

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

$$df = u dx + v dy, \quad (10.1)$$

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

$$g \equiv f - ux. \quad (10.2)$$

It is readily verified that g satisfies the equation

$$dg = -x du + v dy. \quad (10.3)$$

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,

$$dU = -P dV + T dS, \quad (10.4)$$

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

$$H \equiv U + PV. \quad (10.5)$$

Since U , P , and V are all state functions, H is also a state function. In differential form,

$$dH = V dP + T dS, \quad (10.6)$$

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

$$A \equiv U - TS, \quad (10.7)$$

which is also a state function. In differential form,

$$dA = -S dT - P dV, \quad (10.8)$$

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,

$$G \equiv H - TS, \quad (10.9)$$

which is also a state function. In differential form,

$$dG = V dP - S dT, \quad (10.10)$$

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

$$\left(\frac{\partial U}{\partial V} \right)_S = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S} \right)_V = T. \quad (10.11)$$

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 compo-

site system of an ideal paramagnetic gas was considered. Its four characteristic functions are:

$$\begin{aligned}dU &= -P dV + \mu_0 \mathcal{H} d\mathcal{M} + T dS, \\dH &= V dP - \mathcal{M} \mu_0 d\mathcal{H} + T dS, \\dA &= -P dV + \mu_0 \mathcal{H} d\mathcal{M} - S dT,\end{aligned}\tag{10.12}$$

and
$$dG = V dP - \mathcal{M} \mu_0 d\mathcal{H} - S dT.$$

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

[†] 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.

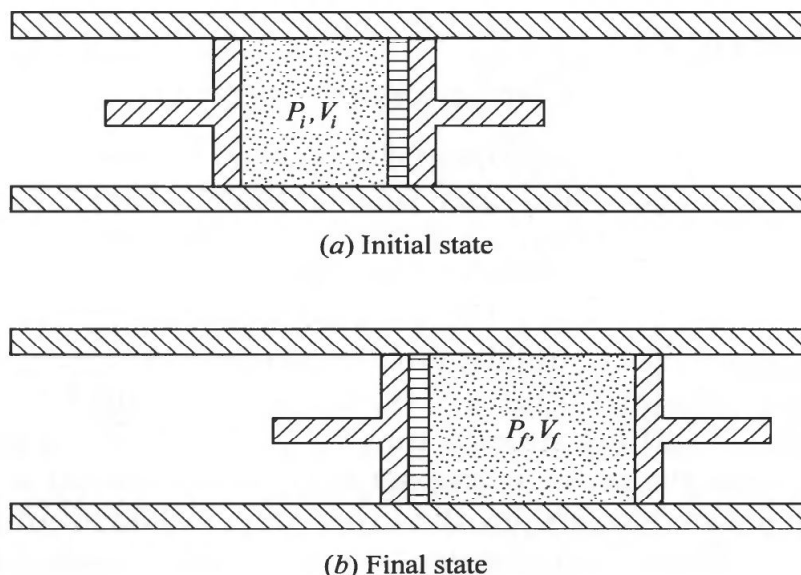


FIGURE 10-1
Throttling process (Joule-Thomson expansion).

equilibrium states, which are described by thermodynamic coordinates. From the first law,

$$(U_f - U_i) = W + Q. \quad (10.13)$$

The throttling process occurs in an adiabatic enclosure, so

$$Q = 0. \quad (10.14)$$

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

$$W = -(P_f V_f - P_i V_i). \quad (10.15)$$

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
$$U_i + P_i V_i = U_f + P_f V_f. \quad (10.16)$$

Of course, the sums in Eq. (10.16) are simply the characteristic function enthalpy introduced in Eq. (10.5); that is,

$$H = U + PV. \quad (10.5)$$

So, Eq. (10.16) becomes

$$H_i = H_f \quad (\text{throttling process}) \quad [\text{property (1)}], \quad (10.17)$$

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),

$$dH = dU + P dV + V dP; \quad (10.18)$$

but,

$$\delta Q = dU + P dV.$$

Therefore,

$$dH = \delta Q + V dP. \quad (10.19)$$

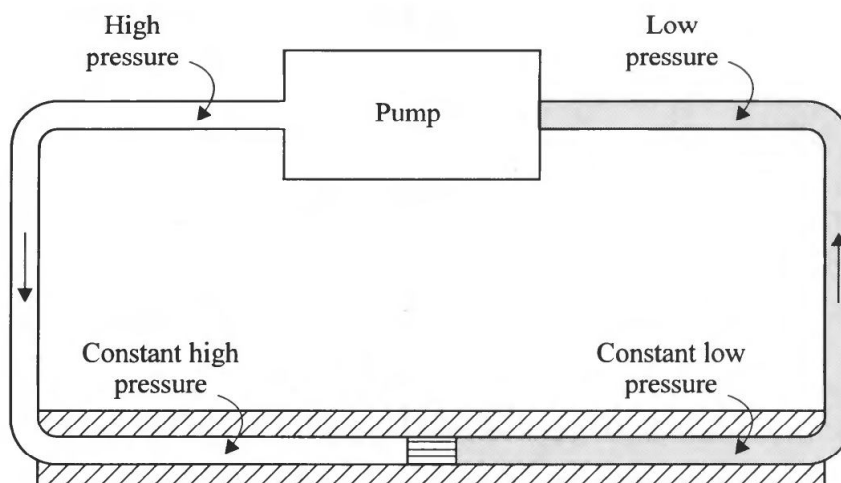


FIGURE 10-2

Apparatus for performing a continuous throttling process.

Dividing both sides by dT , we obtain

$$\frac{dH}{dT} = \frac{\delta Q}{dT} + V \frac{dP}{dT},$$

and, at constant P ,

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P \quad [\text{property (2)}]. \quad (10.20)$$

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,

$$H_f - H_i = \int_i^f C_P dT \quad (\text{all processes}). \quad (10.21)$$

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),

$$dH = \delta Q + V dP.$$

Thus, the change in enthalpy during an *isobaric* process is equal to the heat that is transferred between the system and the surroundings,

$$H_f - H_i = Q_P \quad (\text{isobaric}) \quad [\text{property (3)}]. \quad (10.22)$$

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 transi-

tion, 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

$$dH = \delta Q + V dP,$$

the change of enthalpy for an adiabatic process is

$$H_f - H_i = \int_i^f V dP \quad (\text{adiabatic}) \quad [\text{property (4)}]. \quad (10.23)$$

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

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V. \quad (10.24)$$

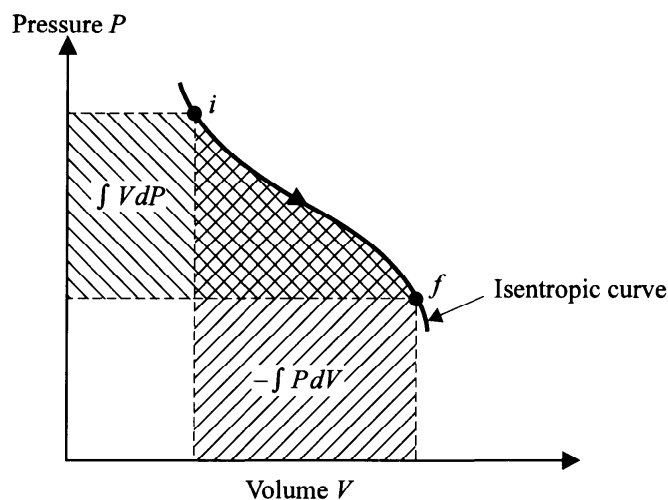


FIGURE 10-3

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)	Throttling process (irreversible)
$U_i = U_f$	$H_i = H_f$
In general	In general
$dU = \delta Q - P dV$	$dH = \delta Q + V dP$
$\left(\frac{\partial U}{\partial T}\right)_V = C_V$	$\left(\frac{\partial H}{\partial T}\right)_P = C_P$
Isochoric process	Isobaric process
$U_f - U_i = Q_V$	$H_f - H_i = Q_P$
For an ideal gas	For an ideal gas
$U_f - U_i = \int_i^f C_V dT$	$H_f - H_i = \int_i^f C_P dT$
Adiabatic process	Adiabatic process
$U_f - U_i = - \int_i^f P dV$	$H_f - H_i = \int_i^f V dP$
Nearby equilibrium states	Nearby equilibrium states
$dU = T dS - P dV$	$dH = T dS + V dP$
$\left(\frac{\partial U}{\partial S}\right)_V = T$	$\left(\frac{\partial H}{\partial S}\right)_P = T$
$\left(\frac{\partial U}{\partial V}\right)_S = -P$	$\left(\frac{\partial H}{\partial P}\right)_S = V$

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*,

$$dA = -P dV,$$

$$\text{or} \quad (A_f - A_i)_T = - \int_i^f (P dV)_T. \quad (10.25)$$

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),

$$\Delta A_T = \Delta U_T - T \Delta S_T,$$

$$\text{or} \quad \Delta A_T = \Delta U_T - \Delta Q_T = \Delta W_T.$$

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,

$$\Delta W_T \begin{matrix} \geq \\ \leq \end{matrix} \Delta U \quad \text{depending on} \quad \Delta Q_T \begin{matrix} \geq \\ \leq \end{matrix} 0.$$

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*,

$$dA = 0,$$

$$\text{and} \quad A = \text{const.} \quad (10.26)$$

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:

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S. \quad (10.27)$$

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:

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S. \quad (10.28)$$

In the case of a *reversible isothermal 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,

$$g' = g'' = g'''. \quad (10.29)$$

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

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y} \quad (10.30)$$

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,

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1.} \quad (10.31)$$

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

$$\boxed{\left(\frac{\partial x}{\partial f}\right)_z = \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z.} \quad (10.32)$$

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:

$$\begin{aligned}
1. \quad dU &= T dS - P dV; \text{ hence, } \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \\
2. \quad dH &= T dS + V dP; \text{ hence, } \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \\
3. \quad dA &= -S dT - P dV; \text{ hence, } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \\
4. \quad dG &= -S dT + V dP; \text{ hence, } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.
\end{aligned} \tag{10.33}$$

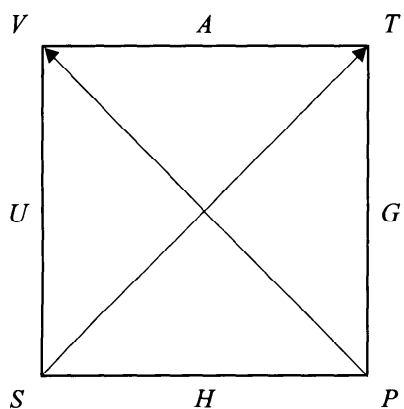
The four equations on the right are known as *Maxwell's relations*. These equations do not refer to a process but express relations that hold at any equilibrium state of a hydrostatic system. Of course, the reciprocals of Maxwell's relations are also valid equations.

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 $T dS = dQ$ 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,

$$T dS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV. \quad (10.34)$$

We shall call Eq. (10.34) the *first $T dS$ 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,

$$T dS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP. \quad (10.35)$$

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 cm³ 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, $V = 2 \times 10^{-5}$ m³, $\beta = 1.81 \times 10^{-4}$ K⁻¹, and $P_f = 1.01 \times 10^8$ Pa. Hence,

$$\begin{aligned}
Q &= -(293 \text{ K})(1.5 \times 10^{-5} \text{ m}^3)(1.81 \times 10^{-4} \text{ K}^{-1})(1.01 \times 10^8 \text{ Pa}) \\
&= -80.3 \text{ N} \cdot \text{m} \\
&= -80.3 \text{ J}.
\end{aligned}$$

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

$$\begin{aligned}
W &= \frac{1}{2} V \kappa (P_f^2 - P_i^2) \\
&\simeq \frac{1}{2} V \kappa P_f^2.
\end{aligned}$$

For example, taking $\kappa = 4.01 \times 10^{-11} \text{ Pa}^{-1}$ for mercury, we get

$$\begin{aligned}
W &= \frac{1}{2} V \kappa P_f^2 \\
&= \frac{1}{2} (1.5 \times 10^{-5} \text{ m}^3) (4.01 \times 10^{-11} \text{ Pa}^{-1}) (1.01 \times 10^8 \text{ Pa})^2 \\
&= 3.07 \text{ J}.
\end{aligned}$$

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

$$\begin{aligned}
\Delta U &= Q + W \\
&= -80.3 \text{ J} + 3.1 \text{ J} \\
&= -77.2 \text{ J}.
\end{aligned}$$

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 cm³ of mercury (specific heat $c_P = 139 \text{ J/kg} \cdot \text{K}$ and specific volume $\nu = 7.38 \times 10^{-5} \text{ m}^3/\text{kg}$) at 20°C is increased isentropically from 0 to 1000 atm, the temperature change will be approximately

$$\begin{aligned} \Delta T &\simeq \frac{T\nu\beta}{c_P} P_f \\ &= \frac{(293 \text{ K})(7.38 \times 10^{-5} \text{ m}^3/\text{kg})(1.81 \times 10^{-4} \text{ K}^{-1})}{139 \text{ J/kg} \cdot \text{K}} (1.01 \times 10^8 \text{ Pa}) \\ &= 2.84 \text{ K}. \end{aligned}$$

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

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P.} \quad (10.36)$$

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

$$\boxed{\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T}, \quad (10.37)$$

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

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

But,

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

Therefore,

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

and

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

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,

$$C_P - C_V = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T. \quad (10.38)$$

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

$$c_P - c_V = P \frac{Tv\beta^2}{\kappa}, \quad (10.39)$$

where ν 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 $c_P = 139 \text{ J/kg} \cdot \text{K}$, $T = 293 \text{ K}$, $\nu = 7.38 \times 10^{-5} \text{ m}^3/\text{kg}$, $\beta = 1.81 \times 10^{-4} \text{ K}^{-1}$, and $\kappa = 4.01 \times 10^{-11} \text{ Pa}^{-1}$. Hence,

$$\begin{aligned} 139 \text{ J/kg} \cdot \text{K} - c_V &= \frac{(293 \text{ K})(7.38 \times 10^{-5} \text{ m}^3/\text{kg})(1.81 \times 10^{-4} \text{ K}^{-1})^2}{4.01 \times 10^{-11} \text{ Pa}^{-1}} \\ &= 17.7 \text{ J/kg} \cdot \text{K}, \end{aligned}$$

and $c_V = 121.3 \text{ J/kg} \cdot \text{K}$.

Finally, the ratio of specific heats γ is

$$\gamma = \frac{c_P}{c_V} = \frac{139 \text{ J/kg} \cdot \text{K}}{121.3 \text{ J/kg} \cdot \text{K}} = 1.15.$$

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,

$$\frac{c_P}{c_V} = \frac{(\partial P / \partial V)_S}{(\partial P / \partial V)_T}. \quad (10.40)$$

The *isentropic compressibility* is defined as

$$\kappa_S \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S, \quad (10.41)$$

and, as usual, the isothermal compressibility is given by

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

We have, therefore,

$$\boxed{\gamma = \frac{c_P}{c_V} = \frac{\kappa}{\kappa_S}}, \quad (10.42)$$

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:

$$(a) \quad A = \int C_V dT - T \int \frac{C_V}{T} dT - nRT \ln V - \text{const. } T + \text{const.}$$

$$(b) \quad G = \int C_P dT - T \int \frac{C_P}{T} dT + nRT \ln P - \text{const. } T + \text{const.}$$

- (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:

$$(a) \quad U = -T \left(\frac{\partial A}{\partial T} \right)_V = -T^2 \left[\frac{\partial(A/T)}{\partial T} \right]_V.$$

$$(b) \quad C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_V.$$

$$(c) \quad H = G - T \left(\frac{\partial G}{\partial T} \right)_P = -T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P \quad (\text{Gibbs-Helmholtz equation}).$$

$$(d) \quad C_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P.$$

- 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:

$$(a) \quad T dS = C_V dT + \frac{\beta T}{\kappa} dV.$$

$$(b) \quad T dS = C_P dT - V\beta T dP.$$

$$(c) \quad T dS = \frac{C_V \kappa}{\beta} dP + \frac{C_P}{\beta V} dV.$$

- 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 $\rho = 8.96 \times 10^3 \text{ kg/m}^3$, volume expansivity $\beta = 49.5 \times 10^{-6} \text{ K}^{-1}$, isothermal compressibility $\kappa = 6.18 \times 10^{-12} \text{ Pa}^{-1}$, and specific heat $c_P = 385 \text{ J/kg} \cdot \text{K}$ to be constant.)

- How much heat is transferred during the compression?
- How much work is done during the compression?
- Determine the change of internal energy.
- 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 $3 \times 10^8 \text{ Pa}$ at 20°C . (Numerical values are given in Table 9.6.)

- 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 , $10^{-3} \text{ m}^3/\text{kg}$	β , 10^{-6} K^{-1}	c_P , $10^3 \text{ J/kg} \cdot \text{K}$
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

$$Pv = RT(1 + BP + CP^2 + \dots)$$

calculate $(\partial u / \partial P)_T$ and its limit as $P \rightarrow 0$.

- (b) Using the same expansion, calculate $(\partial P / \partial v)_T$ and its limit as $P \rightarrow 0$.
 (c) Using parts (a) and (b), calculate $(\partial u / \partial v)_T$ and its limit as $P \rightarrow 0$. (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

$$c_P = -T \frac{d^2 B}{dT^2} P + (c_P)_0,$$

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:

$$(a) \quad C_V = -T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S.$$

$$(b) \quad \left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V \kappa}{\beta T}.$$

$$(c) \quad \frac{(\partial V / \partial T)_S}{(\partial V / \partial T)_P} = \frac{1}{1 - \gamma}.$$

10.20. Derive the following equations:

$$(a) \quad C_P = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_S.$$

$$(b) \quad \left(\frac{\partial P}{\partial T} \right)_S = \frac{C_P}{V\beta T}.$$

$$(c) \quad \frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{\gamma}{\gamma - 1}.$$

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 $\beta = 1.81 \times 10^{-4} \text{ K}^{-1}$, specific heat at constant pressure $c_P = 139 \text{ J/kg} \cdot \text{K}$, isothermal compressibility $\kappa = 3.94 \times 10^{-11} \text{ Pa}^{-1}$ to be constant.)

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

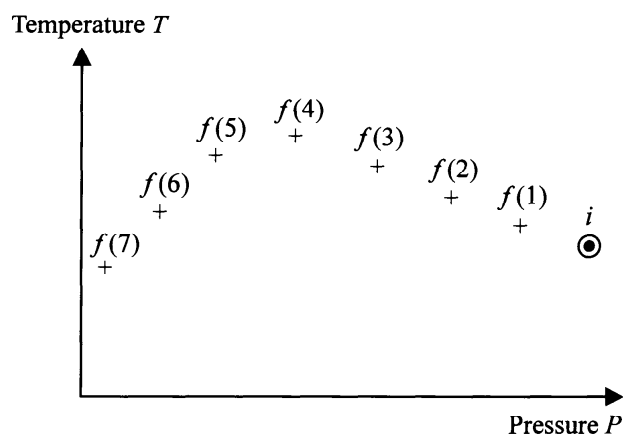


FIGURE 11-1
Isenthalpic states of a gas
undergoing the Joule-Thomson
expansion.

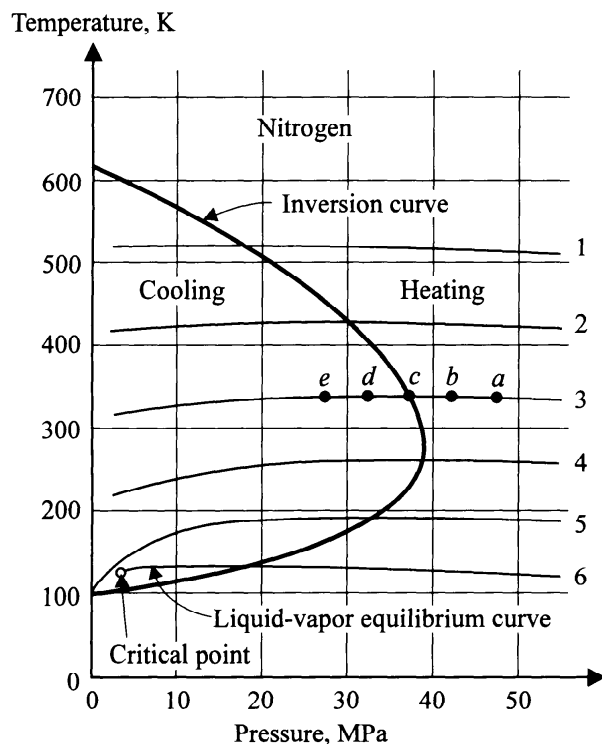
that, if a throttling process takes place between the states (P_i, T_i) and (P_f, T_f) :(4), there is a rise of temperature. Between (P_i, T_i) and (P_f, T_f) :(7), however, there is a drop of temperature. In general, the temperature change of a gas upon passage through a porous plug depends on the three 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,

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h, \quad (11.1)$$

**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 $\mu = (\partial T / \partial P)_h$,

$$\mu = \frac{1}{c_P} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]. \quad (11.2)$$

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

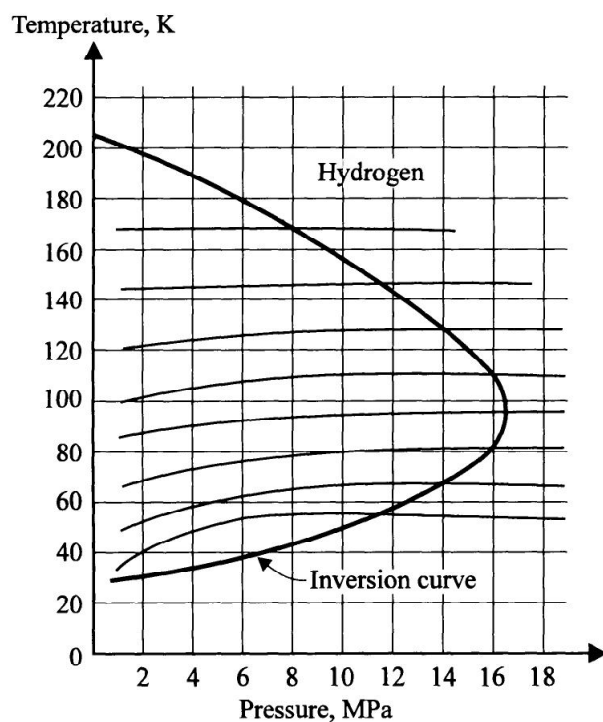


FIGURE 11-3
Isenthalpic curves and inversion curve
for hydrogen.

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
⁴ He	43

maximum inversion temperatures of a few gases. The inversion curve for ⁴He 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

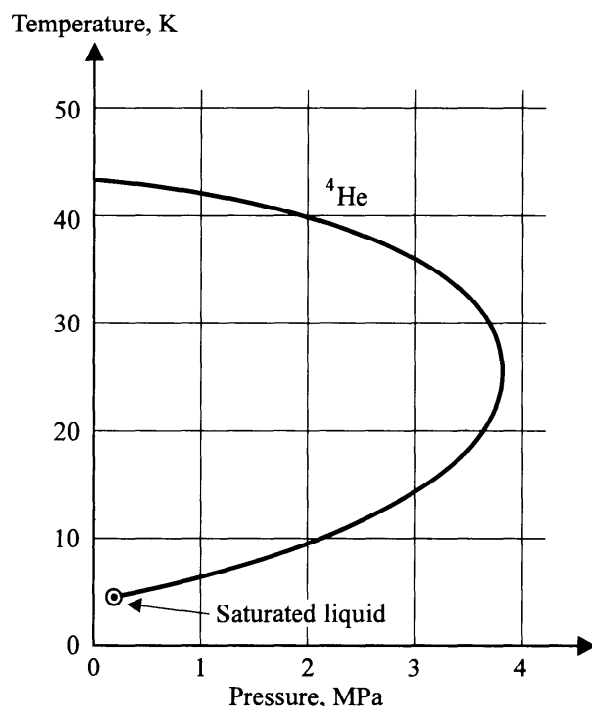


FIGURE 11-4
Inversion curve for ^4He .

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.

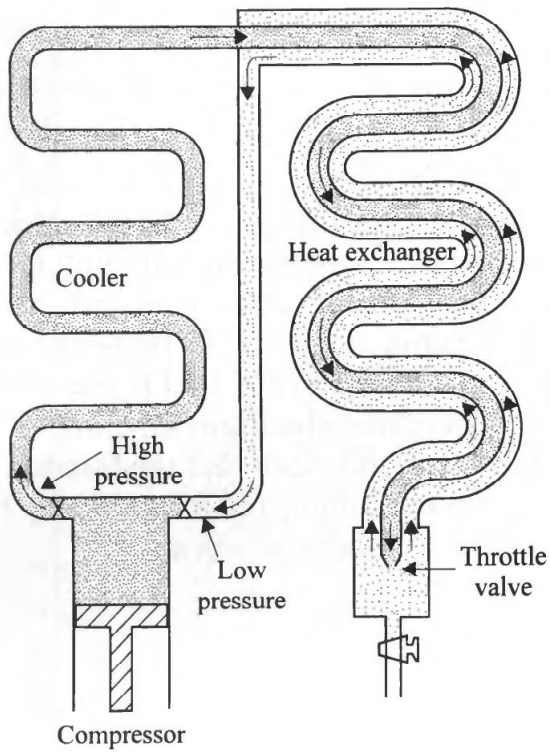
The gas, after precooling, is sent through the middle tube of a long coil of double-walled pipe. After throttling, it flows back through the outer annular space surrounding the middle pipe. For the heat exchanger to be efficient, the temperature of the gas as it leaves must differ only slightly from 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

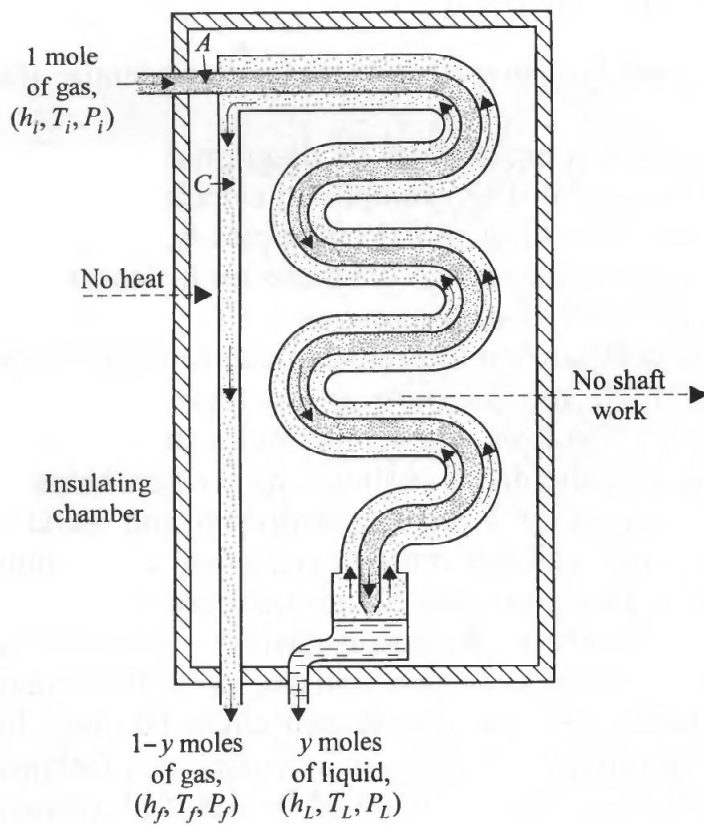
$$h_i = \text{molar enthalpy of entering gas at } (T_i, P_i),$$

$$h_L = \text{molar enthalpy of emerging liquid at } (T_L, P_L),$$

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

$$h_i = y h_L + (1 - y) h_f,$$

or

$$y = \frac{h_f - h_i}{h_f - h_L}. \quad (11.3)$$

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,

$$\mu = 0 \quad \text{at } T = T_i,$$

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.

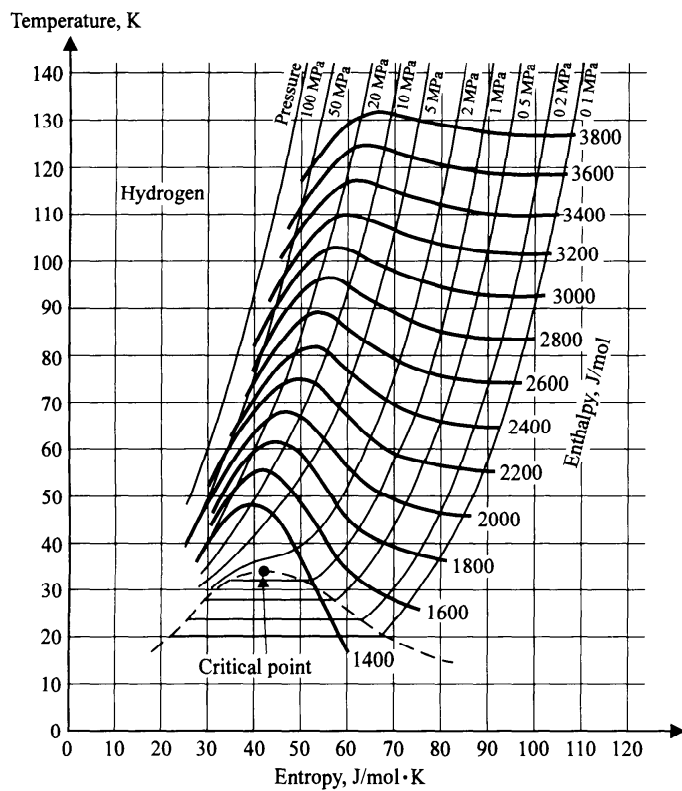


FIGURE 11-7
Temperature-entropy diagram
for hydrogen.

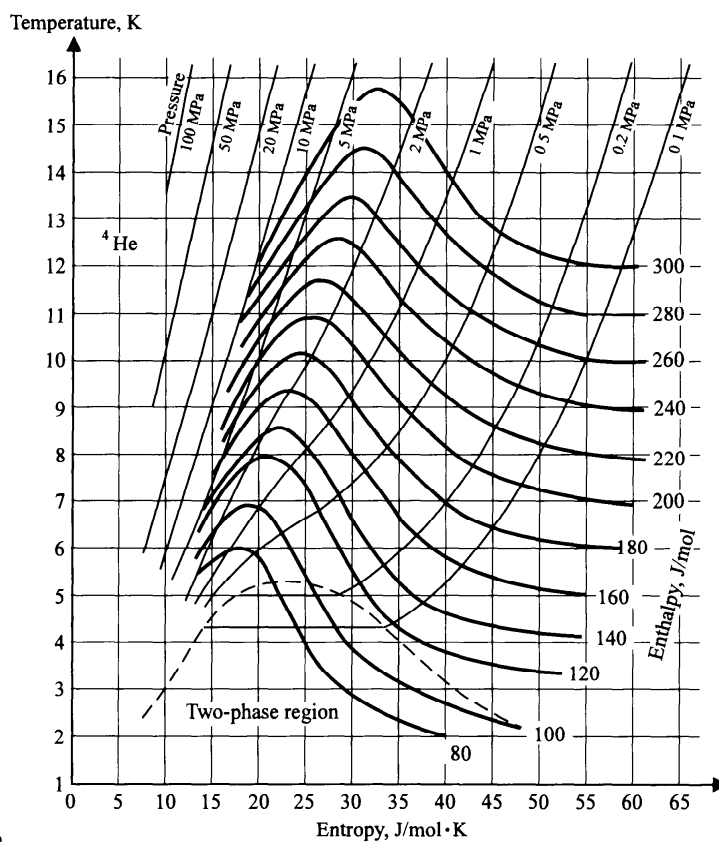


FIGURE 11-8
Temperature-entropy diagram for ^4He .

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

$$S = n_0(1 - x)s^{(i)} + n_0xs^{(f)},$$

and

$$V = n_0(1 - x)v^{(i)} + n_0xv^{(f)},$$

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*

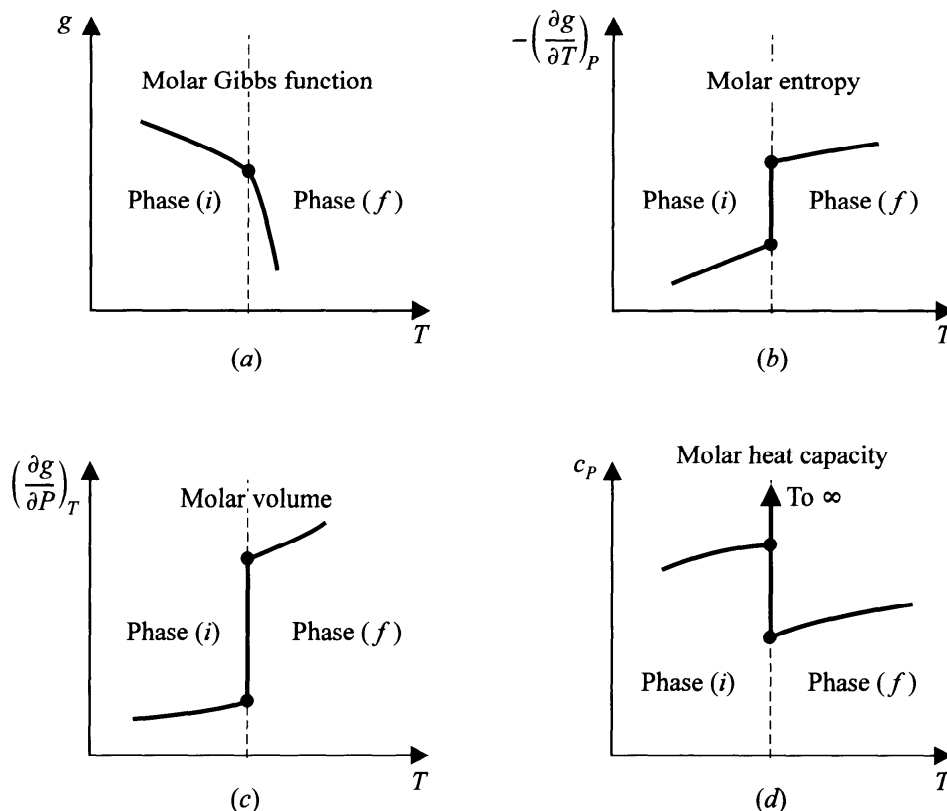


FIGURE 11-9

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,

$$c_P = T \left(\frac{\partial s}{\partial T} \right)_P \rightarrow \infty; \quad \beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \rightarrow \infty; \quad \kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \rightarrow \infty.$$

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,

$$T ds = c_P dT - T v \beta dP,$$

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,

$$T(s^{(f)} - s^{(i)}) = T \frac{dP}{dT} (v^{(f)} - v^{(i)}).$$

The left-hand member of this equation, according to Eq. (10.6), is the isobaric change of molar enthalpy $h^{(f)} - h^{(i)}$. Hence,

$$\boxed{\frac{dP}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{h^{(f)} - h^{(i)}}{T(v^{(f)} - v^{(i)})}.} \quad (11.4)$$

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*. Instead 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

$$\frac{dP}{dT} = \frac{h^{(f)} - h^{(i)}}{T(v^{(f)} - v^{(i)})}.$$

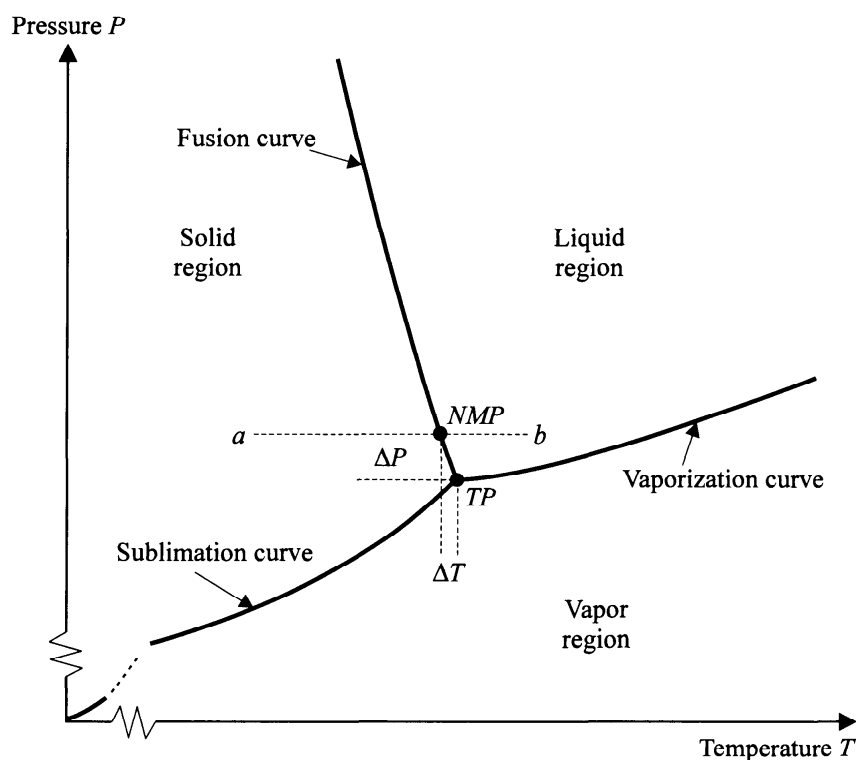
In dealing with phase transitions, it is necessary to indicate, in a simple way, the initial and final phases and the corresponding molar (or specific) enthalpy of transition. The notation used in this book is as follows: a symbol representing any property of the solid phase will be identified with a 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 $T_{TP} = 273.16 \text{ K}$ is higher than the normal melting

point temperature $T_{NMP} = 273.15$ 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 $T = 273$ K, $v' = 19.64 \times 10^{-6}$ m³/mol, $v'' = 18.02 \times 10^{-6}$ m³/mol, $h'' - h' = 6.01$ kJ/mol, and $\Delta P = 1.01 \times 10^5$ 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

[†] 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

$$\eta = \frac{|W|}{|Q_H|}$$

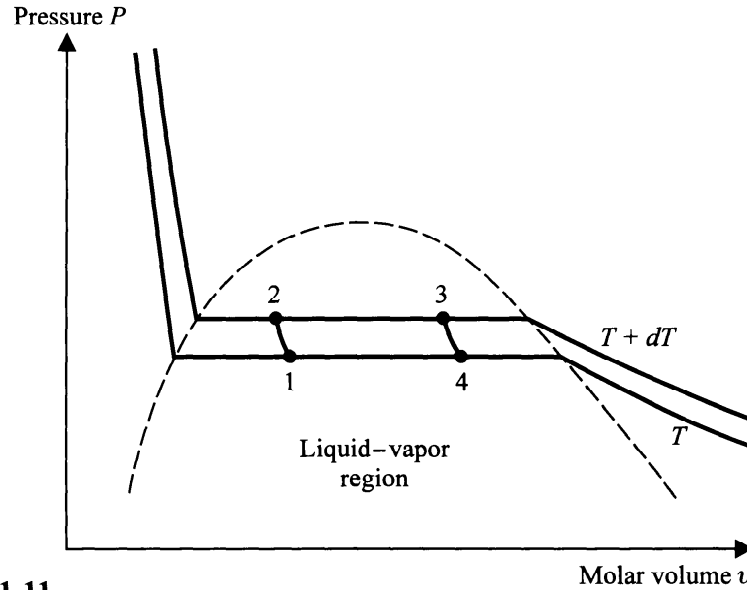
TABLE 11.2

Entropy changes during phase transitions

(All values of normal quantities are obtained at pressure $P = 1.01 \text{ kPa}$)

Substance	Δh_{NMP} , kJ/mol	T , K	Δs_{NMP} , kJ/mol · K	Δh_{NBP} , kJ/mol	T , K	Δs_{NBP} , kJ/mol · K
H ₂ O	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 ($P_{TP} = 518 \text{ kPa}$)	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

$$\frac{|W|}{|Q_H|} = \frac{dT}{T}. \quad (11.5)$$

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 $2 \rightarrow 3$ 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

$$dU(V, S) = -P dV + T dS, \quad (11.6)$$

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, \dots, n_N of N different substances. Since $U(V, S, n_1, n_2, \dots, n_N)$ is a state function, we can expand U as

$$dU(V, S, n) = \left(\frac{\partial U}{\partial V}\right)_{S, n} dV + \left(\frac{\partial U}{\partial S}\right)_{V, n} dS + \left(\frac{\partial U}{\partial n_1}\right)_{V, S, n'} dn_1 + \dots + \left(\frac{\partial U}{\partial n_N}\right)_{V, S, n'} dn_N, \quad (11.7)$$

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

$$\left(\frac{\partial U}{\partial n_j}\right)_{V, S, n'} \equiv \mu_j, \quad (11.8)$$

where μ_j is defined as the *chemical potential* of the j th substance (not to be confused with the Joule-Thomson coefficient, which is also written as μ). Then, Eq. (11.7) can be rewritten as

$$dU(V, S, n) = -P dV + T dS + \mu_1 dn_1 + \dots + \mu_N dn_N,$$

or, the internal energy for an open system is given by

$$dU(V, S, n) = -P dV + T dS + \sum_{j=1}^N \mu_j dn_j. \quad (11.9)$$

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* δW_C , that is,

$$\delta W_C = \sum_{j=1}^N \mu_j dn_j. \quad (11.10)$$

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,

$$dH(P, S, n) = V dP + T dS + \sum_{j=1}^N \mu_j dn_j, \quad (11.11)$$

$$dA(V, T, n) = -P dV - S dT + \sum_{j=1}^N \mu_j dn_j, \quad (11.12)$$

and

$$dG(P, T, n) = V dP - S dT + \sum_{j=1}^N \mu_j dn_j. \quad (11.13)$$

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 $G(P, T, n)$,

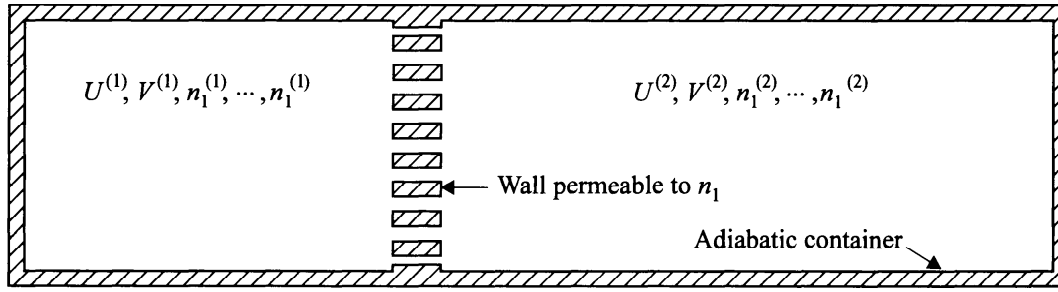
$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{P, T, n'}, \quad (11.14)$$

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, \dots, 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

$$dS = dS^{(1)} + dS^{(2)} = \frac{dU^{(1)}}{T^{(1)}} + \frac{dU^{(2)}}{T^{(2)}} - \frac{\mu_1^{(1)}}{T^{(1)}} dn_1^{(1)} - \frac{\mu_1^{(2)}}{T^{(2)}} dn_1^{(2)}. \quad (11.15)$$

Since matter and internal energy are conserved in the isolated composite system,

$$\begin{aligned} dn_1 &= dn_1^{(1)} + dn_1^{(2)} = 0, \\ dn_1^{(1)} &= -dn_1^{(2)}; \end{aligned} \quad (11.16)$$

and

$$\begin{aligned} dU &= dU^{(1)} + dU^{(2)} = 0, \\ dU^{(1)} &= -dU^{(2)}. \end{aligned} \quad (11.17)$$

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

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} - \left(\frac{\mu_1^{(1)}}{T^{(1)}} - \frac{\mu_1^{(2)}}{T^{(2)}} \right) dn_1^{(1)}. \quad (11.18)$$

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

$$\boxed{\mu_1^{(1)} = \mu_1^{(2)}}; \quad (11.19)$$

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),

$$dS = \frac{\mu_1^{(2)} - \mu_1^{(1)}}{T} dn_1^{(1)} > 0. \quad (11.20)$$

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,

$$dU(V, S, n) = -P dV + T dS + \mu dn, \quad (11.21)$$

$$dH(P, S, n) = V dP + T dS + \mu dn, \quad (11.22)$$

$$dA(V, T, n) = -P dV - S dT + \mu dn, \quad (11.23)$$

and
$$dG(P, T, n) = V dP - S dT + \mu dn. \quad (11.24)$$

Each of the four thermodynamic functions may be changed by a Legendre transformation of the chemical work term μdn to produce a new thermodynamic potential, two of which are new to thermodynamics textbooks.[†]

The transform of the internal energy U is

$$L = U - \mu n, \quad (11.25)$$

where the function $L(V, S, \mu)$ is known as the *Hill energy*, named after the chemist Terrell Hill, which in differential form is

$$dL = -P dV + T dS - n d\mu. \quad (11.26)$$

The transform of the enthalpy H is

$$R = H - \mu n, \quad (11.27)$$

where the function $R(P, S, \mu)$, called the *Ray energy*, named after the physicist John Ray, has its differential form as

$$dR = V dP + T dS - n d\mu. \quad (11.28)$$

The Helmholtz function A yields the *grand function* J by means of the Legendre transform

$$J = A - \mu n, \quad (11.29)$$

where $J(V, T, \mu)$ gives

$$dJ = -P dV - S dT - n d\mu. \quad (11.30)$$

Finally, the transform of the Gibbs function G is

$$Z = G - \mu n = 0, \quad (11.31)$$

which gives the *Guggenheim function* $Z(P, T, \mu)$, given in differential form by

$$dZ = V dP - S dT - n d\mu = 0. \quad (11.32)$$

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,

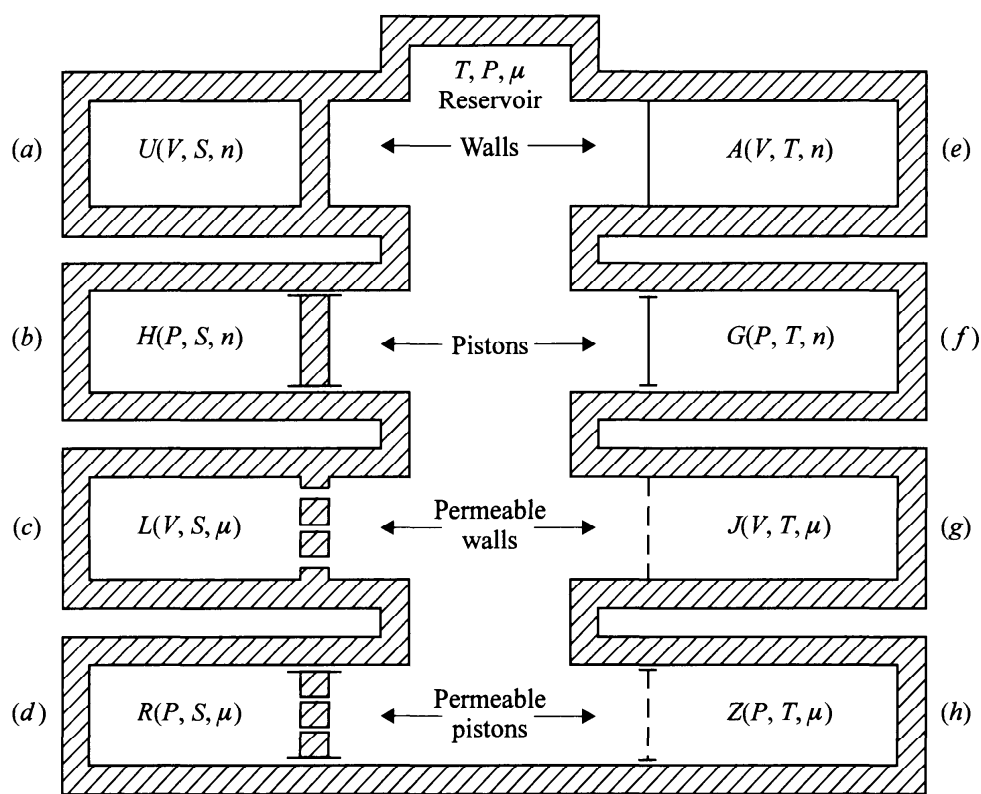


FIGURE 11-13

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

$$\mu_{cP} = T \left(\frac{\partial v}{\partial T} \right)_P - v.$$

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,

$$\mu_{cP} \rightarrow T \frac{dB'}{dT} - B'.$$

- (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 ^4He 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 $-9.05 \times 10^{-5} \text{ m}^3/\text{kg}$, 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/cm³, 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

$$y = \frac{v''[\beta''(T_f - T_i) - \kappa''(P_f - P_i)]}{v_f'' - v_f'}.$$

- (c) Calculate y for $i = 0^\circ\text{C}$, $1.01 \times 10^5 \text{ Pa}$; $f = -5^\circ\text{C}$, $5.98 \times 10^7 \text{ Pa}$; $\beta'' = -67 \times 10^{-6} \text{ K}^{-1}$; $\kappa'' = 12.04 \times 10^{-11} \text{ Pa}^{-1}$; $v_f'' - v_f' = -1.02 \times 10^{-4} \text{ m}^3/\text{kg}$.

- 11.11. (a) Prove that, for a single phase,

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{c_P}{T\nu\beta}.$$

- (b) Calculate $(\partial P/\partial T)_S$ for ice at -3°C , where $c_P = 2.01 \text{ kJ/kg}\cdot\text{K}$, $\nu = 1.09 \times 10^{-3} \text{ m}^3/\text{kg}$, and $\beta = 1.58 \times 10^{-4} \text{ K}^{-1}$.
- (c) Ice is initially at -3°C and $1.01 \times 10^5 \text{ Pa}$. 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, $-1.35 \times 10^7 \text{ Pa/K}$?)

- 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 ($P_i = 1.01 \times 10^5 \text{ Pa}$, $T_i = 273 \text{ K}$).

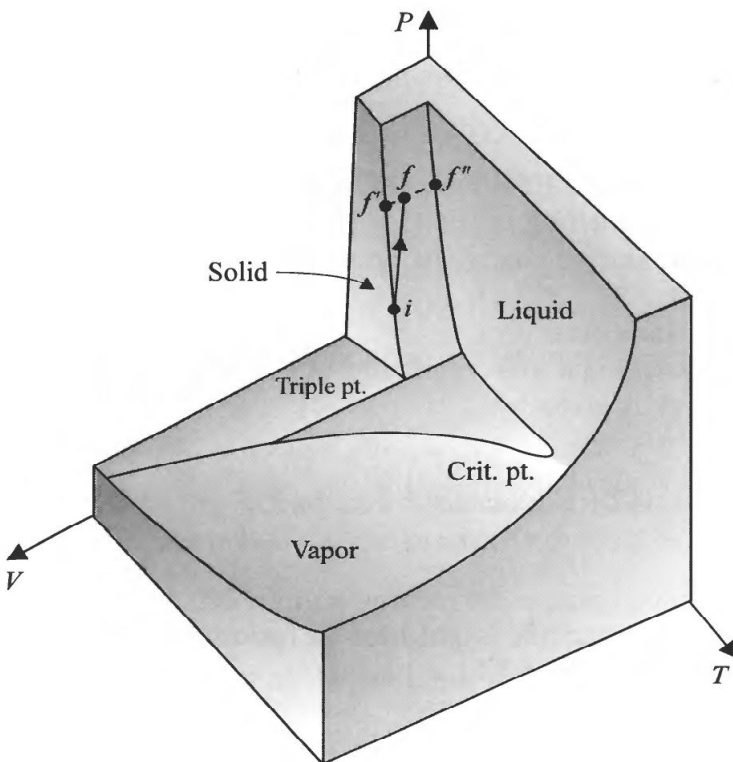


FIGURE P11-1

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 $T_f = 272 \text{ K}$, $P_f = 1.35 \times 10^7 \text{ Pa}$, $c'_p = 2.01 \text{ kJ/kg} \cdot \text{K}$, $v' = 1.09 \times 10^{-3} \text{ m}^3/\text{kg}$, $\beta' = 1.58 \times 10^{-4} \text{ K}^{-1}$, and $\Delta h_F = 334 \text{ kJ/kg}$.

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

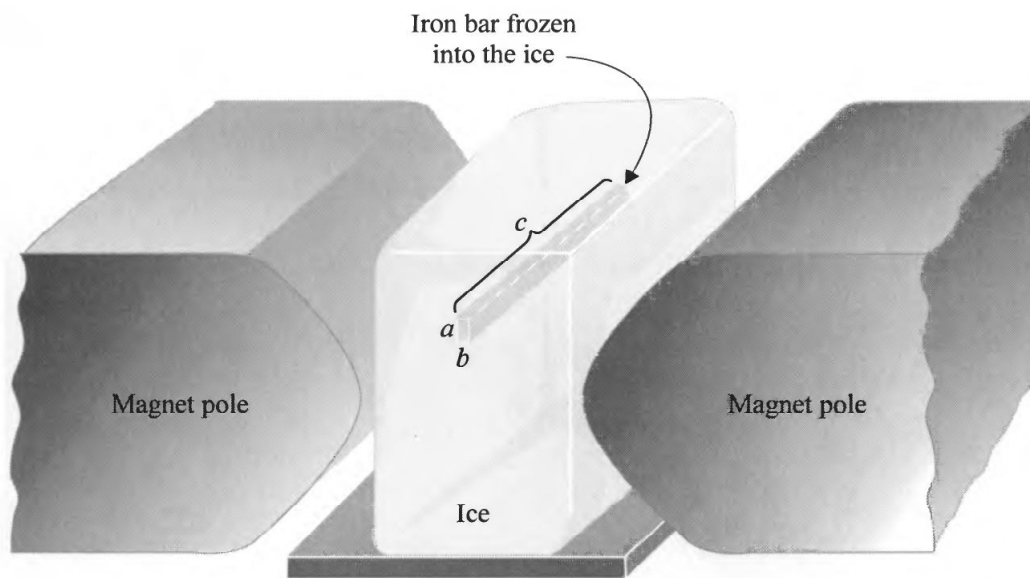


FIGURE P11-2

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 $0.6 \text{ W/m} \cdot \text{K}$, 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 $F = 10^2 \text{ N}$? (Thermal conductivity of steel is $60 \text{ W/m} \cdot \text{K}$.)

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