

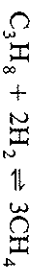
These constitute two independent equations, for the first equation is simply the sum of the two following equations (just as the first chemical reaction is the net result of the two succeeding reactions). The amounts of hydrogen, oxygen, and carbon introduced into the system (in whatever chemical combinations) specify three additional constraints. There are thus five constraints, and there are precisely five mole numbers to be found (the quantities of  $H_2$ ,  $O_2$ ,  $H_2O$ ,  $CO_2$ , and  $CO$ ). The problem is thereby solved in principle.

As we observed earlier, chemical reactions more typically occur in open vessels with only the final pressure and temperature determined. The number of variables is then increased by two (the energy and the volume) but the specification of  $T$  and  $P$  provides two additional constraints. Again the problem is determinate.

We shall return to a more thorough discussion of chemical reactions in Section 6.4. For now it is sufficient to stress that the chemical potential plays a role in matter transfer or chemical reactions fully analogous to the role of temperature in heat transfer or pressure in volume transfer.

## PROBLEMS

2.9-1. The hydrogenation of propane ( $C_3H_8$ ) to form methane ( $CH_4$ ) proceeds by the reaction



Find the relationship among the chemical potentials and show that both the problem and the solution are formally identical to Example 1 on mechanical equilibrium.

# 3

## SOME FORMAL RELATIONSHIPS, AND SAMPLE SYSTEMS

### 3-1 THE EULER EQUATION

Having seen how the fundamental postulates lead to a solution of the equilibrium problem, we now pause to examine in somewhat greater detail the mathematical properties of fundamental equations.

The homogeneous first-order property of the fundamental relation permits that equation to be written in a particularly convenient form, called the Euler form.

From the definition of the homogeneous first-order property we have, for any  $\lambda$

$$U(\lambda S, \lambda X_1, \dots, \lambda X_i, \dots, \lambda X_j) = \lambda U(S, X_1, \dots, X_j) \quad (3.1)$$

Differentiating with respect to  $\lambda$

$$\begin{aligned} \frac{\partial U(\dots, \lambda X_k, \dots)}{\partial (\lambda S)} + \frac{\partial U(\dots, \lambda X_k, \dots)}{\partial \lambda} + \frac{\partial U(\dots, \lambda X_k, \dots)}{\partial (\lambda X_j)} \frac{\partial (\lambda X_j)}{\partial \lambda} \\ + \dots = U(S, X_1, \dots, X_i) \end{aligned} \quad (3.2)$$

or

$$\begin{aligned} \frac{\partial U(\dots, \lambda X_k, \dots)}{\partial (\lambda S)} S + \sum_{j=1}^i \frac{\partial U(\dots, \lambda X_k, \dots)}{\partial (\lambda X_j)} X_j \\ = U(S, X_1, \dots, X_i) \end{aligned} \quad (3.3)$$

it takes the form

$$\frac{\partial U}{\partial S} S + \sum_{j=1}^t \frac{\partial U}{\partial X_j} X_j + \cdots = U \quad (3.4)$$

$$U = TS + \sum_{j=1}^t P_j X_j \quad (3.5)$$

For a simple system in particular we have

$$U = TS - PV + \mu_1 N_1 + \cdots + \mu_r N_r \quad (3.6)$$

The relation 3.5 or 3.6 is the particularization to thermodynamics of the Euler theorem on homogeneous first-order forms. The foregoing development merely reproduces the standard mathematical derivation. We refer to equation 3.5 or 3.6 as the Euler relation.

In the entropy representation the Euler relation takes the form

$$S = \sum_{j=0}^t F_j X_j \quad (3.7)$$

or

$$S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \sum_{k=1}^t \left(\frac{\mu_k}{T}\right) N_k \quad (3.8)$$

## PROBLEMS

**3.1-1.** Write each of the five physically acceptable fundamental equations of Problem 1.9-1 in the Euler form.

## 3-2 THE GIBBS-DUHEM RELATION

In Chapter 2 we arrived at equilibrium criteria involving the temperature, pressure, and chemical potentials. Each of the intensive parameters entered the theory in a similar way, and the formalism is, in fact, symmetric in the several intensive parameters. Despite this symmetry, however, the reader is apt to feel an intuitive response to the concepts of temperature and pressure, which is lacking, at least to some degree, in the case of the chemical potential. It is of interest, then, to note that the intensive parameters are not all independent. There is a relation among

the intensive parameters, and for a single-component system  $\mu$  is a function of  $T$  and  $P$ .

The existence of a relationship among the various intensive parameters is a consequence of the homogeneous first-order property of the fundamental relation. For a single-component system this property permits the fundamental relation to be written in the form  $u = u(s, v)$ , as in equation 2.19; each of the three intensive parameters is then also a function of  $s$  and  $v$ . Elimination of  $s$  and  $v$  from among the three equations of state yields a relation among  $T$ ,  $P$ , and  $\mu$ .

The argument can easily be extended to the more general case, and it again consists of a straightforward counting of variables. Suppose we have a fundamental equation in  $(t + 1)$  extensive variables

$$U = U(S, X_1, X_2, \dots, X_t) \quad (3.9)$$

yielding, in turn,  $t + 1$  equations of state

$$P_k = P_k(S, X_1, X_2, \dots, X_t) \quad (3.10)$$

If we choose the parameter  $\lambda$  of equation 2.14 as  $\lambda = 1/X_t$ , we then have

$$P_k = P_k(S/X_t, X_1/X_t, \dots, X_{t-1}/X_t, 1) \quad (3.11)$$

Thus each of the  $(t + 1)$  intensive parameters is a function of just  $t$  variables. Elimination of these  $t$  variables among the  $(t + 1)$  equations yields the desired relation among the intensive parameters.

To find the explicit functional relationship that exists among the set of intensive parameters would require knowledge of the explicit fundamental equation of the system. That is, the analytic form of the relationship varies from system to system. Given the fundamental relation, the procedure is evident and follows the sequence of steps indicated by equations 3.9 through 3.11.

A differential form of the relation among the intensive parameters can be obtained directly from the Euler relation and is known as the Gibbs-Duhem relation. Taking the infinitesimal variation of equation 3.5, we find

$$dU = T ds + S dT + \sum_{j=1}^t P_j dX_j + \sum_{j=1}^t X_j dP_j \quad (3.12)$$

But, in accordance with equation 2.6, we certainly know that

$$dU = T ds + \sum_{j=1}^t P_j dX_j \quad (3.13)$$

whence, by subtraction we find the Gibbs–Duhem relation

$$S dT + \sum_{j=1}^l X_j dP_j = 0 \quad (3.14)$$

For a single-component simple system, in particular, we have

$$S dT - V dP + N d\mu = 0 \quad (3.15)$$

or

$$d\mu = -s dT + v dP \quad (3.16)$$

The variation in chemical potential is not independent of the variations in temperature and pressure, but the variation of any one can be computed in terms of the variations of the other two.

The Gibbs–Duhem relation presents the relationship among the intensive parameters in differential form. Integration of this equation yields the relation in explicit form, and this is a procedure alternative to that presented in equations 3.9 through 3.11. In order to integrate the Gibbs–Duhem relation, one must know the equations of state that enable one to write the  $X_j$ 's in terms of the  $P_j$ 's, or vice versa.

The number of intensive parameters capable of independent variation is called the number of *thermodynamic degrees of freedom* of a given system. A *simple system of  $r$  components has  $r + 1$  thermodynamic degrees of freedom.*

In the entropy representation the Gibbs–Duhem relation again states that the sum of products of the extensive parameters and the differentials of the corresponding intensive parameters vanishes.

$$\sum_{j=0}^l X_j dF_j = 0 \quad (3.17)$$

or

$$Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - \sum_{k=1}^l N_k d\left(\frac{\mu_k}{T}\right) = 0 \quad (3.18)$$

### PROBLEMS

3.2-1. Find the relation among  $T$ ,  $P$ , and  $\mu$  for the system with the fundamental equation

$$U = \left(\frac{v_0^2 \theta}{R^3}\right) \frac{S^4}{NV^2}$$

### 3-3 SUMMARY OF FORMAL STRUCTURE

Let us now summarize the structure of the thermodynamic formalism in the energy representation. For the sake of clarity, and in order to be explicit, we consider a single-component simple system. The fundamental equation

$$U = U(S, V, N) \quad (3.19)$$

contains *all* thermodynamic information about a system. With the definitions  $T = \partial U / \partial S$ , and so forth, the fundamental equation implies three equations of state

$$T = T(S, V, N) = T(s, v) \quad (3.20)$$

$$P = P(S, V, N) = P(s, v) \quad (3.21)$$

$$\mu = \mu(S, V, N) = \mu(s, v) \quad (3.22)$$

If *all three* equations of state are known, they may be substituted into the Euler relation, thereby recovering the fundamental equation. Thus the *totality of all three equations of state is equivalent to the fundamental equation* and contains all thermodynamic information about a system. Any single equation of state contains less thermodynamic information than the fundamental equation.

If two equations of state are known, the Gibbs–Duhem relation can be integrated to obtain the third. The equation of state so obtained will contain an undetermined integration constant. Thus two equations of state are sufficient to determine the fundamental equation, except for an undetermined constant.

A logically equivalent but more direct and generally more convenient method of obtaining the fundamental equation when two equations of state are given is by direct integration of the molar relation

$$du = T ds - P dv \quad (3.23)$$

Clearly, knowledge of  $T = T(s, v)$  and  $P = P(s, v)$  yields a differential equation in the three variables  $u$ ,  $s$ , and  $v$ , and integration gives

$$u = u(s, v) \quad (3.24)$$

which is a fundamental equation. Again, of course, we have an undetermined constant of integration.

It is always possible to express the internal energy as a function of parameters other than  $S$ ,  $V$ , and  $N$ . Thus we could eliminate  $S$  from  $U = U(S, V, N)$  and  $T = T(S, V, N)$  to obtain an equation of the form  $U = U(T, V, N)$ . However, I stress that such an equation is *not* a fundamental relation and does not contain all possible thermodynamic informa-

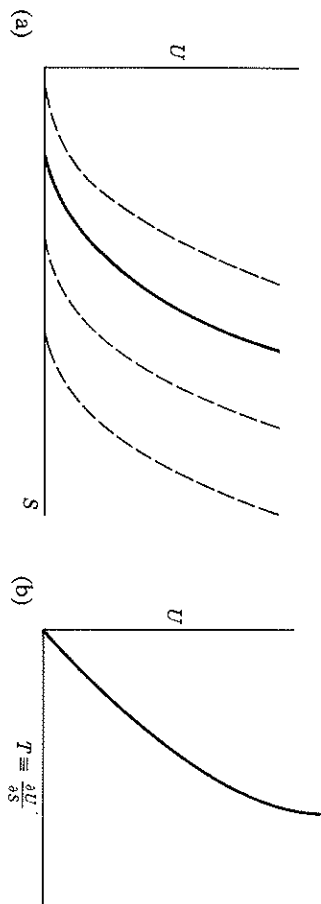


FIGURE 3.1

tion about the system. In fact, recalling the definition of  $T$  as  $\partial U/\partial S$ , we see that  $U = U(T, V, N)$  actually is a partial differential equation. Even if this equation were integrable, it would yield a fundamental equation with undetermined functions. Thus knowledge of the relation  $U = U(S, V, N)$  allows one to compute the relation  $U = U(T, V, N)$ , but knowledge of  $U = U(T, V, N)$  does not permit one inversely to compute  $U = U(S, V, N)$ . Associated with every equation there is both a truth value and an informational content. Each of the equations  $U = U(S, V, N)$  and  $U = U(T, V, N)$  may be true, but only the former has the optimum informational content.

These statements are graphically evident if we focus, for instance, on the dependence of  $U$  on  $S$  at constant  $V$  and  $N$ . Let that dependence be as shown in the solid curve in Fig. 3.1(a). This curve uniquely determines the dependence of  $U$  on  $T$ , shown in Fig. 3.1(b); for each point on the  $U(S)$  curve there is a definite  $U$  and a definite slope  $T = \partial U/\partial S$ , determining a point on the  $U(T)$  curve. Suppose, however, that we are given the  $U(T)$  curve (an equation of state) and we seek to recover the fundamental  $U(S)$  curve. Each of the dotted curves in Fig. 3.1(a) is equally compatible with the given  $U(T)$  curve, for all have the same slope  $T$  at a given  $U$ . The curves differ by an arbitrary displacement, corresponding to the arbitrary "constant of integration" in the solution of the differential equation  $U = U(\partial U/\partial S)$ . Thus, Fig. 3.1(a) implies Fig. 3.1(b), but the reverse is not true. Equivalently stated, only  $U = U(S)$  is a fundamental relation. The formal structure is illustrated by consideration of several specific and explicit systems in the following Sections of this book.

### Example

A particular system obeys the equations

$$U = \frac{1}{2}PV$$

and

$$T^2 = \frac{AU^{3/2}}{VN^{1/2}}$$

where  $A$  is a positive constant. Find the fundamental equation.

### Solution

Writing the two equations in the form of equations of state in the entropy representation (which is suggested by the appearance of  $U$ ,  $V$ , and  $N$  as independent parameters)

$$\begin{aligned} \frac{1}{T} &= A^{-1/2}u^{-3/4}v^{1/2} \\ \frac{P}{T} &= 2A^{-1/2}u^{1/4}v^{-1/2} \end{aligned}$$

Then the differential form of the molar fundamental equation (the analogue of equation 3.23) is

$$\begin{aligned} ds &= \frac{1}{T} du + \frac{P}{T} dv \\ &= A^{-1/2}(u^{-3/4}v^{1/2} du + 2u^{1/4}v^{-1/2} dv) \\ &= 4A^{-1/2}d(u^{1/4}v^{1/2}) \end{aligned}$$

so that

$$s = 4A^{-1/2}u^{1/4}v^{1/2} + s_0$$

and

$$S = 4A^{-1/2}U^{1/4}V^{1/2}N^{1/4} + NS_0$$

The reader should compare this method with the alternative technique of first integrating the Gibbs–Duhem relation to obtain  $\mu(u, v)$ , and then inserting the three equations of state into the Euler equation.

Particular note should be taken of the manner in which  $ds$  is integrated to obtain  $s$ . The equation for  $ds$  in terms of  $du$  and  $dv$  is a *partial differential equation*—it certainly cannot be integrated term by term, nor by any of the familiar methods for ordinary differential equations in one independent variable. We have integrated the equation by "inspection"; simply "recognizing" that  $u^{-3/4}v^{1/2} du + 2u^{1/4}v^{-1/2} dv$  is the differential of  $u^{1/4}v^{1/2}$ .

### PROBLEMS

3.3-1. A particular system obeys the two equations of state

$$T = \frac{3As^2}{v}, \quad \text{the thermal equation of state}$$

and

$$P = \frac{As^3}{v^2}, \quad \text{the mechanical equation of state}$$

where  $A$  is constant.

- a) Find  $\mu$  as a function of  $s$  and  $v$ , and then find the fundamental equation.
- b) Find the fundamental equation of this system by direct integration of the molar form of the equation.

3.3-2. It is found that a particular system obeys the relations

$$U = PV$$

$$P = BT^2$$

where  $B$  is constant. Find the fundamental equation of this system.

3.3-3. A system obeys the equations

$$P = -\frac{NU}{NV - 2AVU}$$

and

$$T = 2C \frac{U^{1/2}V^{1/2}}{N - 2AU} e^{4U/N}$$

Find the fundamental equation.

Hint: To integrate, let

$$s = Du^nv^m e^{-Au}$$

where  $D$ ,  $n$ , and  $m$  are constants to be determined.

3.3-4. A system obeys the two equations  $u = \frac{3}{2}Pv$  and  $u^{1/2} = BTv^{1/3}$ . Find the fundamental equation of this system.

### 3-4 THE SIMPLE IDEAL GAS AND MULTICOMPONENT SIMPLE IDEAL GASES

A "simple ideal gas" is characterized by the two equations

$$PV = NRT \tag{3.25}$$

and

$$U = cNRT \tag{3.26}$$

where  $c$  is a constant and  $R$  is the "universal gas constant" ( $R = N_A k_B = 8.3144 \text{ J/mole K}$ ).

Gases composed of noninteracting monatomic atoms (such as He, Ar, Ne) are observed to satisfy equations 3.25 and 3.26 at temperatures such that  $k_B T$  is small compared to electronic excitation energies (i.e.,  $T \leq 10^4 \text{ K}$ ) and at low or moderate pressures. All such "monatomic ideal gases"

Under somewhat more restrictive conditions of temperature and pressure other real gases may conform to the simple ideal gas equations 3.25 and 3.26, but with other values of the constant  $c$ . For diatomic molecules (such as  $O_2$  or  $NO$ ) there tends to be a considerable region of temperature for which  $c \approx \frac{5}{2}$  and another region of higher temperature for which  $c \approx \frac{7}{2}$  (with the boundary between these regions generally occurring at temperatures on the order of  $10^3 \text{ K}$ ).

Equations 3.25 and 3.26 permit us to determine the fundamental equation. The explicit appearance of the energy  $U$  in one equation of state (equation 3.26) suggests the entropy representation. Rewriting the equations in the correspondingly appropriate form

$$\frac{1}{T} = cR \left( \frac{N}{U} \right) = \frac{cR}{u} \tag{3.27}$$

and

$$\frac{P}{T} = R \left( \frac{N}{V} \right) = \frac{R}{v} \tag{3.28}$$

From these two entropic equations of state we find the third equation of state

$$\frac{\mu}{T} = \text{function of } u, v \tag{3.29}$$

by integration of the Gibbs–Duhem relation

$$d \left( \frac{\mu}{T} \right) = ud \left( \frac{1}{T} \right) + vd \left( \frac{P}{T} \right) \tag{3.30}$$

Finally, the three equations of state will be substituted into the Euler equation

$$S = \left( \frac{1}{T} \right) U + \left( \frac{P}{T} \right) V - \left( \frac{\mu}{T} \right) N \tag{3.31}$$

Proceeding in this way the Gibbs–Duhem relation (3.30) becomes

$$d \left( \frac{\mu}{T} \right) = u \times \left( -\frac{cR}{u^2} \right) du + v \times \left( -\frac{R}{v^2} \right) dv = -cR \frac{du}{u} - R \frac{dv}{v} \tag{3.32}$$

and integrating

$$\frac{\mu}{T} - \left( \frac{\mu}{T} \right)_0 = -cR \ln \frac{u}{u_0} - R \ln \frac{v}{v_0} \tag{3.33}$$

Here  $u_0$  and  $v_0$  are the parameters of a fixed reference state and  $(\mu/T)_0$

relation (3.31)

$$S = Ns_0 + NR \ln \left[ \left( \frac{U}{U_0} \right)^c \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-(c+1)} \right] \quad (3.34)$$

where

$$s_0 = (c + 1)R - \left( \frac{\mu}{T} \right)_0 \quad (3.35)$$

Equation 3.34 is the desired fundamental equation; if the integration constant  $s_0$  were known equation 3.34 would contain all possible thermodynamic information about a simple ideal gas.

This procedure is neither the sole method, nor even the preferred method. Alternatively, and more directly, we could integrate the molar equation

$$ds = \left( \frac{1}{T} \right) du + \left( \frac{P}{T} \right) dv \quad (3.36)$$

which, in the present case, becomes

$$ds = c \left( \frac{R}{u} \right) du + \left( \frac{R}{v} \right) dv \quad (3.37)$$

giving, on integration,

$$s = s_0 + cR \ln \left( \frac{u}{u_0} \right) + R \ln \left( \frac{v}{v_0} \right) \quad (3.38)$$

This equation is equivalent to equation 3.34.

It should, perhaps, be noted that equation 3.37 is integrable term by term, despite our injunction (in Example 3) that such an approach generally is not possible. The segregation of the independent variables  $u$  and  $v$  in separate terms in equation 3.37 is a fortunate but unusual simplification which permits term integration in this special case.

A mixture of two or more simple ideal gases—a “multicomponent simple ideal gas”—is characterized by a fundamental equation which is most simply written in parametric form, with the temperature  $T$  playing the role of the parametric variable.

$$S = \sum_j N_j s_{j0} + \left( \sum_j N_j c_j \right) R \ln \frac{T}{T_0} + \sum_j N_j R \ln \left( \frac{V}{N_j p_0} \right)$$

$$U = \left( \sum_j N_j c_j \right) RT \quad (3.39)$$

Elimination of  $T$  between these equations gives a single equation of the standard form  $S = S(U, V, N_1, N_2, \dots)$ .

Comparison of the individual terms of equations 3.39 with the expression for the entropy of a single-component ideal gas leads to the following interpretation (often referred to as Gibbs's Theorem). *The entropy of a mixture of ideal gases is the sum of the entropies that each gas would have if it alone were to occupy the volume  $V$  at temperature  $T$ .* The theorem is, in fact, true for all ideal gases (Chapter 13).

It is also of interest to note that the first of equations 3.39 can be written in the form

$$S = \sum_j N_j s_{j0} + \left( \sum_j N_j c_j \right) R \ln \frac{T}{T_0} + NR \ln \frac{V}{N p_0} - R \sum_j N_j \ln \frac{N_j}{N} \quad (3.40)$$

and the last term is known as the “entropy of mixing.” *It represents the difference in entropies between that of a mixture of gases and that of a collection of separate gases each at the same temperature and the same density as the original mixture*  $N_j/V_j = N/V$ , (and hence at the same pressure as the original mixture); see Problem 3.4-15. The close similarity, and the important distinction, between Gibbs's theorem and the interpretation of the entropy of mixing of ideal gases should be noted carefully by the reader. An application of the entropy of mixing to the problem of isotope separation will be given in Section 4.4 (Example 4).

Gibbs's theorem is demonstrated very neatly by a simple “thought experiment.” A cylinder (Fig. 3.2) of total volume  $2V_0$  is divided into four chambers (designated as  $\alpha, \beta, \gamma, \delta$ ) by a fixed wall in the center and by two sliding walls. The two sliding walls are coupled together so that their distance apart is always one half the length of the cylinder ( $V_\alpha = V_\gamma$  and  $V_\beta = V_\delta$ ). Initially, the two sliding walls are coincident with the left end and the central fixed partition, respectively, so that  $V_\alpha = V_\gamma = 0$ . The chamber  $\beta$ , of volume  $V_0$ , is filled with a mixture of  $N_A^0$  moles of a simple ideal gas  $A$  and  $N_B^0$  moles of a simple ideal gas  $B$ . Chamber  $\delta$  is initially evacuated. The entire system is maintained at temperature  $T$ .

The left-hand sliding wall is permeable to component  $A$ , but not to component  $B$ . The fixed partition is permeable to component  $B$ , but not to component  $A$ . The right-hand sliding wall is impermeable to either component.

The coupled sliding walls are then pushed quasi-statically to the right until  $V_\beta = V_\delta = 0$  and  $V_\alpha = V_\gamma = V_0$ . Chamber  $\alpha$  then contains pure  $A$  and chamber  $\gamma$  contains pure  $B$ . The initial mixture, of volume  $V_0$ , thereby is separated into two pure components, each of volume  $V_0$ . According to Gibbs's theorem the final entropy should be equal to the initial entropy, and we shall now see directly that this is, in fact, true.

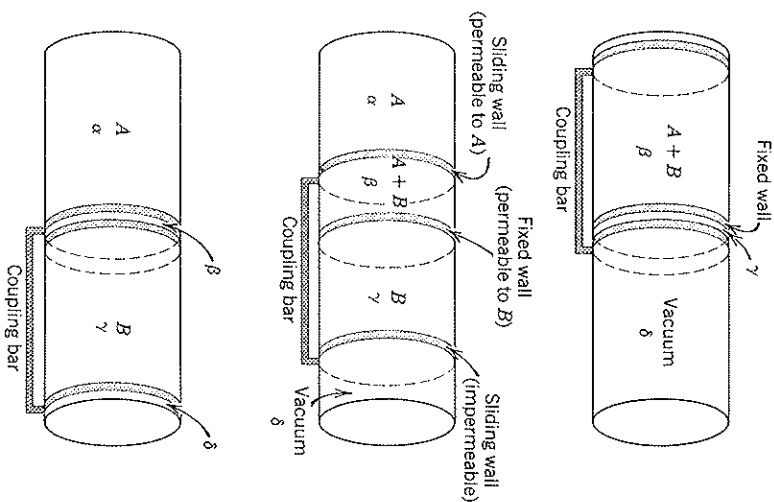


FIGURE 3.2  
Separation of a mixture of ideal gases,  
demonstrating Gibbs's theorem.

We first note that the second of equations 3.39, stating that the energy is a function of only  $T$  and the mole number, ensures that the final energy is equal to the initial energy of the system. Thus  $-T\Delta S$  is equal to the work done in moving the coupled walls.

The condition of equilibrium with respect to transfer of component  $A$  across the left-hand wall is  $\mu_{A,\alpha} = \mu_{A,\beta}$ . It is left to Problem 3.4-14 to show that the conditions  $\mu_{A,\alpha} = \mu_{A,\beta}$  and  $\mu_{B,\beta} = \mu_{B,\gamma}$  imply that

$$P_\alpha = P_\gamma \text{ and } P_\beta = 2P_\alpha$$

That is, *the total force on the coupled moveable walls* ( $P_\alpha - P_\beta + P_\gamma$ ) *vanishes*. Thus no work is done in moving the walls, and consequently no entropy change accompanies the process. The entropy of the original mixture of  $A$  and  $B$ , in a common volume  $V_0$ , is precisely equal to the entropy of pure  $A$  and pure  $B$ , each in a separate volume  $V_0$ . This is Gibbs's theorem.

Finally, we note that the simple ideal gas considered in this section is a special case of the general ideal gas, which encompasses a very wide class

of real gases at low or moderate pressures. The general ideal gas is again characterized by the mechanical equation of state  $PV = NRT$  (equation 3.25), and by an energy that again is a function of the temperature only—but not simply a linear function. The general ideal gas will be discussed in detail in Chapter 13, and statistical mechanical derivations of the fundamental equations will emerge in Chapter 16.

## PROBLEMS

Note that Problems 3.4-1, 3.4-2, 3.4-3, and 3.4-8 refer to “quasi-static processes”; such processes are to be interpreted not as real processes but merely as loci of equilibrium states. Thus we can apply thermodynamics to such quasi-static “processes”; the work done in a quasi-static change of volume (from  $V_1$  to  $V_2$ ) is  $W = -\int P dV$  and the heat transfer is  $Q = \int T dS$ . The relationship of real processes to these idealized “quasi-static processes” will be discussed in Chapter 4.

**3.4-1.** A “constant volume ideal gas thermometer” is constructed as shown (schematically) in Fig. 3.3. The bulb containing the gas is constructed of a material with a negligibly small coefficient of thermal expansion. The point  $A$  is a flexible point marked on the stem of the bulb. The bulb is connected by a mercury reservoir is raised or lowered until the mercury meniscus coincides with the reference point  $A$ . The height  $h$  of the mercury column is then read.

*a)* Show that the pressure of the gas is the sum of the external (atmospheric) pressure plus the height  $h$  of the mercury column multiplied by the weight per unit volume of mercury (as measured at the temperature of interest).

*b)* Using the equation of state of the ideal gas, explain how the temperature of the gas is then evaluated.

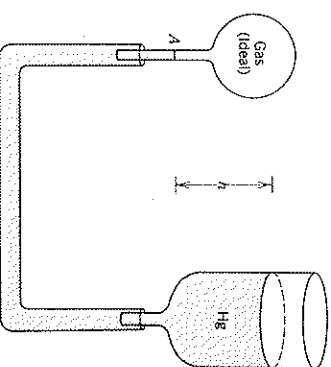


FIGURE 3.3  
Constant-volume ideal gas thermometer.

- c) Describe a "constant pressure ideal gas thermometer" (in which a changing volume is directly measured at constant pressure).
- 3.4.2. Show that the relation between the volume and the pressure of a monatomic ideal gas undergoing a quasi-static adiabatic compression ( $dQ = T dS = 0$ ,  $S = \text{constant}$ ) is

$$Pv^{5/3} = \left( P_0 v_0^{5/3} e^{-2s_0/3R} \right) e^{2s/3R} = \text{constant}$$

Sketch a family of such "adiabats" in a graph of  $P$  versus  $V$ . Find the corresponding relation for a simple ideal gas.

- 3.4.3. Two moles of a monatomic ideal gas are at a temperature of  $0^\circ\text{C}$  and a volume of 45 liters. The gas is expanded adiabatically ( $dQ = 0$ ) and quasi-statically until its temperature falls to  $-50^\circ\text{C}$ . What are its initial and final pressures and its final volume?

*Answer:*  
 $P_a = 0.1 \text{ MPa}, V_f = 61 \times 10^{-3} \text{ m}^3$

- 3.4.4. By carrying out the integral  $\int P dV$ , compute the work done by the gas in Problem 3.4.3. Also compute the initial and final energies, and corroborate that the difference in these energies is the work done.

- 3.4.5. In a particular engine a gas is compressed in the initial stroke of the piston. Measurements of the instantaneous temperature, carried out during the compression, reveal that the temperature increases according to

$$T = \left( \frac{V}{V_0} \right)^\eta T_0$$

where  $T_0$  and  $V_0$  are the initial temperature and volume, and  $\eta$  is a constant. The gas is compressed to the volume  $V_1$  (where  $V_1 < V_0$ ). Assume the gas to be monatomic ideal, and assume the process to be quasi-static.

- Calculate the work  $W$  done on the gas.
- Calculate the change in energy  $\Delta U$  of the gas.
- Calculate the heat transfer  $Q$  to the gas (through the cylinder walls) by using the results of (a) and (b).
- Calculate the heat transfer directly by integrating  $dQ = T dS$ .
- From the result of (c) or (d), for what value of  $\eta$  is  $Q = 0$ ? Show that for this value of  $\eta$  the locus traversed coincides with an adiabat (as calculated in Problem 3.4-2).

- 3.4.6. Find the three equations of state of the "simple ideal gas" (equation 3.34). Show that these equations of state satisfy the Euler relation.

- 3.4.7. Find the four equations of state of a two-component mixture of simple ideal gases (equations 3.39). Show that these equations of state satisfy the Euler relation.

- 3.4.8. If a monatomic ideal gas is permitted to expand into an evacuated region, thereby increasing its volume from  $V$  to  $\lambda V$ , and if the walls are rigid and adiabatic, what is the ratio of the initial and final pressures? What is the ratio of the initial and final temperatures? What is the difference of the initial and final entropies?

- 3.4.9. A tank has a volume of  $0.1 \text{ m}^3$  and is filled with He gas at a pressure of  $5 \times 10^6 \text{ Pa}$ . A second tank has a volume of  $0.15 \text{ m}^3$  and is filled with He gas at a pressure of  $6 \times 10^6 \text{ Pa}$ . A valve connecting the two tanks is opened. Assuming He to be a monatomic ideal gas and the walls of the tanks to be adiabatic and rigid, find the final pressure of the system.

*Hint:* Note that the internal energy is constant.

*Answer:*  
 $P_f = 5.6 \times 10^6 \text{ Pa}$

### 3.4-10.

- If the temperatures within the two tanks of Problem 3.4-9, before opening the valve, had been  $T = 300 \text{ K}$  and  $350 \text{ K}$ , respectively, what would the final temperature be?
- If the first tank had contained He at an initial temperature of  $300 \text{ K}$ , and the second had contained a diatomic ideal gas with  $c = 5/2$  and an initial temperature of  $350 \text{ K}$ , what would the final temperature be?

*Answer:*  
 a)  $T_f = 330 \text{ K}$   
 b)  $T_f = 337 \text{ K}$

- 3.4-11. Show that the pressure of a multicomponent simple ideal gas can be written as the sum of "partial pressures"  $P_j$ , where  $P_j \equiv N_j RT/V$ . These "partial pressures" are purely formal quantities not subject to experimental observation. (From the mechanistic viewpoint of kinetic theory the partial pressure  $P_j$  is the contribution to the total pressure that results from bombardment of the wall by molecules of species  $i$ —a distinction that can be made only when the molecules are noninteracting, as in an ideal gas.)

- 3.4-12. Show that  $\mu_j$ , the electrochemical potential of the  $j$ th component in a multicomponent simple ideal gas, satisfies

$$\mu_j = RT \ln \left( \frac{N_j v_0}{V} \right) + (\text{function of } T)$$

and find the explicit form of the "function of  $T$ ".

- Show that  $\mu_j$  can be expressed in terms of the "partial pressure" (Problem 3.4-11) and the temperature.

- 3.4-13. An impermeable, diathermal, and rigid partition divides a container into two subvolumes, each of volume  $V$ . The subvolumes contain respectively one



mole of  $H_2$  and three moles of Ne. The system is maintained at constant temperature  $T$ . The partition is suddenly made permeable to  $H_2$ , but not to Ne, and equilibrium is allowed to reestablish. Find the mole numbers and the pressure.

**3.4-14.** Use the results of Problems 3.4-11 and 3.4-12 to establish the results  $P_\alpha = P_\gamma$  and  $P_\beta = 2P_\alpha$  in the demonstration of Gibbs's theorem at the end of this section.

**3.4-15.** An impermeable, diathermal and rigid partition divides a container into two subvolumes, of volumes  $nV_0$  and  $mV_0$ . The subvolumes contain, respectively,  $n$  moles of  $H_2$  and  $m$  moles of Ne, each to be considered as a simple ideal gas. The system is maintained at constant temperature  $T$ . The partition is suddenly ruptured and equilibrium is allowed to re-establish. Find the initial pressure in each subvolume and the final pressure. Find the change in entropy of the system. How is this result related to the "entropy of mixing" (the last term in equation 3.40)?

### 3-5 THE "IDEAL VAN DER WAALS FLUID"

Real gases seldom satisfy the ideal gas equation of state except in the limit of low density. An improvement on the mechanical equation of state (3.28) was suggested by J. D. van der Waals in 1873.

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (3.41)$$

Here  $a$  and  $b$  are two empirical constants characteristic of the particular gas. In strictly quantitative terms the success of the equation has been modest, and for detailed practical applications it has been supplanted by more complicated empirical equations with five or more empirical constants. Nevertheless the van der Waals equation is remarkably successful in representing the qualitative features of real fluids, including the gas-liquid phase transition.

The heuristic reasoning that underlies the van der Waals equation is intuitively plausible and informative, although that reasoning lies outside the domain of thermodynamics. The ideal gas equation  $P = RT/v$  is known to follow from a model of point molecules moving independently and colliding with the walls to exert the pressure  $P$ . Two simple corrections to this picture are plausible. The first correction recognizes that the molecules are not point particles, but that each has a nonzero volume  $b/N_A$ . Accordingly, the volume  $V$  in the ideal gas equation is replaced by  $V - Nb$ ; the total volume diminished by the volume  $Nb$  occupied by the molecules themselves.

The second correction arises from the existence of forces between the molecules. A molecule in the interior of the vessel is acted upon by

intermolecular forces in all directions, which thereby tend to cancel. But a molecule approaching the wall of the container experiences a net backward attraction to the remaining molecules, and this force in turn reduces the effective pressure that the molecule exerts on colliding with the container wall. This diminution of the pressure should be proportional to the number of interacting *pairs* of molecules, or upon the square of the number of molecules per unit volume ( $1/v^2$ ); hence the second term in the van der Waals equation.

Statistical mechanics provides a more quantitative and formal derivation of the van der Waals equation, but it also reveals that there are an infinite series of higher order corrections beyond those given in equation 3.41. The truncation of the higher order terms to give the simple van der Waals equation results in an equation with appropriate *qualitative* features and with reasonable (but not optimum) quantitative accuracy.

The van der Waals equation must be supplemented with a thermal equation of state in order to define the system fully. It is instructive not simply to appeal to experiment, but rather to inquire as to the simplest possible (and reasonable) thermal equation of state that can be paired with the van der Waals equation of state. Unfortunately we are not free simply to adopt the thermal equation of state of an ideal gas, for thermodynamic formalism imposes a consistency condition between the two equations of state. We shall be forced to alter the ideal gas equation slightly.

We write the van der Waals equation as

$$P = \frac{R}{v-b} - \frac{a}{v^2} \frac{1}{T} \quad (3.42)$$

and the sought for additional equation of state should be of the form

$$\frac{1}{T} = f(u, v) \quad (3.43)$$

These two equations would permit us to integrate the molar equation

$$ds = \frac{1}{T} du + \frac{P}{T} dv \quad (3.44)$$

to obtain the fundamental equation. However, if  $ds$  is to be a perfect differential, it is required that the mixed second-order partial derivatives should be equal

$$\frac{\partial^2 s}{\partial v \partial u} = \frac{\partial^2 s}{\partial u \partial v} \quad (3.45)$$

OR

$$\frac{\partial}{\partial v} \left( \frac{1}{T} \right)_u = \frac{\partial}{\partial u} \left( \frac{P}{T} \right)_v \quad (3.46)$$

whence

$$\begin{aligned} \frac{\partial}{\partial v} \left( \frac{1}{T} \right)_u &= \frac{\partial}{\partial u} \left( \frac{R}{v-b} - \frac{a}{v^2} \frac{1}{T} \right)_v \\ &= \frac{a}{v^2} \frac{\partial}{\partial u} \left( \frac{1}{T} \right)_v \end{aligned} \quad (3.47)$$

This condition can be written as

$$\frac{\partial}{\partial(1/v)} \left( \frac{1}{T} \right)_u = \frac{\partial}{\partial(u/a)} \left( \frac{1}{T} \right)_v \quad (3.48)$$

That is, the function  $1/T$  must depend on the two variables  $1/v$  and  $u/a$  in such a way that the two derivatives are equal. One possible way of accomplishing this is to have  $1/T$  depend only on the sum  $(1/v + u/a)$ . We first recall that for a simple ideal gas  $1/T = cR/u$ ; this suggests that the simplest possible change consistent with the van der Waals equation is

$$\frac{1}{T} = \frac{cR}{u + a/v} \quad (3.49)$$

For purposes of illustration throughout this text we shall refer to the hypothetical system characterized by the van der Waals equation of state (3.41) and by equation 3.49 as the "ideal van der Waals fluid."

We should note that equation 3.41, although referred to as the "van der Waals equation of state," is not in the appropriate form of an equation of state. However, from equations 3.49 and 3.42 we obtain

$$\frac{P}{T} = \frac{R}{v-b} - \frac{acR}{av^2 + av} \quad (3.50)$$

The two preceding equations are the proper equations of state in the entropy representation, expressing  $1/T$  and  $P/T$  as functions of  $u$  and  $v$ .

With the two equations of state we are now able to obtain the fundamental relation. It is left to the reader to show that

$$S = NR \ln[(v-b)(u+a/v)^c] + Ns_0 \quad (3.51)$$

TABLE 3.1  
Van der Waals Constants and Molar Heat Capacities of Common Gases<sup>a</sup>

Gas	$a$ ( $\text{Pa}\cdot\text{m}^6$ )	$b$ ( $10^{-6}\text{m}^3$ )	$c$
He	0.00346	23.7	1.5
Ne	0.0215	17.1	1.5
H <sub>2</sub>	0.0248	26.6	2.5
A	0.132	30.2	1.5
N <sub>2</sub>	0.136	38.5	2.5
O <sub>2</sub>	0.138	32.6	2.5
CO	0.151	39.9	2.5
CO <sub>2</sub>	0.401	42.7	3.5
N <sub>2</sub> O	0.384	44.2	3.5
H <sub>2</sub> O	0.544	30.5	3.1
Cl <sub>2</sub>	0.659	56.3	2.8
SO <sub>2</sub>	0.680	56.4	3.5

<sup>a</sup> Adapted from Paul S. Epstein, *Textbook of Thermodynamics*, Wiley, New York, 1937.

equation does not satisfy the Nernst theorem, and it cannot be valid at very low temperatures.

We shall see later (in Chapter 9) that the ideal van der Waals fluid is unstable in certain regions of temperature and pressure, and that it spontaneously separates into two phases ("liquid" and "gas"). The fundamental equation (3.51) is a very rich one for the illustration of thermodynamic principles.

The van der Waals constants for various real gases are given in Table 3.1. The constants  $a$  and  $b$  are obtained by empirical curve fitting to the van der Waals isotherms in the vicinity of 273 K; they represent more distant isotherms less satisfactorily. The values of  $c$  are based on the molar heat capacities at room temperatures.

## PROBLEMS

3.5-1. Are each of the listed pairs of equations of state compatible (recall equation 3.46)? If so, find the fundamental equation of the system.

a)  $u = aPv$  and  $Pv^2 = bT$

b)  $U = aPv^2$  and  $Pv^2 = bT$

c)  $P = \frac{u}{v} \cdot \frac{c + buv}{a + buv}$  and  $T = \frac{u}{a + buv}$

3.5-2. Find the relationship between the volume and the temperature of an ideal van der Waals fluid in a quasi-static adiabatic expansion (i.e., in an isentropic