, which are intensive quantities and depend on the x_j's, which, in turn, contain the n_j's in the special form

$$x_j = \frac{n_j}{\sum n_j}.$$

In other words, the chemical potential for a constituent in a phase depends on the composition of that phase, but not on its total mass.

There are many *different* sets of n_j's that satisfy the equations of phase equilibrium and give rise to the same minimum value of the Gibbs function of the heterogeneous system. This may be seen from the fact that

$$G = \mu_1^{(1)} n_1^{(1)} + \cdots + \mu_c^{(1)} n_c^{(1)} + \cdots + \mu_1^{(\varphi)} n_1^{(\varphi)} + \cdots + \mu_c^{(\varphi)} n_c^{(\varphi)},$$

but, at equilibrium, the chemical potentials of the same constituent are the same in all phases and hence may be written without any superscripts. Factoring out the μ_j's, we get

$$G(\text{min}) = \mu_1 (n_1^{(1)} + \cdots + n_1^{(\varphi)}) + \cdots + \mu_c (n_c^{(1)} + \cdots + n_c^{(\varphi)}).$$

Therefore, *the minimum value of the Gibbs function is the same for many different distributions of the total mass among the phases.* Since we cannot find the values of the n_j's at equilibrium, therefore, we may inquire as to whether we can obtain *any* precise information about a heterogeneous system in equilibrium.

As we have seen, the state of the system at equilibrium is determined by the temperature, the pressure, and $c\varphi$ mole fractions. Hence,

$$\text{Total number of variables} = c\varphi + 2.$$

Among these variables, there are two types of equations: (1) equations of phase equilibrium, which are $c(\varphi - 1)$ in number; and (2) equations of the type $\sum x_j = 1$, for each phase, and, therefore, φ such equations altogether. Hence,

$$\text{Total number of equations} = c(\varphi - 1) + \varphi.$$

If there are as many equations as there are variables, then the temperature, pressure, and composition of the whole system at equilibrium are determined. Such a system is called *nonvariant* and is said to have zero variance. If the number of variables exceeds the number of equations by one, then the equilibrium of the system is not determined until one of the variables is arbitrarily chosen. Such a system is called *monovariant* and is said to have a variance of 1. In general, *the excess of variables over equations is called the* **variance** *f*. Thus,

$$\text{Variance} = (\text{number of variables}) - (\text{number of equations}),$$

or

$$f = \quad (c\varphi + 2) \quad - \quad [c(\varphi - 1) + \varphi];$$

whence,

$$\boxed{f = c - \varphi + 2.} \tag{17.5}$$

This is known as the *phase rule*, which was first derived in 1875 by Josiah Willard Gibbs, who was then professor of mathematical physics at Yale University. The phase rule arose from a general theory of the equilibrium of heterogeneous systems that Gibbs developed during the years 1875 to 1878 and published in an obscure journal, *The Transactions of the Connecticut Academy*. The original paper, entitled "On the Equilibrium of Heterogeneous Substances," was almost 300 pages long. In it, Gibbs considered not only chemical effects but also those produced by gravity, capillarity, and nonhomogeneous strains. It stands today as one of the most profound contributions to the world of human thought and, along with Gibbs' researches in vector analysis and statistical mechanics, places him with the greatest of the world's geniuses.

It is a simple matter to remove the restriction that every constituent must be present in every phase. Suppose that constituent B_1 is absent from phase 1. Then, the equation of equilibrium that exists when the constituent is present, namely,

$$\mu_1^{(1)} = -\lambda_1,$$

is now lacking. However, to describe the composition of the first phase, we need one mole fraction fewer than before. Therefore, since both the number of equations and the number of variables have been reduced by one, the difference is the same and the phase rule remains unchanged.

To remove the second restriction — that no chemical reaction takes place — is more difficult and requires solving the problem *de novo*. Before this is done, however, it is worthwhile to consider a few simple applications of the phase rule in its present form.

17.3
SIMPLE APPLICATIONS OF THE PHASE RULE

As simple examples of the use of the phase rule, we shall consider a pure substance, a simple eutectic solution, and a freezing mixture.

1. ***Pure substance.*** In the case of a pure substance, such as water, the phase rule merely confirms what is already known. If there are two phases in equilibrium (say, solid and vapor), the variance is 1. There is one equation of equilibrium, namely,

$$\mu'(T,P) = \mu'''(T,P),$$

where one prime stands for solid and three primes for vapor. We have already shown that, when a phase consists of only one constituent, the chemical potential is equal to the molar Gibbs function. Hence,

$$g' = g'''$$

is the equation of equilibrium among the two coordinates T and P, which will be recognized as the equation of the sublimation curve. If three phases are in equilibrium, the system is nonvariant, and the two equations of equilibrium

$$g' = g''' \qquad \text{and} \qquad g'' = g'''$$

serve to determine both T and P. The phase rule shows that the maximum number of phases of a one-constituent system that exists in equilibrium is three. The various triple points of water confirm this result.

2. ***Simple eutectic alloy or solution.*** Let us consider a system of two constituents, which neither combine to produce a compound nor form a solid solution, but which, in the liquid phase, are miscible in all proportions. A mixture of gold and thallium has these properties. Suppose that we have a liquid alloy consisting of 40 percent thallium and 60 percent gold in an evacuated chamber originally at about 1000°C. A mixture of thallium and gold vapors will constitute the vapor phase, and we shall have $c = 2$ and $\varphi = 2$. It follows that the variance is 2; hence, the composition and temperature having been chosen, the vapor pressure is determined. If the temperature is now progressively lowered, then a solid phase of pure gold will separate from the liquid at a temperature of about 600°C, and the percentage of thallium in the solution is thus increased. At any given concentration, there will be one, and only one, temperature at which the three phases — vapor mixture, liquid solution, and solid gold — will be in equilibrium, because now $c = 2$ and $\varphi = 3$; therefore, $f = 1$.

By enclosing the metals in a cylinder with a piston on which any desired pressure may be exerted, we may exclude the vapor phase and study the variance of the system when only solid and liquid phases are present. In this way, the temperatures and compositions at which equilibrium exists among various phases may be measured and the results plotted on a phase diagram, such as that shown in Fig. 17-1.

Point A on the figure is the melting point (strictly speaking, the triple point) of pure gold, and B that of pure thallium. When two phases, solution and vapor, are present, the system is divariant; and equilibrium may exist at any temperature and composition represented by a point in the *region* above AEB. When the three phases (solution, vapor, and solid gold) are present, the system is monovariant; and equilibrium may exist only at those temperatures and compositions represented by points on the *curve* AE. Similarly, curve BE represents temperatures and compositions at which the monovariant system consisting of three phases — solution, vapor, and solid thallium — is in equilibrium. The complete curve AEB is known as the *liquidus.*

At point E, there are four phases present: solution, vapor, solid gold, and solid thallium. Hence, $c = 2$, $\varphi = 4$, and $f = 0$, so the system is nonvariant. Point E is known as the *eutectic point,* which is the point an alloy or solution has the lowest melting point possible, and the composition at this point as the *eutectic composition.*

Solution and solid gold may coexist at all temperatures and compositions represented by points in region ACE. Below line CE, however, no liquid can exist, and the system consists of a solid with the eutectic mixture plus free

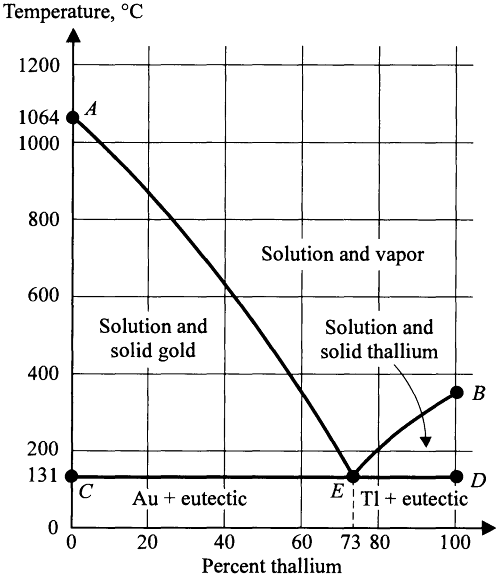


FIGURE 17-1
Phase diagram for eutectic system of gold and thallium.

gold. Solution and solid thallium coexist in region *BED*; and, below *ED*, we have the eutectic mixture plus free thallium. Line *CED* is known as the *solidus*.

There are many different types of eutectic system, each with phase diagrams of different character. All of them, however, may be understood completely in terms of the phase rule.

3. ***Freezing mixture.*** Many years ago, before the commercial use of solid carbon dioxide ("dry ice") as a cooling agent, foods such as ice cream were packed in a container surrounded by a mixture of ice and common salt. If the mixture was thermally insulated and covered, then it maintained a constant temperature of about −21°C. Another practice, which is still current, is to melt the ice that forms on sidewalks and streets by sprinkling salt on it. These phenomena may be clearly understood on the basis of the phase rule.

Consider the phase diagram of sodium chloride and water shown in Fig. 17-2. The point *A* is the triple point of pure water, and *B* is the transition point where the dihydrate $NaCl \cdot 2H_2O$ changes into NaCl. Except for the upper right-hand portion of the figure, the diagram is, in all respects, similar to the simple eutectic diagram of the simple eutectic solution shown in Fig. 17-1. At all points on curve *AE*, the system is monovariant and consists of three phases: solution, vapor, and ice. Similarly, on *EB*, we have solution, vapor, and dihydrate. Point *E* is the eutectic point, which, since in this case the system contains water, is called the *cryohydric point*. The mixture of dihydrate salt and water that forms at the cryohydric point is called a *cryohydrate*.

Only at points below the solidus *CED* can ice and $NaCl \cdot 2H_2O$ exist as solids together. Consequently, when they are mixed at a temperature above

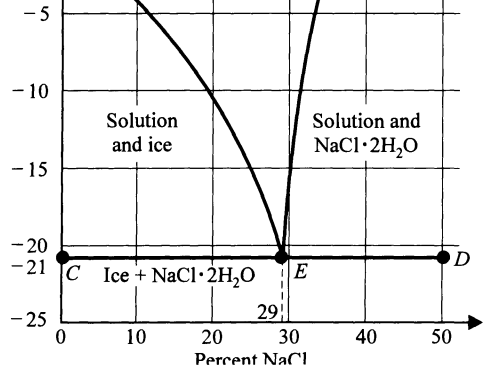


FIGURE 17-2
Phase diagram for a mixture of NaCl and H_2O.

−21°C (as on the sidewalk), they are not in equilibrium and, as a result, the ice melts and the salt dissolves. It should be mentioned at this point that, if the system is open to the air at atmospheric pressure, then there is one more constituent (air), which would ordinarily increase the variance by 1. Since the pressure is constant, however, this extra variance is used up, and the system behaves as before.

If ice, salt, water, and vapor at 0°C are together in a thermally insulated container, they are not in equilibrium, and some ice will melt and dissolve some salt. But, this saturated solution will be too concentrated to be in equilibrium with ice. Ice, therefore, will melt, lowering the concentration of the solution, which will then dissolve more salt. While this is occurring, the temperature of the whole system automatically and spontaneously decreases until the temperature of −21°C is reached. Such a system is known a a *freezing mixture.*

At the transition point *B*, where solid NaCl forms, there are three constituents; hence, one might expect a maximum of five phases to coexist. This is not the case, however, because a chemical reaction

$$\mathrm{NaCl\cdot 2H_2O} \rightleftharpoons \mathrm{NaCl} + \text{solution}$$

takes place. We shall see in the next section that the presence of this reaction causes the system to behave as if there were only two constituents, so that only four phases coexist at the point *B*: solid $NaCl \cdot 2H_2O$, solid NaCl, solution, and vapor.

There are a number of freezing mixtures that are often used for preserving materials at low temperatures. These are listed in Table 17.1.

TABLE 17.1
Freezing mixtures

First constituent	Second constituent	Lowest temperature, °C
NH_4Cl	Ice	−15.4
NaCl	Ice	−21
Alcohol	Ice	−30
$CaCl_2 \cdot 6H_2O$	Ice	−55
Alcohol	Solid CO_2	−72
Ether	Solid CO_2	−77

17.4
PHASE RULE WITH CHEMICAL REACTION

Let us consider a heterogeneous system composed of arbitrary amounts of c constituents, assuming for the sake of simplicity that four of the constituents are chemically active, capable of undergoing the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4.$$

Suppose that there are φ phases and, as only a temporary assumption, that all the constituents are present in all the phases. As before, the Gibbs function of the system is

$$G = \sum_{j=1}^{c} \mu_j^{(1)} n_j^{(1)} + \sum_{j=1}^{c} \mu_j^{(2)} n_j^{(2)} + \cdots + \sum_{j=1}^{c} \mu_j^{(\varphi)} n_j^{(\varphi)}.$$

The equations of constraint for those constituents that do not react are the same type as before; that is, they express the fact that the total number of moles of each inert constituent is constant. In the case of the chemically active constituents, however, the total number of moles of any one is not constant, but is a function of the degree of reaction. Hence, the equations of constraint are

$$\begin{aligned}
n_1^{(1)} + n_1^{(2)} + \cdots + n_1^{(\varphi)} &= (n_0 + n_0')\nu_1(1-\epsilon)\\
n_2^{(1)} + n_2^{(2)} + \cdots + n_2^{(\varphi)} &= (n_0 + n_0')\nu_2(1-\epsilon) + N_2\\
n_3^{(1)} + n_3^{(2)} + \cdots + n_3^{(\varphi)} &= (n_0 + n_0')\nu_3\epsilon\\
n_4^{(1)} + n_4^{(2)} + \cdots + n_4^{(\varphi)} &= (n_0 + n_0')\nu_4\epsilon + N_4\\
n_5^{(1)} + n_5^{(2)} + \cdots + n_5^{(\varphi)} &= \text{const.}\\
\cdots\cdots\cdots\cdots&\cdots\cdots\cdots\cdots\\
n_c^{(1)} + n_c^{(2)} + \cdots + n_c^{(\varphi)} &= \text{const.},
\end{aligned}$$

where n_0, n_0', N_2, and N_4 have their usual meaning. Applying the method of Lagrangian multipliers, we get the equations below (reading across pp. 444 and 445).

Adding, and equating coefficients of the dn_j's to zero, we get the usual $c(\varphi - 1)$ equations of phase equilibrium,

$$\begin{aligned}
\mu_1^{(1)} &= \mu_1^{(2)} = \cdots = \mu_1^{(\varphi)}\\
\mu_2^{(1)} &= \mu_2^{(2)} = \cdots = \mu_2^{(\varphi)}\\
&\cdots\cdots\cdots\cdots\\
\mu_c^{(1)} &= \mu_c^{(2)} = \cdots = \mu_c^{(\varphi)}.
\end{aligned}$$

Equating the coefficient of $d\epsilon$ to zero, we get an extra equation of equilibrium, namely,

$$\lambda_1 \nu_1 + \lambda_2 \nu_2 - \lambda_3 \nu_3 - \lambda_4 \nu_4 = 0,$$

which, since $\lambda_1 = -\mu_1$ of any phase, $\lambda_2 = -\mu_2$ of another phase, etc., becomes

$$\nu_1 \mu_1 + \nu_2 \mu_2 = \nu_3 \mu_3 + \nu_4 \mu_4.$$

This equation will be recognized as the equation of reaction equilibrium, which in the case of ideal gases was found to lead to the law of mass action.

The rest of the argument follows the same lines as before. There are $c(\varphi - 1)$ equations of phase equilibrium, one equation of reaction equilibrium, and φ equations of the type $\sum x_j = 1$. Hence, the total number of equations is

$$c(\varphi - 1) + 1 + \varphi.$$

Since the variables are the same as before, namely, T, P, and the x_j's, of which there are $c\varphi + 2$ in number, the variance is

$$f = c\varphi + 2 - [c(\varphi - 1) + 1 + \varphi],$$

or

$$f = (c - 1) - \varphi + 2. \tag{17.6}$$

The phase rule in this case is seen to be different, in that $c - 1$ now stands where c formerly stood. For the reason given before, this form of the phase rule remains unchanged when every constituent is not present in every phase. We see, therefore, that if there are c constituents, present in arbitrary amounts, and only one chemical reaction, then there is one extra equation of equilibrium and the variance is reduced by 1. It is obvious that, if there were two independent chemical reactions, then there would be two extra equations

---

$$\begin{array}{llllllll}
\multicolumn{7}{l}{\mu_1^{(1)} dn_1^{(1)} + \cdots + \mu_4^{(1)} dn_4^{(1)} + \cdots + \mu_c^{(1)} dn_c^{(1)}} & + \cdots + \\
\lambda_1 \, dn_1^{(1)} & & & & & & & + \cdots + \\
& \lambda_2 \, dn_2^{(1)} & & & & & & + \cdots + \\
& & \lambda_3 \, dn_3^{(1)} & & & & & + \cdots + \\
& & & \lambda_4 \, dn_4^{(1)} & & & & + \cdots + \\
& & & & \lambda_5 \, dn_5^{(1)} & & & + \cdots + \\
& & & & & \cdot & & \cdot \\
& & & & & \quad \cdot & & \cdot \\
& & & & & \qquad \cdot & & \cdot \\
& & & & & & \lambda_c \, dn_c^{(1)} & + \cdots +
\end{array}$$

---

of equilibrium; thus, the phase rule would become $f = (c - 2) - \varphi + 2$. For r independent reactions, we would have

$$f = (c - r) - \varphi + 2. \tag{17.7}$$

The argument up to now has been based on the fact that only three kinds of equations have existed among the variables T, P, and the x_j's: equations of phase equilibrium, equations of reaction equilibrium, and equations of the type $\sum x_j = 1$. It often happens, however, that a chemical reaction takes place in such a manner that additional equations expressing further restrictions upon the x_j's are available. Suppose, for example, that we put an arbitrary amount of solid NH_4HS into an evacuated chamber and two new constituents form, according to the reaction

$$NH_4HS \rightleftharpoons NH_3 + H_2S.$$

Since gaseous NH_3 and H_2S are in the same phase, the restriction always exists that

$$x_{NH_3} = x_{H_2S}.$$

This represents a fourth type of equation, to be added to the three listed at the beginning of this paragraph.

Another example of additional restricting equations among the x_j's is provided by the phenomenon of dissociation in solution. Suppose that we

---

$$\begin{array}{llr}
\mu_1^{(\varphi)} dn_1^{(\varphi)} + \cdots + \mu_4^{(\varphi)} dn_4^{(\varphi)} + \cdots + \mu_c^{(\varphi)} dn_c^{(\varphi)} & & = 0 \\
\lambda_1\, dn_1^{(\varphi)} & + \lambda_1(n_0 + n_0')\nu_1\, d\epsilon & = 0 \\
\quad \lambda_2\, dn_2^{(\varphi)} & + \lambda_2(n_0 + n_0')\nu_2\, d\epsilon & = 0 \\
\qquad \lambda_3\, dn_3^{(\varphi)} & - \lambda_3(n_0 + n_0')\nu_3\, d\epsilon & = 0 \\
\qquad\quad \lambda_4\, dn_4^{(\varphi)} & - \lambda_4(n_0 + n_0')\nu_4\, d\epsilon & = 0 \\
\qquad\qquad \lambda_5\, dn_5^{(\varphi)} & & = 0 \\
\qquad\qquad\quad \cdot & & \cdot \\
\qquad\qquad\quad \cdot & & \cdot \\
\qquad\qquad\quad \cdot & & \cdot \\
\qquad\qquad\qquad \lambda_c dn_c^{(\varphi)} & & = 0.
\end{array}$$

have a heterogeneous system, one of whose phases is a solution of salt 2 in solvent 1. Suppose that the salt dissociates according to the scheme shown in Fig. 17-3(*a*). All the ions, of course, remain in the liquid phase, and no precipitate is formed. Consequently, we have the equation

$$x_3 = x_4,$$

which expresses the fact that the solution is electrically neutral. If multiple dissociation takes place according to the scheme shown in Fig. 17-3(*b*), then there are three independent restricting equations among the x_j's namely,

$$x_3 = x_8 + x_6 + x_4,$$

$$x_5 = x_8 + x_6,$$

and

$$x_7 = x_8.$$

Adding these equations, we get the *dependent* equation

$$x_3 + x_5 + x_7 = 3x_8 + 2x_6 + x_4,$$

expressing the fact of electrical neutrality.

Let us call equations of the preceding type *restricting equations*, and let us suppose that z of them are independent. Then, we may list four types of equations among T, P, and the x_j's, thus:

1. Equations of phase equilibrium [$c(\varphi - 1)$ in number].
2. Equations of reaction equilibrium (r in number).
3. Equations of the type $\sum x_j = 1$ (φ in number).
4. Restricting equations (z in number).

Hence, the total number of equations is

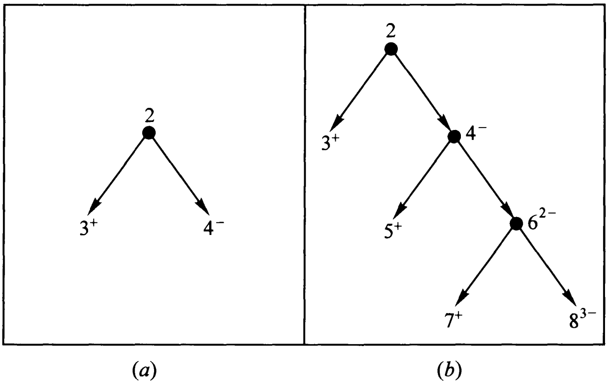


FIGURE 17-3
Dissociations of a salt that give rise to additional restricting equations among the mole fractions: (*a*) single dissociation; (*b*) multiple dissociation.

$$c(\varphi - 1) + r + \varphi + z;$$

and, as usual, the total number of variables is $c\varphi + 2$. Therefore,

$$f = c\varphi + 2 - [c(\varphi - 1) + r + \varphi + z],$$

or

$$f = (c - r - z) - \varphi + 2.$$

If we define the *number of components c' as the total number of constituents minus the number of independent reactions minus the number of independent restricting equations, that is,*

$$\boxed{c' = c - r - z,} \tag{17.8}$$

then we may write the phase rule for components in the same form, thus:

$$\boxed{f = c' - \varphi + 2.} \tag{17.9}$$

17.5
DETERMINATION OF THE NUMBER OF COMPONENTS

The problem of determining the number of components in a heterogeneous system may be somewhat difficult for the beginner. As a result of experience with the behavior of typical heterogeneous systems, the physical chemist is able to determine the number of components by counting the smallest number of constituents whose specification is sufficient to determine the composition of every phase. The validity of this working rule rests upon a few fundamental facts, whose truth we shall demonstrate rigorously in this section.

EXAMPLE 1. First, let us consider a heterogeneous system consisting of a liquid phase composed of a solution of the salt NaH_2PO_4 in water and a vapor phase composed of water vapor. It is important to show that, *so long as no precipitate is formed by virtue of a reaction between the salt and the water, no matter what else we assume to take place in the solution, the number of components c' is two.*

1. *Neglecting all dissociation.* There are two constituents, no chemical reactions, and no restricting equations. Hence,

$$c' = 2 - 0 - 0 = 2.$$

2. *Assuming single dissociation of the salt.* There are four constituents: NaH_2PO_4, H_2O, Na^+, and $H_2PO_4^-$; one chemical reaction,

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-;$$

and one restricting equation,

$$x_{Na^+} = x_{H_2PO_4^-}.$$

Hence, $c' = 4 - 1 - 1 = 2$.

3. *Assuming multiple dissociation of the salt.* There are seven constituents, including water, which does not dissociate, and three independent chemical reactions, as shown in Fig. 17-4(*a*); and two independent restricting equations,

$$x_{\mathrm{Na}^+} = x_{\mathrm{PO}_4^{3-}} + x_{\mathrm{HPO}_4^{2-}} + x_{\mathrm{H_2PO}_4^-}$$

and

$$x_{\mathrm{H}^+} = 2x_{\mathrm{PO}_4^{3-}} + x_{\mathrm{HPO}_4^{2-}}.$$

(By adding the two equations, the *dependent* equation expressing electrical neutrality of the solution is obtained.) Hence, $c' = 7 - 3 - 2 = 2$.

4. *Assuming dissociation of the water also.* There are eight constituents and four independent chemical reactions, as shown in Fig. 17-4(*b*); and two independent restricting equations,

$$x_{\mathrm{Na}^+} = x_{\mathrm{PO}_4^{3-}} + x_{\mathrm{HPO}_4^{2-}} + x_{\mathrm{H_2PO}_4^-}$$

and

$$x_{\mathrm{H}^+} = 2x_{\mathrm{PO}_4^{3-}} + x_{\mathrm{HPO}_4^{2-}} + x_{\mathrm{OH}^-}.$$

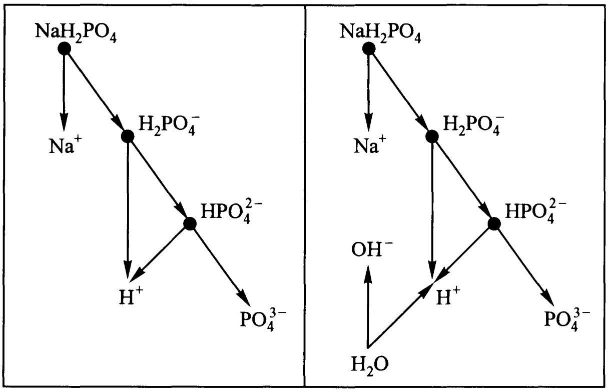
Hence, $c' = 8 - 4 - 2 = 2$.

5. *Assuming association of the water.* A ninth constituent, $(\mathrm{H_2O})_2$, is formed as a result of a fifth independent reaction,

$$\mathrm{H_2O} \rightleftharpoons \tfrac{1}{2}(\mathrm{H_2O})_2.$$

There are still the same two independent restricting equations, and hence $c' = 9 - 5 - 2 = 2$.

It is clear, therefore, that it is a matter of indifference as to what chemical changes take place in the solution. The number of components is always two, provided that no precipitate forms.



(*a*) (*b*)

FIGURE 17-4
Multiple dissociation of $\mathrm{NaH_2PO_4}$: (*a*) without dissociation of $\mathrm{H_2O}$; (*b*) with dissociation of $\mathrm{H_2O}$.

EXAMPLE 2.. To investigate the effect of precipitate, let us consider a mixture of $AlCl_3$ and water. In this case, the $AlCl_3$ combines with the water to form $Al(OH)_3$, some of which precipitates out of the solution, according to the reaction shown in Fig. 17-5. There are eight constituents and only four independent reactions. At first thought, one might imagine that there are five independent reactions, but if we write the equations of reaction equilibrium corresponding to the four dissociations:

$$3\mu_{H_2O} = 3\mu_{H^+} + 3\mu_{OH^-},$$

$$\mu_{AlCl_3} = \mu_{Al^{3+}} + 3\mu_{Cl^-},$$

$$\mu_{Al(HO)_3} = \mu_{Al^{3+}} + 3\mu_{OH^-},$$

and

$$3\mu_{HCl} = 3\mu_{H^+} + 3\mu_{Cl^-},$$

and add the first two equations and subtract the sum of the last two equations, we get

$$3\mu_{H_2O} + \mu_{AlCl_3} = \mu_{Al(OH)_3} + 3\mu_{HCl},$$

which is the equation of reaction equilibrium corresponding to the reaction

$$3H_2O + AlCl_3 \rightleftharpoons Al(OH)_3 + 3HCl,$$

which, therefore, is seen to be a *dependent* reaction.

Since some of the $Al(OH)_3$ has precipitated out, there is only one restricting equation, namely, that expressing the electrical neutrality of the solution,

$$3x_{Al^{3+}} + x_{H^+} = x_{OH^-} + x_{Cl^-}.$$

Consequently, $c' = 8 - 4 - 1 = 3$ and we have an interesting situation in which a heterogeneous system, formed originally by mixing two substances, has three components.

EXAMPLE 3. As a last example, let us consider a system consisting of water vapor and a solution containing arbitrary amounts of NaCl and KNO_3 in water.

1. *Neglecting all dissociations.* There are five constituents; H_2O, NaCl, KNO_3, $NaNO_3$, and KCl; one reaction,

$$NaCl + KNO_3 \rightleftharpoons NaNO_3 + KCl;$$

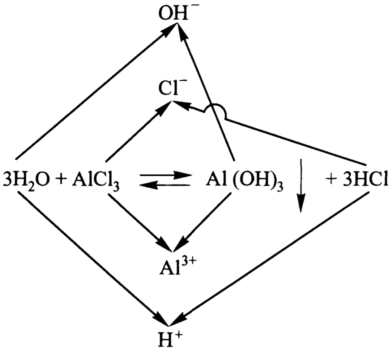


FIGURE 17-5
Dissociation, reaction, and precipitation that occur when $AlCl_3$ is dissolved in water.

and one restricting equation,

$$x_{\mathrm{NaNO_3}} = x_{\mathrm{KCl}}.$$

Hence, the number of components $c' = 5 - 1 - 1 = 3$.

2. *Considering all reactions.* There are eleven constituents, which undergo these reactions:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-},$$
$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-},$$
$$\mathrm{KNO_3} \rightleftharpoons \mathrm{K^+} + \mathrm{NO_3^-},$$
$$\mathrm{NaNO_3} \rightleftharpoons \mathrm{Na^+} + \mathrm{NO_3^-},$$

and

$$\mathrm{KCl} \rightleftharpoons \mathrm{K^+} + \mathrm{Cl^-}.$$

It should be noticed that the reaction

$$\mathrm{NaCl} + \mathrm{KNO_3} \rightleftharpoons \mathrm{NaNO_3} + \mathrm{KCl}$$

is not independent of the preceding five reactions, but that its equation of reaction equilibrium may be obtained by adding the second and third reactions and subtracting the sum of the fourth and fifth reactions.

There are three restricting equations. The first equation,

$$x_{\mathrm{Na^+}} + x_{\mathrm{NaNO_3}} = x_{\mathrm{Cl^-}} + x_{\mathrm{KCl}},$$

expresses the fact that the amount of sodium lost by the NaCl (to form $\mathrm{Na^+}$ and $\mathrm{NaNO_3}$) is equal to the amount of chlorine lost by the NaCl (to form $\mathrm{Cl^-}$ and KCl). The second equation,

$$x_{\mathrm{K^+}} + x_{\mathrm{KCl}} = x_{\mathrm{NO_3^-}} + x_{\mathrm{NaNO_3}},$$

expresses the corresponding fact concerning the loss of potassium and nitrate from $\mathrm{KNO_3}$. The third equation is

$$x_{\mathrm{H^+}} = x_{\mathrm{OH^-}}.$$

(The dependent equation of electrical neutrality is obtained by adding these three equations.) Hence, $c' = 11 - 5 - 3 = 3$.

In the event that we start with arbitrary amounts of all five substances ($\mathrm{H_2O}$, NaCl, $\mathrm{KNO_3}$, $\mathrm{NaNO_3}$, and KCl), there are still eleven constituents and five independent reactions, but only two restricting equations, namely,

$$x_{\mathrm{Na^+}} + x_{\mathrm{K^+}} + x_{\mathrm{H^+}} = x_{\mathrm{Cl^-}} + x_{\mathrm{NO_3^-}} + x_{\mathrm{OH^-}},$$

which expresses electrical neutrality, and

$$x_{\mathrm{H^+}} = x_{\mathrm{OH^-}}.$$

Hence, the number of components, $c' = 11 - 5 - 2 = 4$.

17.6
DISPLACEMENT OF EQUILIBRIUM

Consider a heterogeneous system of φ phases and c constituents, four of which undergo the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4.$$

Any infinitesimal process involving a change in temperature, pressure, and composition of the phases is accompanied by a change in the Gibbs function equal to

$$\begin{aligned} d\boldsymbol{G} = -\boldsymbol{S}\,dT + \boldsymbol{V}\,dP + \mu_1^{(1)}\,dn_1^1 + \cdots + \mu_c^{(1)}\,dn_c^{(1)} \\ + \cdots + \mu_1^{(\varphi)}\,dn_1^{(\varphi)} + \cdots + \mu_c^{(\varphi)}\,dn_c^{(\varphi)}. \end{aligned}$$

In general, during such an infinitesimal change, there is neither equilibrium among the phases nor equilibrium with regard to the chemical reaction. Complete chemical equilibrium would require both phase equilibrium and reaction equilibrium. *Suppose we assume phase equilibrium only.* Then,

$$\begin{aligned} \mu_1^{(1)} &= \mu_1^{(2)} = \cdots = \mu_1^{(\varphi)} \\ \mu_2^{(1)} &= \mu_2^{(2)} = \cdots = \mu_2^{(\varphi)} \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ \mu_c^{(1)} &= \mu_c^{(2)} = \cdots = \mu_c^{(\varphi)}, \end{aligned}$$

and the change in the Gibbs function becomes

$$\begin{aligned} d\boldsymbol{G} = -\boldsymbol{S}\,dT + \boldsymbol{V}\,dP + \mu_1(dn_1^{(1)} + \cdots + dn_1^{(\varphi)}) \\ + \cdots + \mu_4(dn_4^{(1)} + \cdots + dn_4^{(\varphi)}) + \mu_5(dn_5^{(1)} + \cdots + dn_5^{(\varphi)}) \\ + \cdots + \mu_c(dn_c^{(1)} + \cdots + dn_c^{(\varphi)}). \end{aligned}$$

But,

$$\begin{aligned} dn_1^{(1)} + \cdots + dn_1^{(\varphi)} &= -(n_0 + n_0')\nu_1\,d\epsilon \\ dn_2^{(1)} + \cdots + dn_2^{(\varphi)} &= -(n_0 + n_0')\nu_2\,d\epsilon \\ dn_3^{(1)} + \cdots + dn_3^{(\varphi)} &= +(n_0 + n_0')\nu_3\,d\epsilon \\ dn_4^{(1)} + \cdots + dn_4^{(\varphi)} &= +(n_0 + n_0')\nu_4\,d\epsilon \\ dn_5^{(1)} + \cdots + dn_5^{(\varphi)} &= 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ dn_c^{(1)} + \cdots + dn_c^{(\varphi)} &= 0. \end{aligned}$$

Therefore, the change in the Gibbs function during an infinitesimal process in which there is phase equilibrium, but not reaction equilibrium, is given by

$$d\boldsymbol{G} = -\boldsymbol{S}\,dT + \boldsymbol{V}\,dP + (n_0 + n_0')(\nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2)\,d\epsilon.$$

Since, under these circumstances, $\boldsymbol{G}$ is a function of T, P, and ϵ, it follows that

$$\left(\frac{\partial G}{\partial T}\right)_{P,\epsilon} = -S,$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,\epsilon} = V,$$

and
$$\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = (n_0 + n_0')(\nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2).$$

When reaction equilibrium exists at temperature T and pressure P, we must have $(\partial G/\partial\epsilon)_{T,P} = 0$ at $\epsilon = \epsilon_e$. If we go to a slightly different equilibrium state at temperature $T + dT$ and pressure $P + dP$, then the new degree of reaction will be $\epsilon_e + d\epsilon_e$ and the change in $(\partial G/\partial\epsilon)_{T,P}$ during this process is zero. Therefore,

$$d\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} = 0.$$

But,

$$\begin{aligned} d\left(\frac{\partial G}{\partial \epsilon}\right)_{T,P} &= \left(\frac{\partial^2 G}{\partial T\,\partial \epsilon}\right)_{P,T,\epsilon} dT + \left(\frac{\partial^2 G}{\partial P\,\partial \epsilon}\right)_{T,P,\epsilon} dP + \left(\frac{\partial^2 G}{\partial \epsilon^2}\right)_{T,P} d\epsilon = 0 \\ &= \frac{\partial}{\partial \epsilon}\left[\left(\frac{\partial G}{\partial T}\right)_{P,\epsilon}\right]_{T,P} dT + \frac{\partial}{\partial \epsilon}\left[\left(\frac{\partial G}{\partial P}\right)_{T,\epsilon}\right]_{T,P} dP + \left(\frac{\partial^2 G}{\partial \epsilon^2}\right)_{T,P} d\epsilon = 0 \\ &= -\left(\frac{\partial S}{\partial \epsilon}\right)_{T,P} dT + \left(\frac{\partial V}{\partial \epsilon}\right)_{T,P} dP + \left(\frac{\partial^2 G}{\partial \epsilon^2}\right)_{T,P} d\epsilon = 0. \end{aligned}$$

Solving for $d\epsilon = d\epsilon_e$, we get

$$d\epsilon_e = \frac{(\partial S/\partial\epsilon)_{T,P}}{(\partial^2 G/\partial\epsilon^2)_{T,P}} dT - \frac{(\partial V/\partial\epsilon)_{T,P}}{(\partial^2 G/\partial\epsilon^2)_{T,P}} dP. \qquad (17.10)$$

Recognizing that, at thermodynamic equilibrium, $đQ = T\,dS$, or

$$\left(\frac{đQ}{d\epsilon}\right)_{T,P} = T\left(\frac{\partial S}{\partial \epsilon}\right)_{T,P}, \qquad (17.11)$$

we get
$$\left(\frac{\partial \epsilon_e}{\partial T}\right)_P = \frac{(đQ/d\epsilon)_{T,P}}{T(\partial^2 G/\partial\epsilon^2)_{T,P}} \qquad (17.12)$$

$$\left(\frac{\partial \epsilon_e}{\partial P}\right)_T = -\frac{(\partial V/\partial\epsilon)_{T,P}}{(\partial^2 G/\partial\epsilon^2)_{T,P}}. \qquad (17.13)$$

Since G is a minimum at thermodynamic equilibrium, $(\partial^2 G/\partial\epsilon^2)_{T,P}$ is positive. Equation (17.12) states, therefore, that an increase of temperature at constant pressure always causes a reaction to proceed in the direction in which heat is absorbed at constant T and P; whereas, from Eq. (17.13), we see that an increase of pressure at constant temperature causes a reaction to proceed in the direction in which the volume decreases at constant T and P.

PROBLEMS

17.1. All the lettered points in Fig. P17-1 lie in one plane. The line CD separates the plane into two regions: on the left, a wave has the speed w; and on the right, the speed w'. Show by the method of Lagrangian multipliers that the time for the wave to travel the path APB is a minimum when $w/w' = \sin\phi/\sin\phi'$.

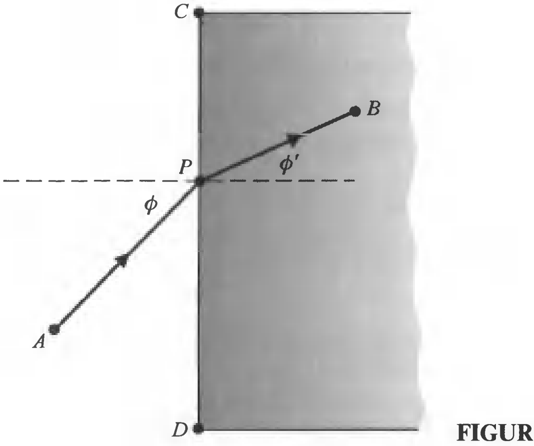


FIGURE P17-1

17.2. A hot metal of mass m, specific heat c_P, and temperature T_i is immersed in a cooler liquid of mass m', specific heat c_P', and temperature T_i'. The entire system is thermally insulated. If the final temperature of the metal is T_f and that of the liquid is T_f', then show by the method of Lagrangian multipliers that the condition for the entropy change of the universe to be a maximum is that $T_f = T_f'$.

17.3. Consider a homogeneous mixture of four ideal gases capable of undergoing the reaction

$$\nu_1 B_1 + \nu_2 B_2 \rightleftharpoons \nu_3 B_3 + \nu_4 B_4.$$

How many components are there if one starts with:
(*a*) Arbitrary amounts of B_1 and B_2 only.
(*b*) Arbitrary amounts of all four gases.
(*c*) ν_1 moles of B_1 and ν_2 moles of B_2 only.

17.4. Consider a system composed of a solid phase of calcium carbonate ($CaCO_3$); a solid phase of calcium oxide (CaO); and a gaseous phase consisting of a mixture of CO_2, $CaCo_3$ vapor, and CaO vapor; all three constituents being present initially in arbitrary amounts. These are the substances that are present in a limekiln, where the reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

occurs.

(*a*) How many components are there, and what is the variance?

(*b*) Assuming the gaseous phase to be a mixture of ideal gases, show that

$$\frac{p_{CaO}p_{CO_2}}{p_{CaCO_3}} = K.$$

(*c*) If solid $CaCO_3$ is introduced into an evacuated chamber, how many components are there, and what is the variance?

17.5. Solid ammonium hydrosulphide (NH_4HS) is mixed with arbitrary amounts of gaseous NH_3 and H_2S, forming a three-constituent system of two phases, undergoing the reaction

$$NH_4HS \rightleftharpoons NH_3 + H_2S.$$

(*a*) How many components are there, and what is the variance?

(*b*) Assuming that the gaseous phase is a mixture of ideal gases, show that

$$\frac{p_{NH_3}p_{H_2S}}{p_{NH_4HS}} = K.$$

(*c*) If solid NH_4HS is placed in an evacuated chamber, how many components are there, and what is the variance?

17.6. How many components are there in a system composed of arbitrary amounts of water, sodium chloride, and barium chloride?

17.7. At high temperature, the following reactions take place:

$$C + CO_2 \rightleftharpoons 2CO,$$

and

$$CO_2 + H_2 \rightleftharpoons CO + H_2O.$$

How many components are there if we start with:

(*a*) Arbitrary amounts of C, CO_2, and H_2?

(*b*) Arbitrary amounts of C, CO_2, H_2, CO, and H_2O?

17.8. Consider a system consisting of a pure liquid phase in equilibrium with a gaseous phase, composed of a mixture of the vapor of the liquid and an inert gas that is insoluble in the liquid. Suppose that the inert gas (sometimes called the *foreign gas*) can flow into or out of the gaseous phase, so that the total pressure can be varied at will.

(*a*) How many components are there, and what is the variance?

(*b*) Assuming the gaseous phase to be a mixture of ideal gases, show that

$$g'' = RT(\phi + \ln p),$$

where g'' is the molar Gibbs function of the liquid, and ϕ and p refer to the vapor.

(*c*) Suppose that a little more foreign gas is added, thus increasing the pressure from P to $P + dP$, at constant temperature. Show that

$$v''dP = RT\frac{dp}{p},$$

where v'' is the molar volume of the liquid, which is practically constant.

(*d*) Integrating at constant temperature from an initial state, where there is no foreign gas, to a final state, where the total pressure is P and the partial vapor pressure is p, show that

$$\ln\frac{p}{P_0}=\frac{v''}{RT}(P-P_0) \qquad \text{(Gibbs' equation)},$$

where P_0 is the vapor pressure when no foreign gas is present.

(*e*) In the case of water at 0°C, at which $P_0 = 4.58$ mm Hg, show that, when there is sufficient air above the water to make the total pressure equal to 10 atm, $p = 4.62$ mm Hg.

17.9. The Gibbs function G of a liquid phase consisting of a solvent and very small amounts of several solutes is

$$G=\mu_0 n_0+\mu_1 n_1+\mu_2 n_2+\cdots,$$

where the subscript zero refers to the solvent, and

$$\mu_j = g_j + RT\ln x_j.$$

(*a*) Using the relation $V=(\partial G/\partial P)_T$, show that

$$V=\sum n_j v_j.$$

(*b*) Using the relation $H=G-T(\partial G/\partial T)_P$, show that

$$H=\sum n_j h_j,$$

which means that there is no heat of dilution.

17.10. A very small amount of sugar is dissolved in water, and the solution is in equilibrium with pure water vapor.

(*a*) Show that the equation of phase equilibrium is

$$g'''=g''+RT\ln\,(1-x),$$

where g''' is the molar Gibbs function of water vapor, g'' is the molar Gibbs function of pure liquid water, and x is the mole fraction of the sugar in solution.

(*b*) For an infinitesimal change in x at constant temperature, show that

$$(v'''-v'')\,dP=RT\,d\ln(1-x).$$

(*c*) Assuming the vapor to behave like an ideal gas and regarding v'' as constant, integrate the preceding equation at constant temperature from an initial state $x=0$, $P=P_0$, to a final state $x=x$, $P=P_x$, and derive

$$\ln\frac{P_x}{P_0}=\ln(1-x)+\frac{v''}{RT}(P_x-P_0),$$

where P_0 is the vapor pressure of the pure liquid and P_x is the vapor pressure of the dilute solution.

(*d*) Justify neglecting the last term on the right, and show that

$$P_x = P_0(1 - x) \qquad \text{(Raoult's law)},$$

or

$$\frac{P_0 - P_x}{P_0} = x.$$

17.11. Consider the system of Prob. 17.10, and let x stand for the mole fraction of the sugar.

(*a*) For an infinitesimal change in x at constant pressure, show that

$$-s''' \, dT = -s'' \, dT + R \ln(1 - x) \, dT + RT \, d \ln(1 - x).$$

(*b*) Substituting for $R \ln(1 - x)$ the value obtained from the equation of phase equilibrium, show that the equation in part (*a*) reduces to

$$0 = \frac{h''' - h''}{T} dT + RT \, d \ln(1 - x).$$

(*c*) Taking into account that $x \ll 1$ and calling $h''' - h''$ the latent heat of vaporization l_V, show that the elevation of the boiling point is

$$\Delta T = \frac{RT^2}{l_V} x.$$

17.12. A very small amount of sugar is dissolved in water, and the solution is in equilibrium with pure ice. The equation of phase equilibrium is

$$g' = g'' + RT \ln(1 - x),$$

where g' is the molar Gibbs function of pure ice, g'' is the molar Gibbs function of pure water, and x is the mole fraction of sugar in solution.

(*a*) For an infinitesimal change in x at constant pressure, show that

$$-s' \, dT = -s'' \, dT + R \ln(1 - x) \, dT + RT \, d \ln(1 - x).$$

(*b*) Substituting for $R \ln(1 - x)$ the value obtained from the equation of phase equilibrium, show that the equation in part (*a*) reduces to

$$\frac{h'' - h'}{T} \, dT = RT \, d \ln(1 - x).$$

(*c*) Taking into account that $x \ll 1$ and calling $h'' - h'$ the latent heat of fusion l_F, show that the depression of the freezing point is

$$\Delta T = -\frac{RT^2}{l_F} x.$$

17.13. In the osmotic pressure apparatus depicted in Fig. P17-2, let the pressure of the pure solvent be P_0 and that of the dilute solution be P, the temperature being T throughout the system. The molar Gibbs function of the pure solvent is g''.

(*a*) Show that, at equilibrium,

$$g''(T, P_0) = g''(T, P) + RT \ln(1 - x),$$

where x is the mole-fraction of the solute.

(*b*) For an infinitesimal change of x at constant T, show that

$$0 = v'' \, dP + RT \, d \ln(1 - x).$$

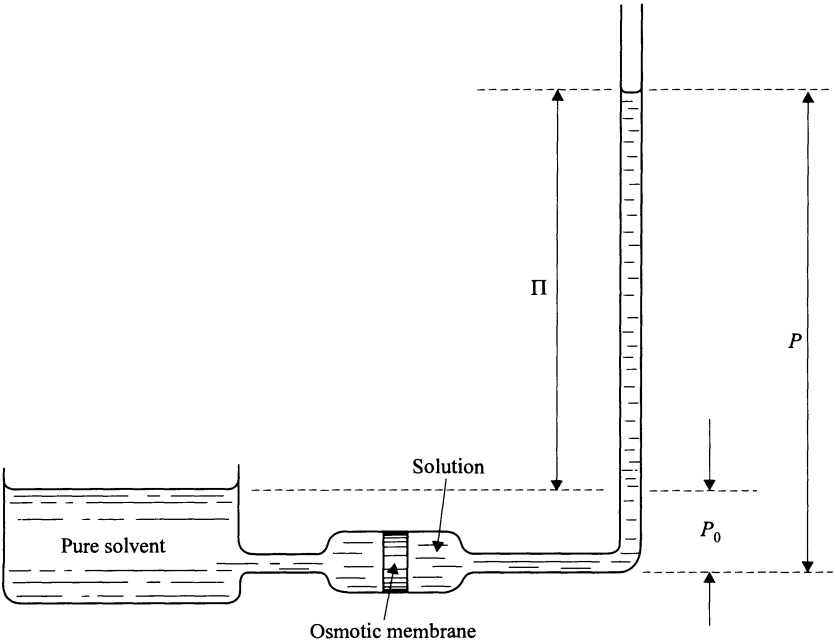


FIGURE P17-2

(*c*) Integrating P from P_0 to P, and x from 0 to x, show that

$$\Pi v'' = xRT,$$

where $\Pi = P - P_0$. Compare this equation with the ideal-gas law.

APPENDIX A

Physical Constants

Constant	Symbol	Rounded value
Molar gas constant	$R = N_A k$	8.315 J/mol · K
Avogadro's number	N_A	6.022×10^{23} particles/mol
Boltzmann's constant	k	1.381×10^{-23} J/K
Stefan-Boltzmann constant	σ	5.671×10^{-8} W/m^2 · K^4
Faraday's constant	F	96,485 C/mol
Elementary charge	e	1.602×10^{-19} C
Electron mass	m_e	9.109×10^{-31} kg
Speed of light in vacuum	c	2.998×10^{8} m/s
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ N/A^2
Permittivity of vacuum	ϵ_0	8.854×10^{-12} F/m
Planck's constant	h	6.626×10^{-34} J · s
Bohr magneton	μ_B	9.274×10^{-24} J/T
Nuclear magneton	μ_N	5.051×10^{-27} J/T
Proton mass	m_p	1.673×10^{-27} kg
Electron-volt	eV	1.602×10^{-29} J
Atomic mass unit	m_u	1.661×10^{-27} kg
Atmosphere of pressure	atm	1.013×10^{5} Pa

APPENDIX B

Method of Lagrangian Multipliers

Let us consider for the sake of simplicity a function f of only four variables, y_1, y_2, y_3, and y_4, that is to be rendered an extremum, subject to the equations of constraint:

$$\psi_1(y_1, y_2, y_3, y_4) = 0,$$

and

$$\psi_2(y_1, y_2, y_3, y_4) = 0.$$

Since there are two equations of constraint, only two of the four y's are independent. Taking the differential of the function f and equating it to zero, we get

$$\frac{\partial f}{\partial y_1} dy_1 + \frac{\partial f}{\partial y_2} dy_2 + \frac{\partial f}{\partial y_3} dy_3 + \frac{\partial f}{\partial y_4} dy_4 = 0.$$

Taking the differential of the equations of constraint, we get

$$\frac{\partial \psi_1}{\partial y_1} dy_1 + \frac{\partial \psi_1}{\partial y_2} dy_2 + \frac{\partial \psi_1}{\partial y_3} dy_3 + \frac{\partial \psi_1}{\partial y_4} dy_4 = 0,$$

and

$$\frac{\partial \psi_2}{\partial y_1} dy_1 + \frac{\partial \psi_2}{\partial y_2} dy_2 + \frac{\partial \psi_2}{\partial y_3} dy_3 + \frac{\partial \psi_2}{\partial y_4} dy_4 = 0.$$

Multiplying the first of the above two equations by λ_1 and the second by λ_2, we have the three equations

$$\frac{\partial f}{\partial y_1} dy_1 + \frac{\partial f}{\partial y_2} dy_2 + \frac{\partial f}{\partial y_3} dy_3 + \frac{\partial f}{\partial y_4} dy_4 = 0,$$

$$\lambda_1 \frac{\partial \psi_1}{\partial y_1} dy_1 + \lambda_1 \frac{\partial \psi_1}{\partial y_2} dy_2 + \lambda_1 \frac{\partial \psi_1}{\partial y_3} dy_3 + \lambda_1 \frac{\partial \psi_1}{\partial y_4} dy_4 = 0,$$

and

$$\lambda_2 \frac{\partial \psi_2}{\partial y_1} dy_1 + \lambda_2 \frac{\partial \psi_2}{\partial y_2} dy_2 + \lambda_2 \frac{\partial \psi_2}{\partial y_3} dy_3 + \lambda_2 \frac{\partial \psi_2}{\partial y_4} dy_4 = 0,$$

where λ_1 and λ_2 are unknown arbitrary functions of y_1, y_2, y_3, and y_4, known as *Lagrangian multipliers.* Adding the three equations, we get

$$\left(\frac{\partial f}{\partial y_1}+\lambda_1\frac{\partial\psi_1}{\partial y_1}+\lambda_2\frac{\partial\psi_2}{\partial y_1}\right)dy_1+\left(\frac{\partial f}{\partial y_2}+\lambda_1\frac{\partial\psi_1}{\partial y_2}+\lambda_2\frac{\partial\psi_2}{\partial y_2}\right)dy_2$$
$$+\left(\frac{\partial f}{\partial y_3}+\lambda_1\frac{\partial\psi_1}{\partial y_3}+\lambda_2\frac{\partial\psi_2}{\partial y_3}\right)dy_3+\left(\frac{\partial f}{\partial y_4}+\lambda_1\frac{\partial\psi_1}{\partial y_4}+\lambda_2\frac{\partial\psi_2}{\partial y_4}\right)dy_4=0.$$

Now, the values to be ascribed to the multipliers λ_1 and λ_2 may be chosen at will. Let us choose λ_1 and λ_2 such that the first two parentheses vanish. This provides two equations,

$$\frac{\partial f}{\partial y_1}+\lambda_1\frac{\partial\psi_1}{\partial y_1}+\lambda_2\frac{\partial\psi_2}{\partial y_1}=0,$$

and

$$\frac{\partial f}{\partial y_2}+\lambda_1\frac{\partial\psi_1}{\partial y_2}+\lambda_2\frac{\partial\psi_2}{\partial y_2}=0,$$

which serve to determine the values of λ_1 and λ_2. We are then left with the equation

$$\left(\frac{\partial f}{\partial y_3}+\lambda_1\frac{\partial\psi_1}{\partial y_3}+\lambda_2\frac{\partial\psi_2}{\partial y_3}\right)dy_3+\left(\frac{\partial f}{\partial y_4}+\lambda_1\frac{\partial\psi_1}{\partial y_4}+\lambda_2\frac{\partial\psi_2}{\partial y_4}\right)dy_4=0.$$

Since two of the four y's are independent, let us regard y_3 and y_4 as the independent variables. Then, it follows that

$$\frac{\partial f}{\partial y_3}+\lambda_1\frac{\partial\psi_1}{\partial y_3}+\lambda_2\frac{\partial\psi_2}{\partial y_3}=0,$$

and

$$\frac{\partial f}{\partial y_4}+\lambda_1\frac{\partial\psi_1}{\partial y_4}+\lambda_2\frac{\partial\psi_2}{\partial y_4}=0.$$

These two equations plus the two equations of constraint constitute four equations that determine the extremal values of y_1, y_2, y_3, and y_4.

It is obvious that this methed may be applied to a function of any number of coordinates subject to any number of equations of constraint. The method of Lagrangian multipliers can be summarized as follows:

1. Write down the differential of the function, and equate it to zero.
2. Take the differential of each equation of constraint, and multiply by as many different Lagrangian multipliers as there are equations of constraint.
3. Add all the equations, factoring the sum so that each differential appears only once.
4. Equate the coefficient of each differential to zero.

Evaluation of the Integral $\int_0^\infty e^{-ax^2}\,dx$

$$\int_0^\infty e^{-ax^2}\,dx = \tfrac{1}{2}\sqrt{\frac{\pi}{a}} \tag{1}$$

To obtain Eq. (1), it must first be recognized that the indefinite integral $\int e^{-ax^2}\,dx$ cannot be evaluated in terms of elementary functions. An appropriate change of variables will allow the definite integral to be evaluated. Equation (1) could equally well be written

$$I = \int_0^\infty e^{-ay^2}\,dy, \tag{2}$$

so that the product of Eqs. (1) and (2) is

$$I^2 = \int_0^\infty e^{-ax^2}\,dx \int_0^\infty e^{-ay^2}\,dy,$$

and

$$I^2 = \int_0^\infty \int_0^\infty e^{-a(x^2+y^2)}\,dx\,dy. \tag{3}$$

Now, change the integration variables to polar coordinates r and θ. Then, $x^2 + y^2 = r^2$ and $dx\,dy = r\,dr\,d\theta$. The area being integrated is the first quadrant, so Eq. (3) becomes

$$
\begin{aligned}
I^2 &= \int_0^\infty \int_0^{\pi/2} e^{-ar^2}\, r\, dr\, d\theta \\
&= \frac{\pi}{2}\int_0^\infty e^{-ar^2} r\, dr \\
&= \frac{\pi}{2}\int_0^\infty \left(-\frac{1}{2a}\right) d(e^{-ar^2}) \\
&= -\frac{\pi}{4a} e^{-ar^2}\Big|_0^\infty \\
&= \frac{\pi}{4a}. \qquad (4)
\end{aligned}
$$

Equation (4) is the square of the definite integral, which is thus

$$I = \int_0^\infty e^{-ax^2}\, dx = \tfrac{1}{2}\sqrt{\frac{\pi}{\alpha}}.$$

APPENDIX D

Riemann Zeta Functions

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^2} = \frac{\pi^2}{12}, \tag{1}$$

$$\zeta(2) = \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}, \tag{2}$$

$$\zeta(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90}. \tag{3}$$

To obtain Eqs. (1) and (2), expand the function

$$f(x) = x^2 \qquad (-\pi \le x \le \pi)$$

in a Fourier series:

$$f(x) = \sum_{n=0}^{\infty} a_n \cos nx,$$

$$a_0 = \frac{1}{\pi}\int_0^{\pi} x^2\, dx = \frac{\pi^2}{3},$$

$$a_n = \frac{2}{\pi}\int_0^{\pi} x^2 \cos nx\, dx = (-1)^n \frac{4}{n^2}.$$

Hence,
$$x^2 = \frac{\pi^2}{3} + 4\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cos nx.$$

Setting $x = 0$ gives Eq. (1), and setting $x = \pi$ gives Eq. (2).

To obtain Eq. (3), expand

$$f(x) = x^4 \qquad (-\pi \le x \le \pi)$$

in a Fourier series:

$$a_0 = \frac{1}{\pi}\int_0^\pi x^4\,dx = \frac{\pi^4}{5},$$

$$a_n = \frac{2}{\pi}\int_0^\pi x^4 \cos nx\,dx = -(-1)^n\frac{8\pi^2}{n^2} - (-1)^n\frac{48}{n^4}.$$

Hence, $$x^4 = \frac{\pi^4}{5} + 8\pi^2\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\cos nx - 48\sum_{n=1}^{\infty}\frac{(-1)^n}{n^4}\cos nx.$$

Setting $x = \pi$ gives

$$\pi^4 = \frac{\pi^4}{5} + 8\pi^2\sum_{n=1}^{\infty}\frac{1}{n^2} - 48\sum_{n=1}^{\infty}\frac{1}{n^4}.$$

Substituting Eq. (2) and solving for $\sum_{n=1}^{\infty}\frac{1}{n^4}$ gives Eq. (3).

APPENDIX E

Thermodynamic Definitions and Formulas

TABLE E.1
Thermodynamic systems and coordinates

System	Intensive coordinate	Extensive coordinate
Hydrostatic system	Pressure P	Volume V
Stretched wire	Force $\mathcal{F}$	Length L
Surface film	Surface tension γ	Area A
Electrochemical cell	Electromotive force (emf) $\mathcal{E}$	Charge Z
Dielectric slab	Electric field E	Polarization $\mathcal{P}$
Paramagnetic rod	Magnetic field $\mu_0\mathcal{H}$	Magnetization $\mathcal{M}$

TABLE E.2
Work done on thermodynamic systems

System	Intensive coordinate (generalized force)	Extensive coordinate (generalized displacement)	Work
Hydrostatic system	P in pascal	V in meter^3	$-P\,dV$ in joule
Stretched wire	$\mathcal{F}$ in newton	L in meter	$\mathcal{F}\,dL$ in joule
Surface film	γ in newton/meter	A in meter^2	$\gamma\,dA$ in joule
Electrochemical cell	$\mathcal{E}$ in volt	Z in coulomb	$\mathcal{E}\,dZ$ in joule
Dielectric slab	E in volt/meter	$\mathcal{P}$ in coulomb · meter	$E\,d\mathcal{P}$ in joule
Paramagnetic rod	$\mu_0\mathcal{H}$ in newton/amp · meter	$\mathcal{M}$ in amp · meter^2	$\mu_0\mathcal{H}\,d\mathcal{M}$ in joule

TABLE E.3

Symbols and definitions for a closed hydrostatic system (constant mass)

Thermal quantity	Symbol	Definition
Temperature	T	
Heat	Q	
Internal energy	U	
Entropy	S	
Enthalpy	H	$U + PV$
Helmholtz function	A	$U - TS$
Gibbs function	G	$H - TS$
Volume expansivity	β	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
Isothermal bulk modulus	B	$-V\left(\frac{\partial P}{\partial V}\right)_T$
Adiabatic (reversible) bulk modulus	B_S	$-V\left(\frac{\partial P}{\partial V}\right)_S$
Isothermal compressibility	κ	$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$
Adiabatic (reversible) compressibility	κ_S	$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$
Heat capacity at constant volume	C_V	$\left(\frac{đQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$
Heat capacity at constant pressure	C_P	$\left(\frac{đQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$
Ratio of heat capacities	γ	$\frac{C_P}{C_V}$
Joule coefficient	η	$\left(\frac{\partial T}{\partial V}\right)_U$
Joule-Thomson coefficient	μ	$\left(\frac{\partial T}{\partial P}\right)_H$
Linear expansivity	α	$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathcal{J}}$
Isothermal Young's modulus	Y	$\frac{L}{A}\left(\frac{\partial \mathcal{J}}{\partial L}\right)_T$
Adiabatic (reversible) Young's modulus	Y_S	$\frac{L}{A}\left(\frac{\partial \mathcal{J}}{\partial L}\right)_S$

TABLE E.4

Thermodynamic formulas for a closed hydrostatic system (constant mass)

Zeroth law of thermodynamics for three systems in thermal equilibrium:

$$T_A = T_B = T_C.$$

First law of thermodynamics, where heat and work are positive when added to the system:

$$\begin{aligned} U_2 - U_1 &= Q + W, \\ dU &= đQ + đW. \end{aligned}$$

Second law of thermodynamics, where the equality applies to reversible processes and the inequality to irreversible processes:

$$\Delta S \geq 0.$$

Third law of thermodynamics:

$$\lim_{T \to 0} \Delta S_T = 0.$$

$$\begin{aligned} dU &= T\,dS - P\,dV, \\ dH &= T\,dS + V\,dP, \\ dA &= -S\,dT - P\,dV, \\ dG &= -S\,dT + V\,dP. \end{aligned}$$

Maxwell's relations:

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V, \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P, \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V, \\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P. \end{aligned}$$

Basic thermodynamic equations:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_S, \\ C_P &= \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_S, \end{aligned}$$

$$\begin{aligned} T\,dS &= C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV = C_V\,dT + \frac{\beta T}{\kappa}\,dV, \\ T\,dS &= C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_P\,dT - V\beta T\,dP, \\ T\,dS &= C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV = \frac{C_V\kappa}{\beta}\,dP + \frac{C_P}{\beta V}\,dV, \end{aligned}$$

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V,$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P,$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T = \frac{TV\beta^2}{\kappa},$$

$$\gamma = \frac{C_P}{C_V} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T} = \frac{\kappa}{\kappa_S},$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] = \frac{V}{C_P}(\beta T - 1),$$

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] = -\frac{1}{C_V}\left(\frac{\beta T}{\kappa} - P\right).$$

First derivatives of T, P, V, and S:

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{\kappa}{\beta},$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{V\beta},$$

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P},$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa},$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V\kappa},$$

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

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

$$\left(\frac{\partial V}{\partial P}\right)_T = -V\kappa,$$

$$\left(\frac{\partial V}{\partial S}\right)_T = \frac{\kappa}{\beta},$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T},$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\beta,$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{V\beta T} = \frac{\gamma\beta,}{(\gamma - 1)\kappa},$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{V\beta T}{C_P} = \frac{(\gamma - 1)\kappa}{\gamma\beta},$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\beta T}{C_V\kappa} = -\frac{\gamma - 1}{V\beta},$$

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V},$$

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V\beta T} = \frac{\gamma\beta}{(\gamma - 1)\kappa},$$

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{\gamma}{V\kappa},$$

$$\left(\frac{\partial P}{\partial S}\right)_V = \frac{\beta T}{C_V\kappa} = \frac{\gamma - 1}{V\beta},$$

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V\kappa}{\beta T} = -\frac{V\beta}{\gamma - 1},$$

$$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{V\kappa}{\gamma},$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{V\beta T}{C_P} = \frac{(\gamma - 1)\kappa}{\gamma\beta},$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T},$$

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{C_V\kappa}{\beta T} = \frac{V\beta}{\gamma - 1},$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{\kappa}.$$

Note: Equations appropriate for a stretched wire, surface film, electrochemical cell, dielectric slab, or paramagnetic rod can be generated from any of the formulas in Tables E.3 or E.4 by replacing P with $-\mathcal{J}$, $-\gamma$, $-\mathcal{E}$, $-E$, or $-\mu_0\mathcal{H}$, **and** V with L, A, Z, $\mathcal{P}$, or $\mathcal{M}$, respectively.

Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{S^{(f)} - S^{(i)}}{V^{(f)} - V^{(i)}} = \frac{H^{(f)} - H^{(i)}}{T(V^{(f)} - V^{(i)})}.$$

TABLE E.5

Thermodynamic formulas for an open hydrostatic system (varying mass)

First law of thermodynamics for N constituents, each comprised of n_j moles:

$$\begin{aligned} dU(V,S,n) &= -P\,dV + T\,dS + \mu_1\,dn_1 + \cdots + \mu_j\,dn_j + \cdots + \mu_N\,dn_N \\ &= -P\,dV + T\,dS + \sum_{j=1}^{N} \mu_j\,dn_j, \end{aligned}$$

where
$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,n}$$

and
$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n}.$$

Chemical work $đW_C$ is given by

$$đW_C = \sum_{j=1}^{N} \mu_j\,dn_j,$$

and the chemical potential μ_j is given by

$$\mu_j = \left(\frac{\partial U}{\partial n_j}\right)_{V,S,\text{ all } n \text{ except } n_j}.$$

The chemical potential is expressed more commonly in terms of the Gibbs function $G(P,T,n)$ as

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{P,T,\text{ all } n \text{ except } n_j}.$$

Thermodynamic functions for open systems:

Hill energy $L(V,S,\mu)$, $dL = -P\,dV + T\,dS - n\,d\mu$;

Ray energy $R(P,S,\mu)$, $dR = V\,dP + T\,dS - n\,d\mu$;

Grand function $J(V,T,\mu)$, $dJ = -P\,dV - S\,dT - n\,d\mu$;

Guggenheim function $Z(P,T,\mu)$, $dZ = V\,dP - S\,dT - n\,d\mu$.

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Answers to Selected Problems

1.1. 1.5356 K
1.2. 373.124 K
1.3. (*a*) 4.01 K
1.7. 211.23°F
1.9. 211.95°F

2.4. (*a*) 4.02×10^7 Pa, (*b*) 17.4°C
2.5. 320 atm
2.6. (*b*) 20.3 N
2.7. (*d*) 7 N, 10^7 Pa, -1.83×10^{-3} K^{-1}
2.8. -1.498×10^{-4} N/m · K, -1.738×10^{-4} N/m · K
2.10. $\mathcal{E} = 1.0$ V, $d\mathcal{E}/dT = -1.28 \times 10^{-5}$ V/°C

3.2. (*b*) -3.17×10^3 J
3.4. (*b*) 7.75×10^{10} J
3.5. -9.2×10^2 J
3.7. 9.67×10^{-2} J
3.11. -6.69×10^3 J
3.14. (*a*) 125.7 J, (*b*) 0.8 J, (*c*) 126.5 J

4.6. 1.225 V
4.17. 1.124×10^{-3} J/mol
4.19. 0.458 W/m · K
4.21. 4.59×10^{-3} K
4.22. 0.120 kg
4.23. 1.61×10^{-2} m^2
4.24. 1356 K
4.25. 5768 K
4.26. (*c*) 2.34
4.27. 13.5 min

5.1. (*b*) 50.2 K; (*c*) ΔT = 7226 K, meteor will melt and burn
5.2. 760 mm
5.3. 1.25 m
5.4. 1.7 g
5.5. $3T_0$
5.10. (*b*) −96.75 ft · lb
5.11. 400 ft
5.12. (*b*) 571 K
5.13. 1.02×10^3 J
5.16. (*c*) −9.77 K/km
5.21. 319 m/s
5.22. 1.27
5.23. 80% He, 20% Ne

6.2. $\eta = 0.572$
6.7. (*a*) Q = 148.5 J, U = 148.5 J; (*b*) W = −148.5 J, U = 0; (*c*) W = 6.908 J,
Q = −6.908 J, η= 0.954

7.1. $P_2 = 5.66\ P_0$, V_2 = 17.7 liters
$P_3 = 1.34\ P_0$
$P_4 = 0.237\ P_0$, V_4 = 212 liters
7.2. $P_2 = 32\ P_0$, V_2 = 1.63 liters
$P_4 = 0.0625\ P_0$, V_4 = 208 liters
7.3. No, it violates Carnot's theorem and, therefore, is impossible.
7.4. $|Q_L|$ = 73.20 J, W = 26.8 J, η= 0.268
7.10. (*b*) 32.9 m^3; (*c*) T_0 = 307.9 K, T_1 = 76.97 K, T_{max} = 720.8 K; (*e*) 41.13 m^3;
(*f*) 1215 J; (*g*) −579.3 J

8.6. (*a*) 0, (*b*) 8.33 J/K, (*c*) 5.82 J/K, (*d*) 5.82 J/K
8.7. (*a*) 1311 K, −1126 J/K, 185 J/K; (*b*) 1310 K, −1210 J/K, 98 J/K
8.10. 0.0301 R
8.11. 1.5 atm, 300 K, 0.0566 J/K
8.12. (*a*) $\frac{4}{9}\ V_0$, (*b*) $\frac{3}{2}\ T_0$, (*c*) $\frac{21}{4}\ T_0$, (*d*) $\frac{19}{4}\ nC_VT_0$, (*e*) $\frac{1}{2}\ nC_VT_0$, (*f*) 0,
(*g*) $nC_P \ln \frac{21}{4} - nR \ln \frac{27}{8}$, (*h*) $nC_P \ln \frac{63}{84} - 2nR \ln \frac{27}{8}$
8.14. (*a*) 6.28 J/K, (*b*) 1.385 J/K, (*c*) 3.64 J/K
8.15. (*a*) 1.83×10^{-5} J/K, (*b*) 1.83×10^{-5} J/K
8.16. (*a*) 3740 J/mol, (*b*) 3740 J/mol, (*d*) −2296 J/mol, (*e*) −1444 J/mol, (*f*) 3.82 J/mol · K

9.6. (*a*) 2256 kJ/kg, (*b*) 420 kJ/kg
9.7. 3087 kJ/kg

10.9. (*a*) −139.91 J, (*b*) 44.24 J, (*c*) −95.67 J, (*d*) 0.727 K
10.10. (*a*) −3641 J, (*b*) 4183 J, (*c*) 497 J
10.11. 0°C: -4.41×10^{-4} K; 5°C: 1.04×10^{-4} K; 50°C: 3.03×10^{-3} K
10.22. 605 J

11.3. (*a*) 37 K; (*b*) 20.6 K, 35 atm
11.7. -7.47×10^{-8} K/Pa
11.9. 600.76 K

11.11. (*b*) 4.32×10^7 Pa/K; (*c*) 270.7 K, 3.03×10^7 Pa
11.12. (*d*) 6.21%
11.13. (*c*) 7.2×10^{-6} m/s

12.1. $2 \text{ x} 10^{11}$
12.2. (*b*) 1.03×10^{48}, (*c*) 2.4×10^{19} atoms
12.4. 5.96×10^7
12.13. Krypton-86 lamp at 77 K
12.14. (*a*) 7729 K, (*b*) 7.73×10^6 K, (*c*) 7.73×10^9 K
12.15. 2.41×10^{15} atoms/s
12.16. $k' = A<w>/4V$
12.17. 3.24 s
12.18. 2.47×10^{-2} Pa

14.4. (*a*) $\delta = 3$, (*b*) $\gamma = 1$, (*c*) $\alpha = 0$

15.2. 1250 J

16.5. (*a*) 0.315 atm, (*b*) 0.612, (*c*) 61.0 kJ/mol
16.6. 94.2 kJ/mol
16.7. 37%, 78%
16.8. 100%
16.10. 660 J/K
16.11. 1.95×10^{-4} K^{-1}

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