# 8

# STABILITY OF THERMODYNAMIC SYSTEMS

## 8-1 INTRINSIC STABILITY OF THERMODYNAMIC SYSTEMS

The basic extremum principle of thermodynamics implies both that $dS = 0$ and that $d^2S < 0$, the first of these conditions stating that the entropy is an extremum and the second stating that the extremum is, in particular, a maximum. We have not yet fully exploited the second condition, which determines the *stability* of predicted equilibrium states. Similarly, in classical mechanics the stable equilibrium of a rigid pendulum is at the position of minimum potential energy. A so-called "unstable equilibrium" exists at the inverted point where the potential energy is maximum.

Considerations of stability lead to some of the most interesting and significant predictions of thermodynamics. In this chapter we investigate the conditions under which a system is stable. In Chapter 9 we consider phase transitions, which are the consequences of instability.

Consider two identical subsystems, each with a fundamental equation $S = S(U, V, N)$, separated by a totally restrictive wall. Suppose the dependence of $S$ on $U$ to be qualitatively as sketched in Fig. 8.1. If we were to remove an amount of energy $\Delta U$ from the first subsystem and transfer it to the second subsystem the total entropy would change from its initial value of $2S(U, V, N)$ to $S(U + \Delta U, V, N) + S(U - \Delta U, V, N)$. With the shape of the curve shown in the figure the resultant entropy would be larger than the initial entropy! If the adiabatic restraint were removed in such a system energy would flow spontaneously across the wall; one subsystem thereby would increase its energy (and its temperature) at the expense of the other. Even within one subsystem the system would find it advantageous to transfer energy from one region to another, developing internal inhomogeneities. Such a loss of homogeneity is the hallmark of a phase transition.

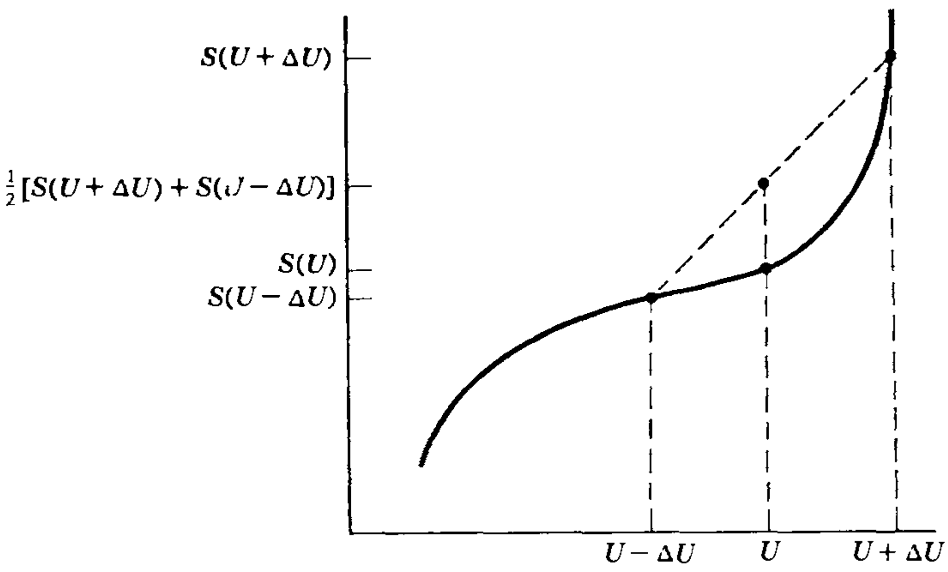

FIGURE 8.1
For a convex fundamental relation, as shown, the average entropy is increased by transfer of energy between two subsystems; such a system is unstable.

It is evident from Fig. 8.1 that the condition of stability is the *concavity* of the entropy.[1]

$$S(U + \Delta U, V, N) + S(U - \Delta U, V, N) \leq 2S(U, V, N) \qquad \text{(for all } \Delta) \tag{8.1}$$

For $\Delta U \to 0$ this condition reduces to its differential form

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \leq 0 \tag{8.2}$$

However this differential form is less restrictive than the concavity condition (8.1), which must hold for *all* $\Delta U$ rather than for $\Delta U \to 0$ only.

It is evident that the same considerations apply to a transfer of volume

$$S(U, V + \Delta V, N) + S(U, V - \Delta V, N) \leq 2S(U, V, N) \tag{8.3}$$

or in differential form

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_{U,N} \leq 0 \tag{8.4}$$

A fundamental equation that does not satisfy the concavity conditions might be obtained from a statistical mechanical calculation or from

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[1] R. B. Griffiths, *J. Math. Phys.* **5**, 1215 (1964). L. Galgani and A. Scotti, *Physica* **40**, 150 (1968); **42**, 242 (1969); *Pure and Appl Chem.* **22**, 229 (1970).

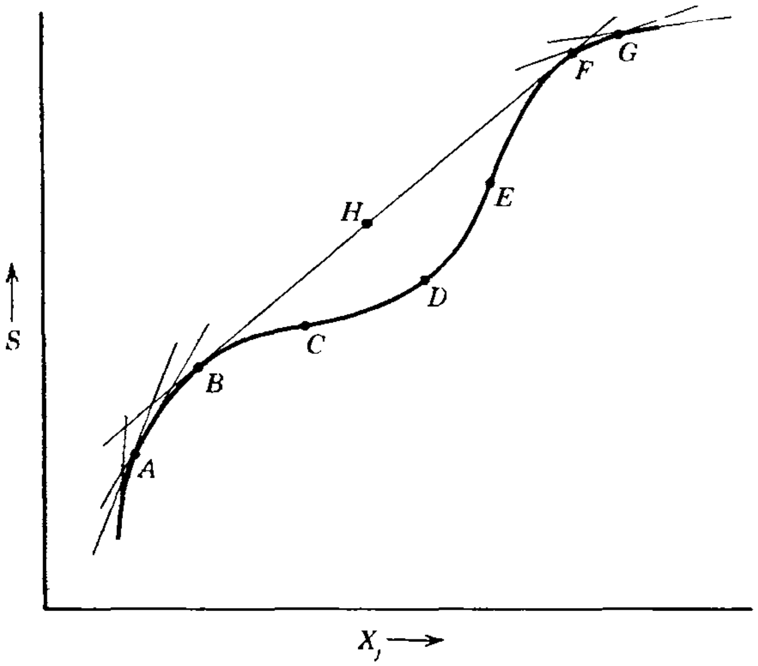

FIGURE 8.2
The underlying fundamental relation *ABCDEFG* is unstable. The stable fundamental relation is *ABHFG*. Points on the straight line *BHF* correspond to inhomogeneous combinations of the two phases at *B* and *F*.

extrapolation of experimental data. The stable thermodynamic fundamental equation is then obtained from this "underlying fundamental equation" by the construction shown in Fig. 8.2. The family of tangent lines that lie everywhere *above* the curve (the superior tangents) are drawn; *the thermodynamic fundamental equation is the envelope of these superior tangent lines.*

In Fig. 8.2 the portion *BCDEF* of the underlying fundamental relation is unstable and is replaced by the straight line *BHF*. It should be noted that only the portion *CDE* fails to satisfy the differential (or "local") form of the stability condition (8.2), whereas the entire portion *BCDEF* violates the global form (8.1). The portions of the curve *BC* and *EF* are said to be "locally stable" but "globally unstable."

A point on a straight portion (*BHF* in Fig. 8.2) of the fundamental relation corresponds to a phase separation in which part of the system is in state *B* and part in state *F*, as we shall see in some detail in Chapter 9.

In the three-dimensional $S-U-V$ subspace the global condition of stability requires that the entropy surface $S(U, V, \dots)$ lie everywhere below its tangent *planes*. That is, for arbitrary $\Delta U$ and $\Delta V$

$$S(U + \Delta U, V + \Delta V, N) + S(U - \Delta U, V - \Delta V, N) \leq 2S(U, V, N) \tag{8.5}$$

from which equations 8.2 and 8.4 again follow, as well as the additional requirement (see Problem 8.1-1) that

$$\frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2}-\left(\frac{\partial^2 S}{\partial U\,\partial V}\right)^2 \geqslant 0 \tag{8.6}$$

We shall soon obtain this equation by an alternative method, by applying the analogue of the simple curvature condition 8.2 to the Legendre transforms of the entropy.

To recapitulate, stability requires that the entropy surface lie everywhere below its family of tangent planes. The local conditions of stability are weaker conditions. They require not only that $(\partial^2 S/\partial U^2)_{V,N}$ and $(\partial^2 S/\partial V^2)_{U,N}$ be negative, but that $[(\partial^2 S/\partial U^2)(\partial^2 S/\partial V^2)] - (\partial^2 S/\partial U\,\partial V)^2$ must be positive. The condition $\partial^2 S/\partial U^2 \leqslant 0$ ensures that the curve of intersection of the entropy surface with the plane of constant $V$ (passing through the equilibrium point) have negative curvature. The condition $\partial^2 S/\partial V^2 < 0$ similarly ensures that the curve of intersection of the entropy surface with the plane of constant $U$ have negative curvature. These two "partial curvatures" are not sufficient to ensure concavity, for the surface could be "fluted," curving downward along the four directions $\pm U$ and $\pm V$, but curving upward along the four diagonal directions (between the $U$ and $V$ axes). It is this fluted structure that is forbidden by the third differential stability criterion (8.6).

In physical terms the local stability conditions ensure that inhomogeneities of either $u$ or $v$ separately do not increase the entropy, and also that a coupled inhomogeneity of $u$ and $v$ together does not increase the entropy.

For magnetic systems analogous relations hold, with the magnetic moment replacing the volume.[2]

Before turning to the full physical implications of these stability conditions it is useful first (Section 8.2) to consider their analogues for other thermodynamic potentials. We here take note only of the most easily interpreted inequality (equation 8.3), which suggests the type of information later to be inferred from all the stability conditions. Equation 8.2 requires that

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_{V,N} = -\frac{1}{NT^2 c_v} \leqslant 0 \tag{8.7}$$

whence *the molar heat capacity must be positive in a stable system*. The remaining stability conditions will place analogous restrictions on other physically significant observables.

Finally, and in summary, in an $r + 2$ dimensional thermodynamic space $(S, X_0, X_1, \ldots, X_r)$ *stability requires that the entropy hyper-surface lie everywhere below its family of tangent hyper-planes.*

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[2] R. B. Griffiths, *J. Math. Phys.* 5, 1215 (1964)

## PROBLEMS

**8.1-1.** To establish the inequality 8.6 expand the left-hand side of 8.5 in a Taylor series to second order in $\Delta U$ and $\Delta V$. Show that this leads to the condition

$$S_{UU}(\Delta U)^2 + 2S_{UV}\Delta U\Delta V + S_{VV}(\Delta V)^2 \leq 0$$

Recalling that $S_{UU} \equiv \partial^2 S/\partial U^2 \leq 0$, show that this can be written in the form

$$(S_{UU}\Delta U + S_{UV}\Delta V)^2 + (S_{UU}S_{VV} - S_{UV}^2)(\Delta V)^2 \geqslant 0$$

and that this condition in turn leads to equation 8.6.

**8.1-2.** Consider the fundamental equation of a monatomic ideal gas and show that $S$ is a concave function of $U$ and $V$, and also of $N$.

## 8-2 STABILITY CONDITIONS FOR THERMODYNAMIC POTENTIALS

The reformulation of the stability criteria in energy representation requires only a straightforward transcription of language. Whereas the entropy is maximum, the energy is minimum; thus the concavity of the entropy surface is replaced by *convexity* of the energy surface.

The stable energy surface lies *above* its tangent planes

$$U(S + \Delta S, V + \Delta V, N) + U(S - \Delta S, V - \Delta V, N) \geq 2U(S, V, N) \tag{8.8}$$

The local conditions of convexity become

$$\frac{\partial^2 U}{\partial S^2} = \frac{\partial T}{\partial S} \geq 0 \qquad \frac{\partial^2 U}{\partial V^2} = -\frac{\partial P}{\partial V} \geq 0 \tag{8.9}$$

and for cooperative variations of $S$ and $V$

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S\,\partial V}\right)^2 \geq 0 \tag{8.10}$$

This result can be extended easily to the Legendre transforms of the energy, or of the entropy. We first recall the properties of Legendre transformations (equation 5.31)

$$P = \frac{\partial U}{\partial X} \qquad \text{and} \qquad X = -\frac{\partial U[P]}{\partial P} \tag{8.11}$$

whence

$$\frac{\partial X}{\partial P} = -\frac{\partial^2 U[P]}{\partial P^2} = \frac{1}{\dfrac{\partial^2 U}{\partial X^2}} \tag{8.12}$$

Hence the sign of $\partial^2 U[P]/\partial P^2$ is the negative of the sign of $\partial^2 U/\partial X^2$. *If $U$ is a convex function of $X$ then $U[P]$ is a concave function of $P$.* It follows that the Helmholtz potential is a concave function of the temperature and a convex function of the volume

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0 \qquad \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0 \tag{8.13}$$

The enthalpy is a convex function of the entropy and a concave function of the pressure

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} \geq 0 \qquad \left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \leq 0 \tag{8.14}$$

The Gibbs potential is a concave function of both temperature and pressure

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0 \qquad \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \leq 0 \tag{8.15}$$

In summary, for constant $N$ the *thermodynamic potentials* (the energy and its Legendre transforms) *are convex functions of their extensive variables and concave functions of their intensive variables.* Similarly for constant $N$ the *Massieu functions* (the entropy and its Legendre transforms) *are concave functions of their extensive variables and convex functions of their intensive variables.*

## PROBLEMS

**8.2-1.** *a*) Show that in the region $X > 0$ the function $Y = X^n$ is concave for $0 < n < 1$ and convex for $n < 0$ or $n > 1$.

The following four equations are asserted to be fundamental equations of physical systems.

(*b*) $F = A\left(\dfrac{N^5 T}{V^3}\right)^{\frac{1}{2}}$ (*c*) $G = BT^{\frac{1}{2}}P^2N$

(*d*) $H = \dfrac{CS^2P^{\frac{1}{2}}}{N}$ (*e*) $U = D\left(\dfrac{S^3V^4}{N^5}\right)^{\frac{1}{2}}$

Which of these equations violate the criteria of stability? Assume $A$, $B$, $C$, and $D$ to be positive constants. Recall the "fluting condition" (equation 8.10).

**8.2-2.** Prove that

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = \frac{\dfrac{\partial^2 U}{\partial S^2}\dfrac{\partial^2 U}{\partial V^2} - \left(\dfrac{\partial^2 U}{\partial S\,\partial V}\right)^2}{\dfrac{\partial^2 U}{\partial S^2}}$$

*Hint*: Note that $(\partial^2 F/\partial V^2)_T = -(\partial P/\partial V)_T$, and consider $P$ formally to be a function of $S$ and $V$.

This identity casts an interesting perspective on the formalism. The quantity in square brackets measures the curvature of the energy along a direction intermediate between the $S$ and $V$ axes (recall the discussion of "fluting" after equation 8.6). The primary curvature condition on $F$, along the $V$ axis, is redundant with the "fluting" condition on $U$. *Only primary curvature conditions need be invoked if all potentials are considered.*

**8.2-3.** Show that stability requires equations 8.15 and

$$\left(\frac{\partial^2 G}{\partial T^2}\right)\left(\frac{\partial^2 G}{\partial P^2}\right) - \left(\frac{\partial^2 G}{\partial T\,\partial P}\right)^2 \geqslant 0$$

(Recall Problem 8.1-1.)

## 8-3 PHYSICAL CONSEQUENCES OF STABILITY

We turn finally to a direct interpretation of the local stability criteria in terms of limitations on the signs of quantities such as $c_v$, $c_p$, $\alpha$, and $\kappa_T$. The first such inference was obtained in equations 8.2 or 8.7, where we found that $c_v \geq 0$. Similarly, the convexity of the Helmholtz potential with respect to the volume gives

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V\kappa_T} \geq 0 \tag{8.16}$$

or

$$\kappa_T > 0 \tag{8.17}$$

The fact that both $c_v$ and $\kappa_T$ are positive (equations 8.7 and 8.17) has further implications which become evident when we recall the identities of

Problem 3.9-5

$$c_p - c_v = \frac{Tv\alpha^2}{\kappa_T} \tag{8.18}$$

and

$$\frac{\kappa_s}{\kappa_T} = \frac{c_v}{c_p} \tag{8.19}$$

From these it follows that stability requires

$$c_p \geq c_v \geq 0 \tag{8.20}$$

and

$$\kappa_T \geq \kappa_s \geq 0 \tag{8.21}$$

Thus both heat capacities and both compressibilities must be positive in a stable system. *Addition of heat, either at constant pressure or at constant volume, necessarily increases the temperature of a stable system—the more so at constant volume than at constant pressure. And decreasing the volume, either isothermally or isentropically, necessarily increases the pressure of a stable system—the more so isothermally than isentropically.*

## PROBLEMS

**8.3-1.** Explain on intuitive grounds why $c_p \geq c_v$ and why $\kappa_T \geq \kappa_S$.
*Hint*: Consider the energy input and the energy output during constant-pressure and constant-volume heating processes.

**8.3-2.** Show that the fundamental equation of a monatomic ideal gas satisfies the criteria of intrinsic stability.

**8.3-3.** Show that the van der Waals equation of state does not satisfy the criteria of intrinsic stability for all values of the parameters. Sketch the curves of $P$ versus $V$ for constant $T$ (the isotherms of the gas) and show the region of local instability.

## 8-4 LE CHATELIER'S PRINCIPLE; THE QUALITATIVE EFFECT OF FLUCTUATIONS

The physical content of the stability criteria is known at *Le Chatelier's Principle*. According to this principle the criterion for stability is that *any* *inhomogeneity that somehow develops in a system should induce a process that tends to eradicate the inhomogeneity.*

As an example, suppose that a container of fluid is in equilibrium and an incident photon is suddently absorbed at some point within it, locally heating the fluid slightly. Heat flows away from this heated region and, by the stability condition (that the specific heat is positive), this flow of heat tends to *lower* the local temperature toward the ambient value. The initial homogeneity of the system thereby is restored.

Similarly, a longitudinal vibrational wave in a fluid system induces local regions of alternately high and low density. The regions of increased density, and hence of increased pressure, tend to expand, and the regions of low density contract. The stability condition (that the compressibility is positive) ensures that these responses tend to restore the local pressure toward homogeneity.

In fact local inhomogeneities always occur in physical systems even in the absence of incident photons or of externally induced vibrations. In a gas, for instance, the individual molecules move at random, and by pure chance this motion produces regions of high density and other regions of low density.

From the perspective of statistical mechanics all systems undergo continual local fluctuations. The equilibrium state, static from the viewpoint of classical thermodynamics, is incessantly dynamic. Local inhomogeneities continually and spontaneously generate, only to be attenuated and dissipated in accordance with the Le Chatelier principle.

An informative analogy exists between a thermodynamic system and a model of a marble rolling within a "potential well." The stable state is at the minimum of the surface. The criterion of stability is that the surface be convex.

In a slightly more sophisticated viewpoint we can conceive of the marble as being subject to Brownian motion—perhaps being buffeted by some type of random collisions. These are the mechanical analogues of the spontaneous fluctuations that occur in all real systems. The potential minimum does not necessarily coincide with the instantaneous position of the system, but rather with its "expected value"; it is this "expected value" that enters thermodynamic descriptions. The curvature of the potential well then plays a crucial and continual role, restoring the system toward the "expected state" after each Brownian impact (fluctuation). This "induced restoring force" is the content of the Le Chatelier principle.

We note in passing that in the atypical but important case in which the potential well is both shallow and asymmetric, the time-averaged position may deviate measurably from the "expected state" at the potential minimum. In such a case classical thermodynamics makes spurious predictions which deviate from observational data, for thermodynamic measurements yield *average* values (recall Chapter 1). Such a pathological case arises at higher-order phase transitions—the correct theory of which was developed in the 1970s. We shall explore that area in Chapter 11.

## 8-5 THE LE CHATELIER-BRAUN PRINCIPLE

Returning to the physical interpretation of the stability criteria, a more subtle insight than that given by the Le Chatelier principle is formulated in the Le Chatelier–Braun principle.

Consider a system that is taken out of equilibrium by some action or fluctuation. According to the Le Chatelier principle the perturbation directly induces a process that attenuates the perturbation. But various other secondary processes are also induced, indirectly. The content of the Le Chatelier–Braun principle is that these indirectly induced processes also act to attenuate the initial perturbation.

A simple example may clarify the principle. Consider a subsystem contained within a cylinder with diathermal walls and a loosely fitting piston, all immersed within a "bath" (a thermal and pressure reservoir). The piston is moved outward slightly, either by an external agent or by a fluctuation. The primary effect is that the internal pressure is decreased—the pressure difference across the piston then acts to push it inward; this is the Le Chatelier principle. A second effect is that the initial expansion $dV$ alters the temperature of the subsystem; $dT = (\partial T/\partial V)_S \, dV = -(T\alpha/Nc_v\kappa_T)\, dV$. This change of temperature may have either sign, depending on the sign of $\alpha$. Consequently there is a flow of heat through the cylinder walls, inward if $\alpha$ is positive and outward if $\alpha$ is negative (sign $\text{đ}Q = \operatorname{sign}\alpha$). This flow of heat, in turn, tends to change the pressure of the system: $dP = (1/T)(\partial P/\partial S)_V \, \text{đ}Q = (\alpha/NT^2 c_v \kappa_T)\, \text{đ}Q$. The pressure is increased for either sign of $\alpha$. Thus a secondary induced process (heat flow) also acts to diminish the initial perturbation. This is the Le Chatelier–Braun principle.

To demonstrate both the Le Chatelier and the Le Chatelier–Braun principles formally, let a spontaneous fluctuation $dX_1^f$ occur in a composite system. This fluctuation is accompanied by a change in the intensive parameter $P_1$ of the subsystem

$$dP_1^f = \frac{\partial P_1}{\partial X_1} dX_1^f \tag{8.22}$$

The fluctuation $dX_1^f$ also alters the intensive parameter $P_2$

$$dP_2^f = \frac{\partial P_2}{\partial X_1} dX_1^f \tag{8.23}$$

Now we can inquire as to the changes in $X_1$ and $X_2$ which are driven by these two deviations $dP_1^f$ and $dP_2^f$. We designate the driven change in $dX_j$ by $dX_j^r$, the superscript indicating "response." The signs of $dX_1^r$ and $dX_2^r$ are determined by the minimization of the total energy (at constant total entropy)

$$d(U + U^{\text{res}}) = (P_1 - P_1^{\text{res}})\,dX_1^r + (P_2 - P_2^{\text{res}})\,dX_2^r \leq 0 \tag{8.24}$$

$$= dP_1^f dX_1^r + dP_2^f dX_2^r \leq 0 \tag{8.25}$$

Hence, since $dX_1^r$ and $dX_2^r$ are independent

$$dP_1^f dX_1^r \leq 0 \tag{8.26}$$

and

$$dP_2^f dX_2^r \leq 0 \tag{8.27}$$

From the first of these and equation 8.22

$$\frac{dP_1}{dX_1}\,dX_1^f dX_1^r \leq 0 \tag{8.28}$$

and similarly

$$\frac{dP_2}{dX_1}\,dX_1^f dX_2^f \leq 0 \tag{8.29}$$

We examine these two results in turn. The first, equation 8.28, is the formal statement of the Le Chatelier principle. For multiplying by $dP_1/dX_1$, which is positive by virtue of the convexity criterion of stability,

$$\frac{dP_1}{dX_1}\,dX_1^f \cdot \frac{dP_1}{dX_1}\,dX_1^r \leq 0 \tag{8.30}$$

or

$$dP_1^f dP_1^{r(1)} \leq 0 \tag{8.31}$$

That is, the response $dX_1^r$ produces a change $dP_1^{r(1)}$ in the intensive parameter $P_1$ that is opposite in sign to the change $dP_1^f$ induced by the initial fluctuation.

The second inequality, (8.29), can be rewritten by the Maxwell relation

$$\frac{\partial P_2}{\partial X_1} = \frac{\partial P_1}{\partial X_2} \tag{8.32}$$

in the form

$$dX_1^f \cdot \left( \frac{\partial P_1}{\partial X_2} dX_2^r \right) \leq 0 \tag{8.33}$$

Then, multiplying by the positive quantity $dP_1/dX_1$

$$\left( \frac{\partial P_1}{\partial X_1} dX_1^f \right) \left( \frac{dP_1}{dX_2} dX_2^r \right) \leq 0 \tag{8.34}$$

or

$$\left( dP_1^f \right) \left( dP_1^{r(2)} \right) \leq 0 \tag{8.35}$$

That is, the response $dX_2^r$ produces a change $dP_1^{r(2)}$ in the intensive parameter $P_1$ which is opposite in sign to the change in $P_1$ directly induced by the initial fluctuation. This is the Le Chatelier–Braun principle.

Finally, it is of some interest to note that equation 8.33 is subject to another closely correlated interpretation. Multiplying by the positive quantity $dP_2/dX_2$

$$\left( \frac{\partial P_2}{\partial X_1} dX_1^f \right) \left( \frac{\partial P_2}{\partial X_2} dX_2^r \right) \leq 0 \tag{8.36}$$

or

$$\left( dP_2^f \right) \left( dP_2^{r(2)} \right) \leq 0 \tag{8.37}$$

That is, the response in $X_2$ produces a change in $P_2$ opposite in sign to the change induced by the initial fluctuation in $X_1$.

## PROBLEMS

**8.5-1.** A system is in equilibrium with its environment at a common temperature and a common pressure. The entropy of the system is increased slightly (by a fluctuation in which heat flows into the system, or by the purposeful injection of heat into the system). Explain the implications of both the Le Chatelier and the Le Chatelier–Braun principles to the ensuing processes, proving your assertions in detail.

# 9

# FIRST-ORDER PHASE TRANSITIONS

## 9-1 FIRST-ORDER PHASE TRANSITIONS IN SINGLE COMPONENT SYSTEMS

Ordinary water is liquid at room temperature and atmospheric pressure, but if cooled below 273.15 K it solidifies; and if heated above 373.15 K it vaporizes. At each of these temperatures the material undergoes a precipitous change of properties—a "phase transition." At high pressures water undergoes several additional phase transitions from one solid form to another. These distinguishable solid phases, designated as "ice I," "ice II," "ice III," ..., differ in crystal structure and in essentially all thermodynamic properties (such as compressibility, molar heat capacity, and various molar potentials such as $u$ or $f$). The "phase diagram" of water is shown in Fig. 9.1.

Each transition is associated with a linear region in the thermodynamic fundamental relation (such as $BHF$ in Fig. 8.2), and each can be viewed as the result of failure of the stability criteria (convexity or concavity) in the underlying fundamental relation.

In this section we shall consider systems for which the underlying fundamental relation is unstable. By a qualitative consideration of fluctuations in such systems we shall see that *the fluctuations are profoundly influenced by the details of the underlying fundamental relation*. In contrast, *the average values of the extensive parameters reflect only the stable thermodynamic fundamental relation.*

Consideration of the manner in which the form of the underlying fundamental relation influences the thermodynamic fluctuations will provide a physical interpretation of the stability considerations of Chapter 8 and of the construction of Fig. 8.2 (in which the thermodynamic fundamental relation is constructed as the envelope of tangent planes).

A simple mechanical model illustrates the considerations to follow by an intuitively transparent analogy. Consider a semicircular section of pipe, closed at both ends. The pipe stands vertically on a table, in the form of

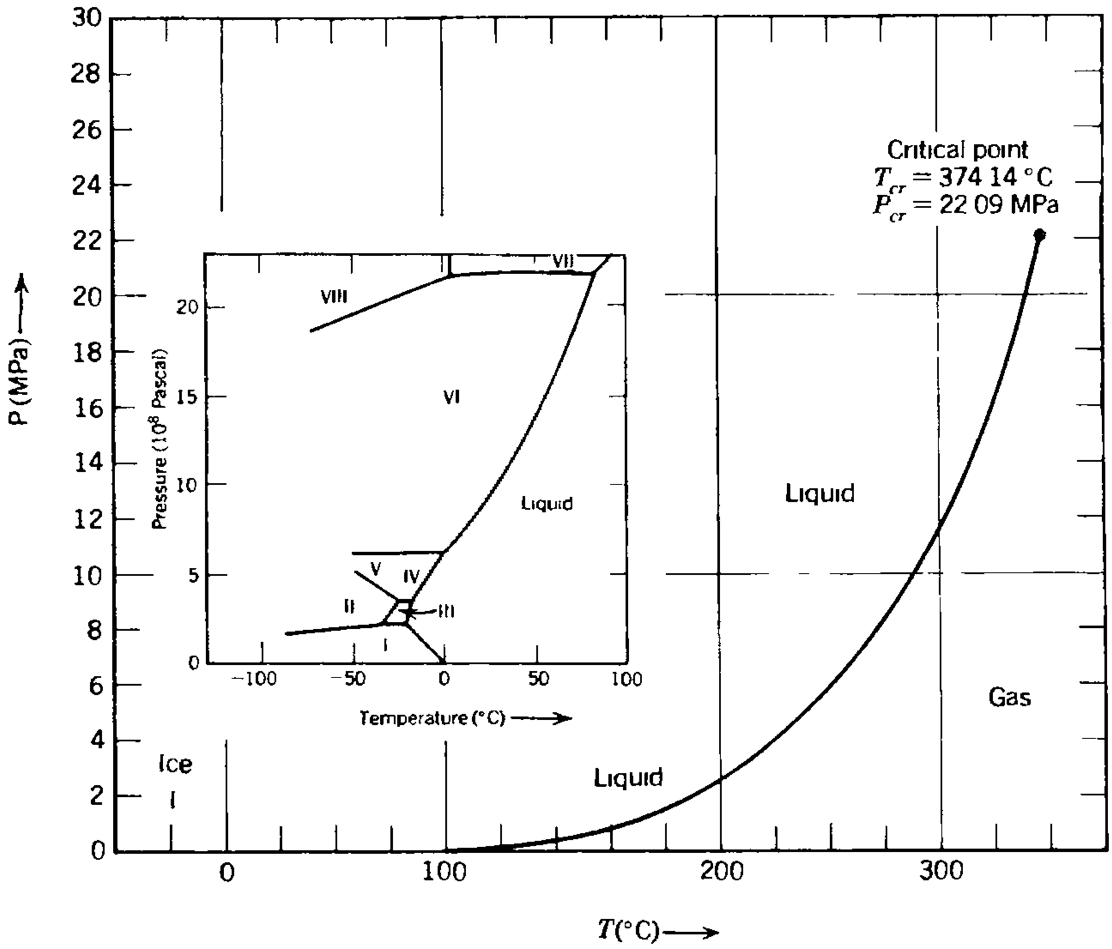

FIGURE 9.1

Phase diagram of water. The region of gas-phase stability is represented by an indiscernibly narrow horizontal strip above the positive temperature axis in the phase diagram (small figure). The background graph is a magnification of the vertical scale to show the gas phase and the gas–liquid coexistence curve.

an inverted U (Fig. 9.2). The pipe contains a freely-sliding internal piston separating the pipe into two sections, each of which contains one mole of a gas. The symmetry of the system will prove to have important consequences, and to break this symmetry we consider that each section of the pipe contains a small metallic "ball bearing" (i.e., a small metallic sphere). The two ball bearings are of dissimilar metals, with different coefficients of thermal expansion.

At some particular temperature, which we designate as $T_c$, the two spheres have equal radii; at temperatures above $T_c$ the right-hand sphere is the larger.

The piston, momentarily brought to the apex of the pipe, can fall into either of the two legs, compressing the gas in that leg and expanding the gas in the other leg. In either of these competing equilibrium states the pressure difference exactly compensates the effect of the weight of the piston.

In the absence of the two ball bearings the two competing equilibrium states would be fully equivalent. But with the ball bearings present the

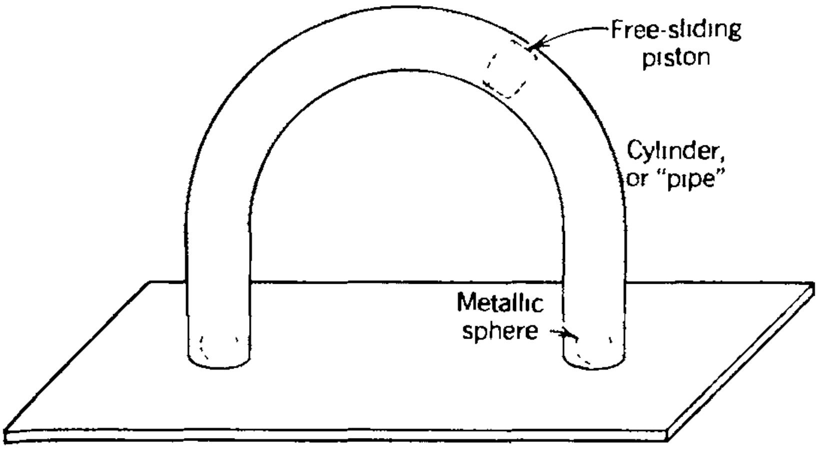

FIGURE 9.2
A simple mechanical model.

more stable equilibrium position is that to the left if $T > T_c$, and it is that to the right if $T < T_c$.

From a thermodynamic viewpoint the Helmholtz potential of the system is $F = U - TS$, and the energy $U$ contains the gravitational potential energy of the piston as well as the familiar thermodynamic energies of the two gases (and, of course, the thermodynamic energies of the two ball bearings, which we assume to be small and/or equal). Thus the Helmholtz potential of the system has two local minima, the lower minimum corresponding to the piston being on the side of the smaller sphere.

As the temperature is lowered through $T_c$ the two minima of the Helmholtz potential shift, the absolute minimum changing from the left-hand to the right-hand side.

A similar shift of the equilibrium position of the piston from one side to the other can be induced at a given temperature by tilting the table—or, in the thermodynamic analogue, by adjustment of some thermodynamic parameter other than the temperature.

The shift of the equilibrium state from one local minimum to the other constitutes a *first-order phase transition*, induced either by a change in temperature or by a change in some other thermodynamic parameter.

*The two states between which a first-order phase transition occurs are distinct, occurring at separate regions of the thermodynamic configuration space.*

To anticipate "critical phenomena" and "second-order phase transitions" (Chapter 10) it is useful briefly to consider the case in which the ball bearings are identical or absent. Then at low temperatures the two competing minima are equivalent. However as the temperature is increased the two equilibrium positions of the piston rise in the pipe, approaching the apex. Above a particular temperature $T_{cr}$, there is only one equilibrium position, with the piston at the apex of the pipe. Inversely, lowering the temperature from $T > T_{cr}$ to $T < T_{cr}$, the single equilibrium state bifurcates into two (symmetric) equilibrium states. The temperature $T_{cr}$ is the "critical temperature," and the transition at $T_{cr}$ is a "second-order phase transition."

*The states between which a second-order phase transition occurs are contiguous states in the thermodynamic configuration space.*

In this chapter we consider first-order phase transitions. Second-order transitions will be discussed in Chapter 10. We shall there also consider the "mechanical model" in quantitative detail, whereas we here discuss it only qualitatively.

Returning to the case of dissimilar spheres, consider the piston residing in the higher minimum—that is, in the same side of the pipe as the larger ball bearing. Finding itself in such a minimum of the Helmholtz potential, the piston will remain temporarily in that minimum though undergoing thermodynamic fluctuations ("Brownian motion"). After a sufficiently long time a giant fluctuation will carry the piston "over the top" and into the stable minimum. It then will remain in this deeper minimum until an even larger (and enormously less probable) fluctuation takes it back to the less stable minimum, after which the entire scenario is repeated. The probability of fluctuations falls so rapidly with increasing amplitude (as we shall see in Chapter 19) that *the system spends almost all of its time in the more stable minimum.* All of this dynamics is ignored by macroscopic thermodynamics, which concerns itself only with the stable equilibrium state.

To discuss the dynamics of the transition in a more thermodynamic context it is convenient to shift our attention to a familiar thermodynamic system that again has a thermodynamic potential with two local minimum separated by an unstable intermediate region of concavity. Specifically we consider a vessel of water vapor at a pressure of 1 atm and at a temperature somewhat above 373.15 K (i.e., above the "normal boiling point" of water). We focus our attention on a small subsystem—a spherical region of such a (variable) radius that at any instant it contains one milligram of water. This subsystem is effectively in contact with a thermal reservoir and a pressure reservoir, and the condition of equilibrium is that the Gibbs potential $G(T, P, N)$ of the small subsystem be minimum. The two independent variables which are determined by the equilibrium conditions are the energy $U$ and the volume $V$ of the subsystem.

If the Gibbs potential has the form shown in Fig. 9.3, where $X_j$ is the volume, the system is stable in the lower minimum. This minimum corresponds to a considerably larger volume (or a smaller density) than does the secondary local minimum.

Consider the behavior of a fluctuation in volume. Such fluctuations occur continually and spontaneously. The slope of the curve in Fig. 9.3 represents an intensive parameter (in the present case a difference in pressure) which acts as a restoring "force" driving the system back toward density homogeneity in accordance with Le Chatelier's principle. Occa-

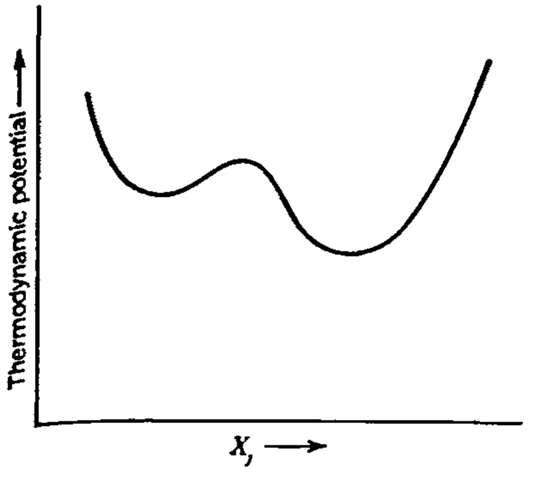

FIGURE 9.3
Thermodynamic potential with multiple minima.

sionally a fluctuation may be so large that it takes the system over the maximum, to the region of the secondary minimum. The system then settles in the region of this secondary minimum—but only for an instant. A relatively small (and therefore much more frequent) fluctuation is all that is required to overcome the more shallow barrier at the secondary minimum. The system quickly returns to its stable state. Thus very small droplets of high density (liquid phase!) occasionally form in the gas, live briefly, and evanesce.

If the secondary minimum were far removed from the absolute minimum, with a very high intermediate barrier, the fluctuations from one minimum to another would be very improbable. In Chapter 19 it will be shown that the probability of such fluctuations decreases exponentially with the height of the intermediate free-energy barrier. In solid systems (in which interaction energies are high) it is not uncommon for multiple minima to exist with intermediate barriers so high that transitions from one minimum to another take times on the order of the age of the universe! Systems trapped in such secondary "metastable" minima are *effectively* in stable equilibrium (as if the deeper minimum did not exist at all).

Returning to the case of water vapor at temperatures somewhat above the "boiling point," let us suppose that we lower the temperature of the entire system. The form of the Gibbs potential varies as shown schematically in Fig. 9.4. At the temperature $T_4$ the two minima become equal, and below this temperature the high density (liquid) phase becomes absolutely stable. Thus $T_4$ is the temperature of the phase transition (at the prescribed pressure).

If the vapor is cooled very gently through the transition temperature the system finds itself in a state that had been absolutely stable but that is now metastable. Sooner or later a fluctuation within the system will "discover" the truly stable state, forming a nucleus of condensed liquid. This nucleus then grows rapidly, and the entire system suddenly undergoes the transition. In fact the time required for the system to discover the

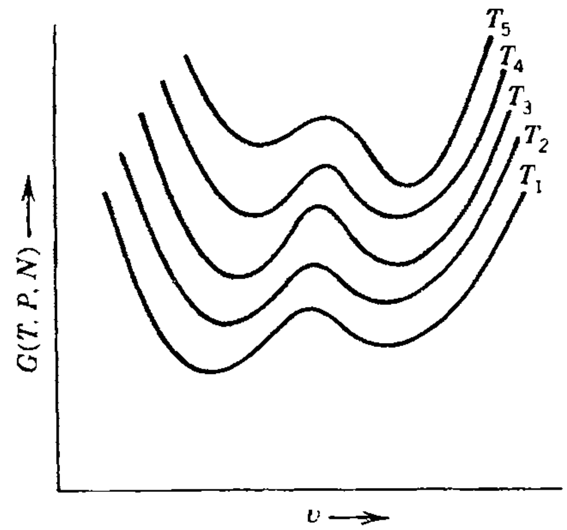

FIGURE 9.4
Schematic variation of Gibbs potential with volume (or reciprocal density) for various temperatures ($T_1 < T_2 < T_3 < T_4 < T_5$). The temperature $T_4$ is the transition temperature. The high density phase is stable below the transition temperature.

preferable state by an "exploratory" fluctuation is unobservably short in the case of the vapor to liquid condensation. But in the transition from liquid to ice the delay time is easily observed in a pure sample. The liquid so cooled below its solidification (freezing) temperature is said to be "supercooled." A slight tap on the container, however, sets up longitudinal waves with alternating regions of "condensation" and "rarefaction," and these externally induced fluctuations substitute for spontaneous fluctuations to initiate a precipitous transition.

A useful perspective emerges when the values of the Gibbs potential at each of its minima are plotted against temperature. The result is as shown schematically in Fig. 9.5. If these minimum values were taken from Fig. 9.4 there would be only two such curves, but any number is possible. At equilibrium the smallest minimum is stable, so the true Gibbs potential is the lower envelope of the curves shown in Fig. 9.5. The discontinuities in the entropy (and hence the latent heat) correspond to the discontinuities in slope of this envelope function.

Figure 9.5 should be extended into an additional dimension, the additional coordinate $P$ playing a role analogous to $T$. The Gibbs potential is then represented by the lower envelope *surface*, as each of the three

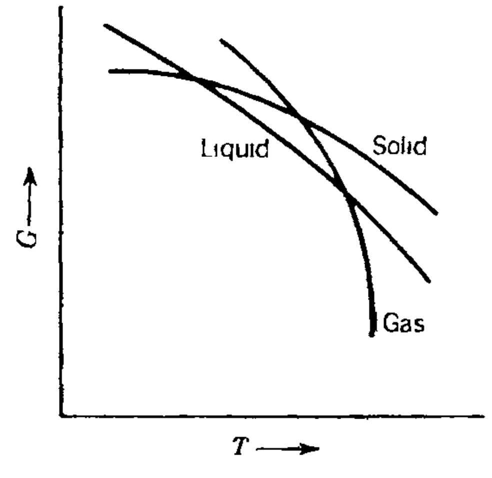

FIGURE 9.5
Minima of the Gibbs potential as a function of $T$

single-phase surfaces intersect. The projection of these curves of intersection onto the $P-T$ plane is the now familiar phase diagram (e.g., Fig. 9.1).

A phase transition occurs as the state of the system passes from one envelope surface, across an intersection curve, to another envelope surface.

The variable $X_j$, or $V$ in Fig. 9.4, can be any extensive parameter. In a transition from paramagnetic to ferromagnetic phases $X_j$ is the magnetic moment. In transitions from one crystal form to another (e.g., from cubic to hexagonal) the relevant parameter $X_j$ is a crystal symmetry variable. In a solubility transition it may be the mole number of one component. We shall see examples of such transitions subsequently. All conform to the general pattern described.

At a first-order phase transition the molar Gibbs potential of the two phases are equal, but other molar potentials ($u$, $f$, $h$, etc.) are discontinuous across the transition, as are the molar volume and the molar entropy. The two phases inhabit different regions in "thermodynamic space," and equality of any property other than the Gibbs potential would be a pure coincidence. The discontinuity in the molar potentials is the defining property of a first-order transition.

As shown in Fig. 9.6, as one moves along the liquid–gas coexistence curve away from the solid phase (i.e., toward higher temperature), the discontinuities in molar volume and molar energy become progressively smaller. The two phases become more nearly alike. Finally, at the terminus of the liquid–gas coexistence curve, the two phases become indistinguishable. The first-order transition degenerates into a more subtle transition, a *second-order transition*, to which we shall return in Chapter 10. The terminus of the coexistence curve is called a *critical point*.

The existence of the critical point precludes the possibility of a sharp distinction between the generic term *liquid* and the generic term *gas*. In crossing the liquid–gas coexistence curve in a first-order transition we distinguish two phases, one of which is "clearly" a gas and one of which is

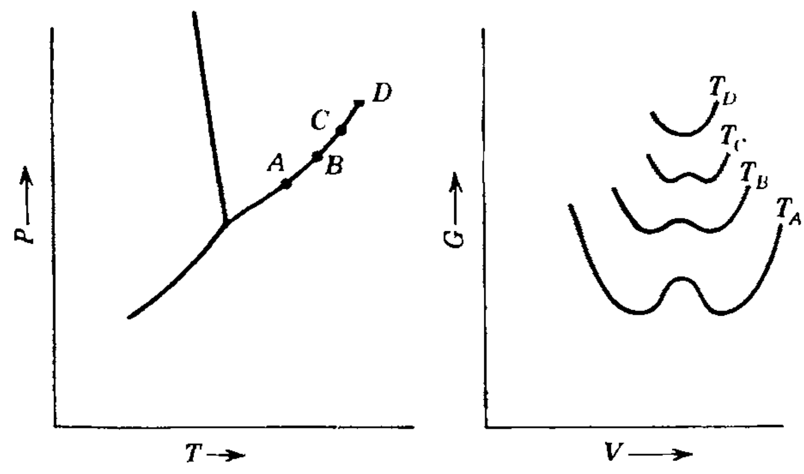

FIGURE 9.6
The two minima of $G$ corresponding to four points on the coexistence curve. The minima coalesce at the critical point $D$.

"clearly" a liquid. But starting at one of these (say the liquid, immediately above the coexistence curve) we can trace an alternate path that skirts around the critical point and arrives at the other state (the "gas") without ever encountering a phase transition! Thus the terms *gas* and *liquid* have more intuitive connotation than strictly defined denotation. Together liquids and gases constitute the *fluid phase*. Despite this we shall follow the standard usage and refer to "the liquid phase" and "the gaseous phase" in a liquid–gas first-order transition.

There is another point of great interest in Fig. 9.1: the opposite terminus of the liquid–gas coexistence curve. This point is the coterminus of three coexistence curves, and it is a unique point at which gaseous, liquid, and solid phases coexist. Such a state of three-phase compatibility is a "triple point"—in this case the triple point of water. The uniquely defined temperature of the triple point of water is assigned the (arbitrary) value of 273.16 K to define the Kelvin scale of temperature (recall Section 2.6).

## PROBLEM

**9.1-1.** The slopes of all three curves in Fig. 9.5 are shown as negative. Is this necessary? Is there a restriction on the curvature of these curves?

## 9-2 THE DISCONTINUITY IN THE ENTROPY—LATENT HEAT

Phase diagrams, such as Fig. 9.1, are divided by coexistence curves into regions in which one or another phase is stable. At any point on such a curve the two phases have precisely equal molar Gibbs potentials, and both phases can coexist.

Consider a sample of water at such a pressure and temperature that it is in the "ice" region of Fig. 9.1*a*. To increase the temperature of the ice one must supply roughly 2.1 kJ/kg for every kelvin of temperature increase (the specific heat capacity of ice). If heat is supplied at a constant rate the temperature increases at an approximately constant rate. But when the temperature reaches the "melting temperature," on the solid–liquid coexistence line, the temperature ceases to rise. As additional heat is supplied ice melts, forming liquid water at the same temperature. It requires roughly 335 kJ to melt each kg of ice. At any moment the amount of liquid water in the container depends on the quantity of heat that has entered the container since the arrival of the system at the coexistence curve (i.e., at the melting temperature). When finally the requisite amount of heat has been supplied, and the ice has been entirely melted, continued heat input again results in an increase in temperature—now at a rate determined by the specific heat capacity of liquid water ($\simeq$ 4.2 kJ/kg-K).

The quantity of heat required to melt one mole of solid is the *heat of fusion* (or the *latent heat of fusion*). It is related to the difference in molar entropies of the liquid and the solid phase by

$$\ell_{LS} = T\left[s^{(L)} - s^{(S)}\right] \tag{9.1}$$

where $T$ is the melting temperature at the given pressure.

More generally, the latent heat in any first-order transition is

$$\ell = T\Delta s \tag{9.2}$$

where $T$ is the temperature of the transition and $\Delta s$ is the difference in molar entropies of the two phases. Alternatively, the latent heat can be written as the difference in the molar enthalpies of the two phases

$$\ell = \Delta h \tag{9.3}$$

which follows immediately from the identity $h = Ts + \mu$ (and the fact that $\mu$, the molar Gibbs function, is equal in each phase). The molar enthalpies of each phase are tabulated for very many substances.

If the phase transition is between liquid and gaseous phases the latent heat is called the *heat of vaporization*, and if it is between solid and gaseous phases it is called the *heat of sublimation*.

At a pressure of one atmosphere the liquid–gas transition (boiling) of water occurs at 373.15 K, and the latent heat of vaporization is then 40.7 kJ/mole (540 cal/g).

In each case the latent heat must be put *into* the system as it makes a transition from the low-temperature phase to the high-temperature phase. Both the molar entropy and the molar enthalpy are greater in the high-temperature phase than in the low-temperature phase.

It should be noted that the method by which the transition is induced is irrelevant—the latent heat is independent thereof. Instead of heating the ice at constant pressure (crossing the coexistence curve of Fig. 9.1*a* "horizontally"), the pressure could be increased at constant temperature (crossing the coexistence curve "vertically"). In either case the same latent heat would be drawn from the thermal reservoir.

The functional form of the liquid–gas coexistence curve for water is given in "saturated steam tables"—the designation "saturated" denoting that the steam is in equilibrium with the liquid phase. ("Superheated steam tables" denote compilations of the properties of the vapor phase alone, at temperatures above that on the coexistence curve at the given pressure). An example of such a saturated steam table is given in Table 9.1, from Sonntag and Van Wylen. The properties $s$, $u$, $v$ and $h$ of each

ABLE 9 1

Steam Table"; Properties of the Gaseous and Liquid Phases on the Coexistence Curve of Water[a]

| | | Specific Volume | | Internal Energy | | | Enthalpy | | | Entropy | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| emp. C | Press. kPa $P$ | Sat. Liquid $v_f$ | Sat. Vapor $v_g$ | Sat. Liquid $u_f$ | Evap. $u_{fg}$ | Sat. Vapor $u_g$ | Sat. Liquid $h_f$ | Evap. $h_{fg}$ | Sat. Vapor $h_g$ | Sat. Liquid $s_f$ | Evap. $s_{fg}$ | Sat. Vapor $s_g$ |
| .01 | 0.6113 | 0.001 000 | 206.14 | .00 | 2375.3 | 2375.3 | .01 | 2501.3 | 2501.4 | .0000 | 9.1562 | 9.1562 |
| 5 | 0.8721 | 0.001 000 | 147.12 | 20.97 | 2361.3 | 2382.3 | 20.98 | 2489 6 | 2510.6 | .0761 | 8.9496 | 9 0257 |
| 10 | 1.2276 | 0.001 000 | 106 38 | 42.00 | 2347.2 | 2389.2 | 42.01 | 2477.7 | 2519.8 | .1510 | 8.7498 | 8.9008 |
| 15 | 1.7051 | 0.001 001 | 77.93 | 62.99 | 2333.1 | 2396.1 | 62.99 | 2465.9 | 2528.9 | .2245 | 8.5569 | 8.7814 |
| 20 | 2.339 | 0.001 002 | 57.79 | 83.95 | 2319.0 | 2402.9 | 83.96 | 2454.1 | 2538.1 | .2966 | 8.3706 | 8.6672 |
| 25 | 3.169 | 0.001 003 | 43.36 | 104.88 | 2304.9 | 2409.8 | 104.89 | 2442.3 | 2547.2 | .3674 | 8.1905 | 8.5580 |
| 30 | 4.246 | 0.001 004 | 32.89 | 125.78 | 2290.8 | 2416.6 | 125.79 | 2430.5 | 2556.3 | .4369 | 8.0164 | 8.4533 |
| 35 | 5.628 | 0.001 006 | 25.22 | 146.67 | 2276.7 | 2423.4 | 146.68 | 2418.6 | 2565.3 | .5053 | 7.8478 | 8.3531 |
| 40 | 7.384 | 0 001 008 | 19.52 | 167.56 | 2262.6 | 2430.1 | 167.57 | 2406.7 | 2574.3 | .5725 | 7.6845 | 8 2570 |
| 45 | 9.593 | 0.001 010 | 15.26 | 188 44 | 2248.4 | 2436 8 | 188.45 | 2394.8 | 2583.2 | .6387 | 7.5261 | 8 1648 |
| 50 | 12.349 | 0 001 012 | 12.03 | 209.32 | 2234.2 | 2443.5 | 209.33 | 2382 7 | 2592.1 | .7038 | 7 3725 | 8.0763 |
| 55 | 15.758 | 0.001 015 | 9 568 | 230.21 | 2219.9 | 2450.1 | 230.23 | 2370.7 | 2600.9 | .7679 | 7.2234 | 7 9913 |
| 60 | 19 940 | 0.001 017 | 7.671 | 251.11 | 2205.5 | 2456.6 | 251.13 | 2358.5 | 2609.6 | .8312 | 7.0784 | 7 9096 |
| 65 | 25.03 | 0.001 020 | 6.197 | 272.02 | 2191.1 | 2463 1 | 272.06 | 2346.2 | 2618.3 | .8935 | 6 9375 | 7.8310 |
| 70 | 31.19 | 0.001 023 | 5 042 | 292 95 | 2176.6 | 2469.6 | 292.98 | 2333.8 | 2626.8 | .9549 | 6 8004 | 7.7553 |
| 75 | 38.58 | 0.001 026 | 4 131 | 313 90 | 2162.0 | 2475 9 | 313.93 | 2321.4 | 2635.3 | 1.0155 | 6 6669 | 7.6824 |
| 80 | 47.39 | 0 001 029 | 3.407 | 334.86 | 2147.4 | 2482.2 | 334.91 | 2308.8 | 2643.7 | 1.0753 | 6.5369 | 7 6122 |
| 85 | 57 83 | 0.001 033 | 2 828 | 355 84 | 2132.6 | 2488.4 | 355.90 | 2296.0 | 2651 9 | 1.1343 | 6.4102 | 7.5445 |
| 90 | 70 14 | 0.001 036 | 2.361 | 376 85 | 2117 7 | 2494 5 | 376.92 | 2283.2 | 2660 1 | 1.1925 | 6.2866 | 7.4791 |
| 95 | 84 55 | 0 001 040 | 1 982 | 397 88 | 2102 7 | 2500 6 | 397 96 | 2270 2 | 2668 1 | 1 2500 | 6 1659 | 7 4159 |

| | Press. in MPa | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 | 0.101 35 | 0.001 044 | 1.6729 | 418.94 | 2087.6 | 2506 5 | 419.04 | 2257.0 | 2676.1 | 1.3069 | 6.0480 | 7 3549 |
| 105 | 0.120 82 | 0.001 048 | 1.4194 | 440.02 | 2072.3 | 2512.4 | 440.15 | 2243.7 | 2683.8 | 1.3630 | 5 9328 | 7.2958 |
| 110 | 0.143 27 | 0.001 052 | 1.2102 | 461.14 | 2057.0 | 2518.1 | 461.30 | 2230.2 | 2691.5 | 1.4185 | 5 8202 | 7.2387 |
| 115 | 0.169 06 | 0 001 056 | 1.0366 | 482 30 | 2041.4 | 2523.7 | 482.48 | 2216.5 | 2699.0 | 1.4734 | 5.7100 | 7.1833 |
| 120 | 0.198 53 | 0.001 060 | 0.8919 | 503 50 | 2025.8 | 2529.3 | 503.71 | 2202.6 | 2706.3 | 1.5276 | 5.6020 | 7.1296 |
| 125 | 0.2321 | 0.001 065 | 0.7706 | 524 74 | 2009.9 | 2634 6 | 524 99 | 2188.5 | 2713.5 | 1.5813 | 5.4962 | 7 0775 |
| 130 | 0.2701 | 0.001 070 | 0.6685 | 546.02 | 1993.9 | 2539.9 | 546 31 | 2174.2 | 2720.5 | 1.6344 | 5.3925 | 7.0269 |
| 135 | 0.3130 | 0.001 075 | 0.5822 | 567.35 | 1977.7 | 2545 0 | 567.69 | 2159.6 | 2727.3 | 1.6870 | 5.2907 | 6 9777 |
| 140 | 0.3613 | 0.001 080 | 0.5089 | 588.74 | 1961.3 | 2550.0 | 589 13 | 2144.7 | 2733.9 | 1.7391 | 5.1908 | 6.9299 |
| 145 | 0.4154 | 0.001 085 | 0.4463 | 610.18 | 1944.7 | 2554.9 | 610.63 | 2129.6 | 2740.3 | 1.7907 | 5.0926 | 6.8833 |
| 150 | 0.4758 | 0.001 091 | 0.3928 | 631.68 | 1927.9 | 2559.5 | 632.20 | 2114.3 | 2746.5 | 1.8418 | 4.9960 | 6.8379 |
| 155 | 0.5431 | 0.001 096 | 0.3468 | 653.24 | 1910.8 | 2564.1 | 653.84 | 2098.6 | 2752.4 | 1.8925 | 4.9010 | 6 7935 |
| 160 | 0.6178 | 0.001 102 | 0.3071 | 674.87 | 1893.5 | 2568.4 | 675.55 | 2082.6 | 2758.1 | 1.9427 | 4.8075 | 6 7502 |
| 165 | 0.7005 | 0.001 108 | 0.2727 | 696.56 | 1876.0 | 2572.5 | 697.34 | 2066.2 | 2763.5 | 1.9925 | 4.7153 | 6.7078 |
| 170 | 0.7917 | 0.001 114 | 0.2428 | 718.33 | 1858.1 | 2576.5 | 719.21 | 2049 5 | 2768.7 | 2.0419 | 4.6244 | 6.6663 |
| 175 | 0.8920 | 0.001 121 | 0.2168 | 740.17 | 1840.0 | 2580 2 | 741.17 | 2032.4 | 2773.6 | 2 0909 | 4 5347 | 6.6256 |
| 180 | 1.0021 | 0.001 127 | 0.194 05 | 762.09 | 1821.6 | 2583.7 | 763.22 | 2015.0 | 2778.2 | 2.1396 | 4.4461 | 6.5857 |
| 185 | 1.1227 | 0.001 134 | 0.179 09 | 784.10 | 1802.9 | 2587.0 | 785.37 | 1997.1 | 2782.4 | 2.1879 | 4.3586 | 6.5465 |
| 190 | 1.2544 | 0.001 141 | 0.156 54 | 806.19 | 1783.8 | 2590.0 | 807.62 | 1978.8 | 2786.4 | 2.2359 | 4.2720 | 6.5079 |
| 195 | 1.3978 | 0.001 149 | 0.141 05 | 828.37 | 1764.4 | 2592.8 | 829.98 | 1960.0 | 2790.0 | 2.2835 | 4.1863 | 6.4698 |
| 200 | 1.5538 | 0.001 157 | 0.127 36 | 850.65 | 1744.7 | 2595.3 | 852.45 | 1940.7 | 2793 2 | 2 3309 | 4.1014 | 6.4323 |
| 205 | 1 7230 | 0.001 164 | 0.115 21 | 873.04 | 1724 5 | 2597.5 | 875.04 | 1921.0 | 2796.0 | 2.3780 | 4.0172 | 6.3952 |
| 210 | 1 9062 | 0.001 173 | 0.104 41 | 895.53 | 1703.9 | 2599.5 | 897.76 | 1900.7 | 2798.5 | 2.4248 | 3.9337 | 6 3585 |
| 215 | 2.104 | 0.001 181 | 0.094 79 | 918.14 | 1682.9 | 2601.1 | 920.62 | 1879 9 | 2800.5 | 2 4714 | 3.8507 | 6 3221 |

TABLE 9.1 (continued)

| | | Specific Volume | | Internal Energy | | | Enthalpy | | | Entropy | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. °C $T$ | Press. MPa $P$ | Sat. Liquid $v_f$ | Sat. Vapor $v_g$ | Sat. Liquid $u_f$ | Evap. $u_{fg}$ | Sat. Vapor $u_g$ | Sat. Liquid $h_f$ | Evap. $h_{fg}$ | Sat. Vapor $h_g$ | Sat. Liquid $s_f$ | Evap. $s_{fg}$ | Sat. Vapor $s_g$ |
| 220 | 2.318 | 0.001 190 | 0.086 19 | 940.87 | 1661.5 | 2602.4 | 943.62 | 1858.5 | 2802.1 | 2.5178 | 3.7683 | 6.2861 |
| 225 | 2.548 | 0.001 199 | 0.078 49 | 963.73 | 1639.6 | 2603.3 | 966.78 | 1836.5 | 2803.3 | 2.5639 | 3.6863 | 6.2503 |
| 230 | 2.795 | 0.001 209 | 0.071 58 | 986.74 | 1617.2 | 2603.9 | 990.12 | 1813.8 | 2804.0 | 2.6099 | 3.6047 | 6.2146 |
| 235 | 3.060 | 0.001 219 | 0.065 37 | 1009.89 | 1594.2 | 2604.1 | 1013.62 | 1790.5 | 2804.2 | 2.6558 | 3.5233 | 6.1791 |
| 240 | 3.344 | 0.001 229 | 0.059 76 | 1033.21 | 1570.8 | 2604.0 | 1037.32 | 1766.5 | 2803.8 | 2.7015 | 3.4422 | 6.1437 |
| 245 | 3.648 | 0.001 240 | 0.054 71 | 1056.71 | 1546.7 | 2603.4 | 1061.23 | 1741.7 | 2803.0 | 2.7472 | 3.3612 | 6.1083 |
| 250 | 3.973 | 0.001 251 | 0.050 13 | 1080.39 | 1522.0 | 2602.4 | 1085.36 | 1716.2 | 2801.5 | 2.7927 | 3.2802 | 6.0730 |
| 255 | 4.319 | 0.001 263 | 0.045 98 | 1104.28 | 1496.7 | 2600.9 | 1109.73 | 1689.8 | 2799.5 | 2.8383 | 3.1992 | 6.0375 |
| 260 | 4.688 | 0.001 276 | 0.042 21 | 1128.39 | 1470.6 | 2599.0 | 1134.37 | 1662 5 | 2796.9 | 2.8838 | 3.1181 | 6.0019 |
| 265 | 5.081 | 0.001 289 | 0.038 77 | 1152.74 | 1443.9 | 2596.6 | 1159.28 | 1634.4 | 2793.6 | 2.9294 | 3.0368 | 5.9662 |
| 270 | 5.499 | 0.001 302 | 0.035 64 | 1177.36 | 1416.3 | 2593.7 | 1184.51 | 1605.2 | 2789 7 | 2.9751 | 2 9551 | 5.9301 |
| 275 | 5.942 | 0.001 317 | 0.032 79 | 1202.25 | 1387.9 | 2590.2 | 1210.07 | 1574.9 | 2785.0 | 3.0208 | 2.8730 | 5 8938 |
| 280 | 6.412 | 0.001 332 | 0.030 17 | 1227.46 | 1358.7 | 2586.1 | 1235.99 | 1543.6 | 2779.6 | 3.0668 | 2.7903 | 5.8571 |
| 285 | 6.909 | 0.001 348 | 0.027 77 | 1253.00 | 1328.4 | 2581.4 | 1262.31 | 1511.0 | 2773.3 | 3.1130 | 2.7070 | 5.8199 |
| 290 | 7.436 | 0.001 366 | 0.025 57 | 1278.92 | 1297.1 | 2576.0 | 1289.07 | 1477.1 | 2766.2 | 3.1594 | 2 6227 | 5.7821 |
| 295 | 7.993 | 0.001 384 | 0.023 54 | 1305.2 | 1264.7 | 2569.9 | 1316.3 | 1441.8 | 2758.1 | 3.2062 | 2.5375 | 5.7437 |
| 300 | 8.581 | 0.001 404 | 0.021 67 | 1332.0 | 1231.0 | 2563.0 | 1344.0 | 1404.9 | 2749.0 | 3.2534 | 2 4511 | 5.7045 |
| 305 | 9.202 | 0.001 425 | 0.019 948 | 1359.3 | 1195.9 | 2555.2 | 1372.4 | 1366 4 | 2738.7 | 3.3010 | 2.3633 | 5.6643 |
| 310 | 9.856 | 0.001 447 | 0.018 350 | 1387.1 | 1159.4 | 2546.4 | 1401.3 | 1326.0 | 2727.3 | 3.3493 | 2.2737 | 5.6230 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 315 | 10.547 | 0.001 472 | 0 016 867 | 1415.5 | 1121.1 | 2536.6 | 1431.0 | 1283 5 | 2714.5 | 3 3982 | 2.1821 | 5.5804 |
| 320 | 11.274 | 0.001 499 | 0.015 488 | 1444.6 | 1080.9 | 2525.5 | 1461.5 | 1238.6 | 2700.1 | 3.4480 | 2.0882 | 5.5362 |
| 330 | 12.845 | 0.001 561 | 0.012 996 | 1505.3 | 993.7 | 2498.9 | 1525.3 | 1140.6 | 2665.9 | 3.5507 | 1.8909 | 5.4417 |
| 340 | 14.586 | 0.001 638 | 0.010 797 | 1570.3 | 894.3 | 2464.6 | 1594.2 | 1027.9 | 2622.0 | 3.6594 | 1 6763 | 5.3357 |
| 350 | 16.513 | 0.001 740 | 0.008 813 | 1641.9 | 776.6 | 2418.4 | 1670.6 | 893.4 | 2563.9 | 3.7777 | 1.4335 | 5.2112 |
| 360 | 18.651 | 0.001 893 | 0.006 945 | 1725.2 | 626.3 | 2351.5 | 1760.5 | 720.5 | 2481.0 | 3.9147 | 1.1379 | 5.0526 |
| 370 | 21.03 | 0.002 213 | 0.004 925 | 1844.0 | 384.5 | 2228.5 | 1890.5 | 441.6 | 2332.1 | 4.1106 | .6865 | 4.7971 |
| 374.14 | 22.09 | 0.003 155 | 0.003 155 | 2029.6 | 0 | 2029.6 | 2099.3 | 0 | 2099.3 | 4.4298 | 0 | 4.4298 |

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[a] From R E Sonntag and G J Van Wylen, *Introduction to Thermodynamics, Classical and Statistical*", John Wiley & Sons, New York, 1982 (adapted from J H Keenan, F G Keyes, P. G Hill, and J G Moore, *Steam Tables*, John Wiley & Sons, New York, 1978)

phase are conventionally listed in such tables; the latent heat of the transition is the difference in the molar enthalpies of the two phases, or it can also be obtained as $T\Delta s$.

Similar data are compiled in the thermophysical data literature for a wide variety of other materials.

The molar volume, like the molar entropy and the molar energy, is discontinuous across the coexistence curve. For water this is particularly interesting in the case of the solid–liquid coexistence curve. It is common experience that ice floats in liquid water. The molar volume of the solid (ice) phase accordingly is *greater* than the molar volume of the liquid phase—an uncommon attribute of $H_2O$. The much more common situation is that in which the solid phase is more compact, with a smaller molar volume. One mundane consequence of this peculiar property of $H_2O$ is the proclivity of frozen plumbing to burst. A compensating consequence, to which we shall return in Section 9.3, is the possibility of ice skating. And, underlying all, this peculiar property of water is essential to the very possibility of life on earth. If ice were more dense than liquid water the frozen winter surfaces of lakes and oceans would sink to the bottom; new surface liquid, unprotected by an ice layer, would again freeze (and sink) until the entire body of water would be frozen solid ("frozen under" instead of "frozen over").

## PROBLEMS

**9.2-1.** In a particular solid–liquid phase transition the point $P_0, T_0$ lies on the coexistence curve. The latent heat of vaporization at this point is $\ell_0$. A nearby point on the coexistence curve has pressure $P_0 + p$ and temperature $T_0 + t$; the local slope of the coexistence curve in the $P$–$T$ plane is $p/t$. Assuming $v$, $c_p$, $\alpha$, and $\kappa_T$ to be known in each phase in the vicinity of the states of interest, find the latent heat at the point $P_0 + p$, $T_0 + t$.

**9.2-2.** Discuss the equilibrium that eventually results if a solid is placed in an initially evacuated closed container and is maintained at a given temperature. Explain why the solid–gas coexistence curve is said to define the "vapor pressure of the solid" at the given temperature.

## 9-3 THE SLOPE OF COEXISTENCE CURVES; THE CLAPEYRON EQUATION

The coexistence curves illustrated in Fig. 9.1 are less arbitrary than is immediately evident; the slope $dP/dT$ of a coexistence curve is fully determined by the properties of the two coexisting phases.

The slope of a coexistence curve is of direct physical interest. Consider cubes of ice at equilibrium in a glass of water. Given the ambient pressure, the temperature of the mixed system is determined by the liquid–solid coexistence curve of water; if the temperature were not on the coexistence curve some ice would melt, or some liquid would freeze, until the temperature would again lie on the coexistence curve (or one phase would become depleted). At 1 atm of pressure the temperature would be 273.15 K. If the ambient pressure were to decrease—perhaps by virtue of a change in altitude (the glass of water is to be served by the flight attendant in an airplane), or by a variation in atmospheric conditions (approach of a storm)—then the temperature of the glass of water would appropriately adjust to a new point on the coexistence curve. If $\Delta P$ were the change in pressure then the change in temperature would be $\Delta T = \Delta P/(dP/dT)_{cc}$, where the derivative in the denominator is the slope of the coexistence curve.

Ice skating, to which we have made an earlier allusion, presents another interesting example. The pressure applied to the ice directly beneath the blade of the skate shifts the ice across the solid–liquid coexistence curve (vertically upward in Fig. 9.1*a*), providing a lubricating film of liquid on which the skate slides.

The possibility of ice skating depends on the negative slope of the liquid–solid coexistence curve of water. The existence of the ice on the upper surface of the lake, rather than on the bottom, reflects the larger molar volume of the solid phase of water as compared to that of the liquid phase. The connection of these two facts, which are not independent, lies in the Clapeyron equation, to which we now turn.

Consider the four states shown in Fig. 9.7. States $A$ and $A'$ are on the coexistence curve, but they correspond to different phases (to the left-hand and right-hand regions respectively.) Similarly for the states $B$ and $B'$. The pressure difference $P_B - P_A$ (or, equivalently, $P_{B'} - P_{A'}$) is assumed to be infinitesimal ($= dP$), and similarly for the temperature difference $T_B - T_A$ ($= dT$). The slope of the curve is $dP/dT$.

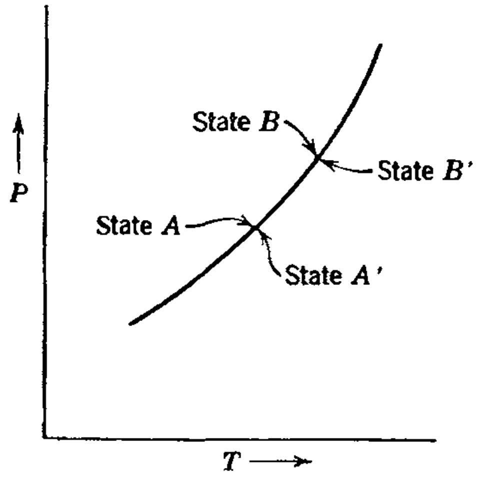

FIGURE 9 7
Four coexistence states.

Phase equilibrium requires that

$$\mu_A = \mu_{A'} \tag{9.4}$$

and

$$\mu_B = \mu_{B'} \tag{9.5}$$

whence

$$\mu_B - \mu_A = \mu_{B'} - \mu_{A'} \tag{9.6}$$

But

$$\mu_B - \mu_A = -s\,dT + v\,dP \tag{9.7}$$

and

$$\mu_{B'} - \mu_{A'} = -s'\,dT + v'\,dP \tag{9.8}$$

in which $s$ and $s'$ are the molar entropies and $v$ and $v'$ are the molar volumes in each of the phases. By inserting equations 9.7 and 9.8 in equation 9.6 and rearranging the terms, we easily find

$$\frac{dP}{dT} = \frac{s' - s}{v' - v} \tag{9.9}$$

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} \tag{9.10}$$

in which $\Delta s$ and $\Delta v$ are the discontinuities in molar entropy and molar volume associated with the phase transition. According to equation 9.2 the latent heat is

$$\ell = T\Delta s \tag{9.11}$$

whence

$$\frac{dP}{dT} = \frac{\ell}{T\Delta v} \tag{9.12}$$

This is the Clapeyron equation.

The Clapeyron equation embodies the Le Chatelier principle. Consider a solid–liquid transition with a positive latent heat ($s_\ell > s_s$) and a positive difference of molar volumes ($v_\ell > v_s$). The slope of the phase curve is correspondingly positive. Then an increase in pressure at constant temperature tends to drive the system to the more dense (solid) phase (alleviating the pressure increase), and an increase in temperature tends to drive the system to the more entropic (liquid) phase. Conversely, if $s_\ell > s_s$ but $v_\ell < v_s$, then the slope of the coexistence curve is negative, and an increase of the pressure (at constant $T$) tends to drive the system to the liquid phase—again the more dense phase.

In practical problems in which the Clapeyron equation is applied it is often sufficient to neglect the molar volume of the liquid phase relative to the molar volume of the gaseous phase ($v_g - v_\ell \simeq v_g$), and to approximate the molar volume of the gas by the ideal gas equation ($v_g \simeq RT/P$). This "Clapeyron–Clausius approximation" may be used where appropriate in the problems at the end of this section.

**Example**

A light rigid metallic bar of rectangular cross section lies on a block of ice, extending slightly over each end. The width of the bar is 2 mm and the length of the bar in contact with the ice is 25 cm. Two equal masses, each of mass $M$, are hung from the extending ends of the bar. The entire system is at atmospheric pressure and is maintained at a temperature of $T = -2°\text{C}$. What is the minimum value of $M$ for which the bar will pass through the block of ice by "regelation"? The given data are that the latent heat of fusion of water is 80 cal/gram, that the density of liquid water is 1 gram/cm$^3$, and that ice cubes float with $\simeq 4/5$ of their volume submerged.

Solution

The Clapeyron equation permits us to find the pressure at which the solid-liquid transition occurs at $T = -2°\text{C}$. However we must first use the "ice cube data" to obtain the difference $\Delta v$ in molar volumes of liquid and solid phases. The data given imply that the density of ice is 0.8 g/cm$^3$. Furthermore $v_{\text{liq}} \simeq 18\ \text{cm}^3/\text{mole}$, and therefore $v_{\text{solid}} \simeq 22.5 \times 10^{-6}\ \text{m}^3/\text{mole}$. Thus

$$\left.\frac{dP}{dT}\right)_{cc} = \frac{\ell}{T\Delta v} = \frac{(80 \times 4.2 \times 18)\ \text{J/mole}}{271 \times (-4.5 \times 10^{-6})\ \text{K}-\text{m}^3/\text{mole}} = -5 \times 10^6\ \text{Pa/K}$$

so that the pressure difference required is

$$P \simeq -5 \times 10^6 \times (-2) \simeq 10^7\ \text{Pa}$$

This pressure is to be obtained by a weight $2Mg$ acting on the area $A = 5 \times 10^{-5}\ \text{m}^2$,

$$\begin{aligned} M &= \tfrac{1}{2}\Delta P \frac{A}{g} \\ &= \tfrac{1}{2}(10^7\ \text{Pa})(5 \times 10^{-5}\ \text{m}^2) \Big/ \left(9.8\ \frac{\text{m}}{\text{s}^2}\right) = 2.6\ \text{Kg} \end{aligned}$$

## PROBLEMS

**9.3-1.** A particular liquid boils at 127°C at a pressure of 800 mm Hg. It has a heat of vaporization of 1000 cal/mole. At what temperature will it boil if the pressure is raised to 810 mm Hg?

**9.3-2.** A long vertical column is closed at the bottom and open at the top; it is partially filled with a particular liquid and cooled to $-5\,^\circ\mathrm{C}$. At this temperature the fluid solidifies below a particular level, remaining liquid above this level. If the temperature is further lowered to $-5.2^\circ\mathrm{C}$ the solid–liquid interface moves upward by 40 cm. The latent heat (per unit mass) is 2 cal/g, and the density of the liquid phase is 1 g/cm$^3$. Find the density of the solid phase. Neglect thermal expansion of all materials.
*Hint*: Note that the pressure at the original position of the interface remains constant.

*Answer:*
2.6 g/cm$^3$

**9.3-3.** It is found that a certain liquid boils at a temperature of 95°C at the top of a hill, whereas it boils at a temperature of 105°C at the bottom. The latent heat is 1000 cal/mole. What is the approximate height of the hill?

**9.3-4.** Two weights are hung on the ends of a wire, which passes over a block of ice. The wire gradually passes through the block of ice, but the block remains intact even after the wire has passed completely through it. Explain why less mass is required if a semi-flexible wire is used, rather than a rigid bar as in the Example.

**9.3-5.** In the vicinity of the triple point the vapor pressure of liquid ammonia (in Pascals) is represented by

$$\ln P = 24.38 - \frac{3063}{T}$$

This is the equation of the liquid–vapor boundary curve in a $P$–$T$ diagram. Similarly, the vapor pressure of solid ammonia is

$$\ln P = 27.92 - \frac{3754}{T}$$

What are the temperature and pressure at the triple point? What are the latent heats of sublimation and vaporization? What is the latent heat of fusion at the triple point?

**9.3-6.** Let $x$ be the mole fraction of solid phase in a solid–liquid two-phase system. If the temperature is changed at constant total volume, find the rate of change of $x$; that is, find $dx/dT$. Assume that the standard parameters $v$, $\alpha$, $\kappa_T$, $c_P$ are known for each phase.

**9.3-7.** A particular material has a latent heat of vaporization of $5 \times 10^3$ J/mole, constant along the coexistence curve. One mole of this material exists in two-phase (liquid–vapor) equilibrium in a container of volume $V = 10^{-2}$ m$^3$, at a temperature of 300 K and a pressure of $10^5$ Pa. The system is heated at constant volume, increasing the pressure to $2.0 \times 10^5$ Pa. (Note that this is *not* a small $\Delta P$.) The vapor phase can be treated as a monatomic ideal gas, and the molar volume of the liquid can be neglected relative to that of the gas. Find the initial and final mole fractions of the vapor phase [$x \equiv N_g/(N_g + N_\ell)$].

**9.3-8.** Draw the phase diagram, in the $B_e$–$T$ plane, for a simple ferromagnet; assume no magnetocrystalline anisotropy and assume the external field $B_e$ to be always parallel to a fixed axis in space. What is the slope of the coexistence curve? Explain this slope in terms of the Clapeyron equation.

**9.3-9.** A system has coexistence curves similar to those shown in Fig. 9.6*a*, but with the liquid–solid coexistence curve having a positive slope. Sketch the isotherms in the $P$–$v$ plane for temperature $T$ such that
(a) $T < T_t$, (b) $T = T_t$, (c) $T_t \le T < T_{\text{crit}}$, (d) $T_t < T \le T_{\text{crit}}$, (e) $T = T_{\text{crit}}$, (f) $T \gtrsim T_{\text{crit}}$.
Here $T_t$ and $T_{\text{crit}}$ denote the triple point and critical temperatures, respectively.

## 9-4 UNSTABLE ISOTHERMS AND FIRST-ORDER PHASE TRANSITIONS

Our discussion of the origin of first-order phase transitions has focused, quite properly, on the multiple minima of the Gibbs potential. But although the Gibbs potential may be the fundamental entity at play, a more common description of a thermodynamic system is in terms of the form of its isotherms. For many gases the shape of the isotherms is well represented (at least semiquantitatively) by the van der Waals equation of state (recall Section 3.5)

$$P = \frac{RT}{(v - b)} - \frac{a}{v^2} \tag{9.13}$$

The shape of such van der Waals isotherms is shown schematically in the $P$–$v$ diagram of Fig. 9.8.

As pointed out in Section 3.5 the van der Waals equation of state can be viewed as an "underlying equation of state," obtained by curve fitting, by inference based on plausible heuristic reasoning, or by statistical mechanical calculations based on a simple molecular model. Other empirical or semiempirical equations of state exist, and they all have isotherms that are similar to those shown in Fig. 9.8.

We now explore the manner in which isotherms of the general form shown reveal and define a phase transition.

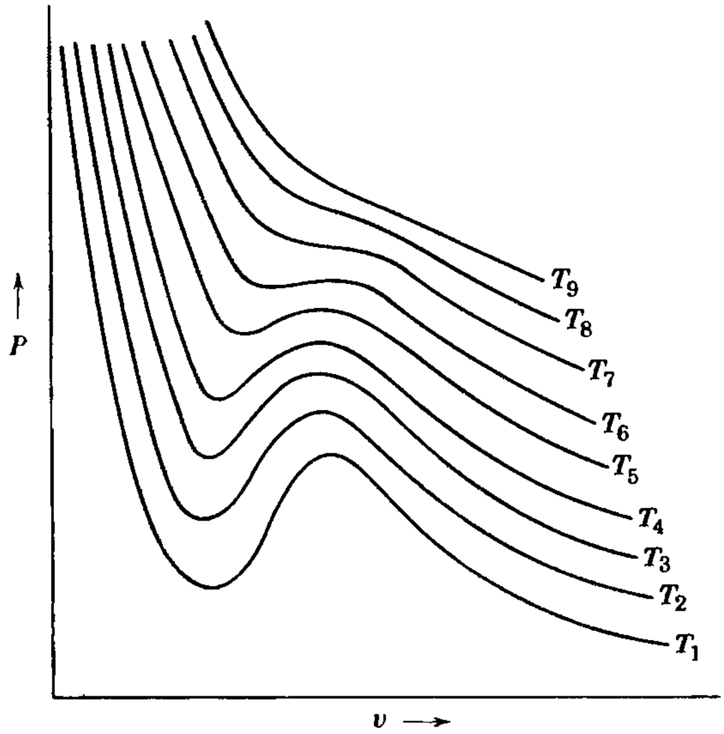

FIGURE 9.8
van der Waals isotherms (schematic). $T_1 < T_2 < T_3 \ldots$

It should be noted immediately that the isotherms of Fig. 9.8 do not satisfy the criteria of intrinsic stability everywhere, for one of these criteria (equation 8.21) is $\kappa_T > 0$, or

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \tag{9.14}$$

This condition clearly is violated over the portion *FKM* of a typical isotherm (which, for clarity, is shown separately in Fig. 9.9). Because of this violation of the stability condition a portion of the isotherm must be unphysical, superseded by a phase transition in a manner which will be explored shortly.

The molar Gibbs potential is essentially determined by the form of the isotherm. From the Gibbs–Duhem relation we recall that

$$d\mu = -s\,dT + v\,dP \tag{9.15}$$

whence, integrating at constant temperature

$$\mu = \int v\,dP + \phi(T) \tag{9.16}$$

where $\phi(T)$ is an undetermined function of the temperature, arising as the "constant of integration." The integrand $v(P)$, for constant temperature, is given by Fig. 9.9, which is most conveniently represented with $P$ as

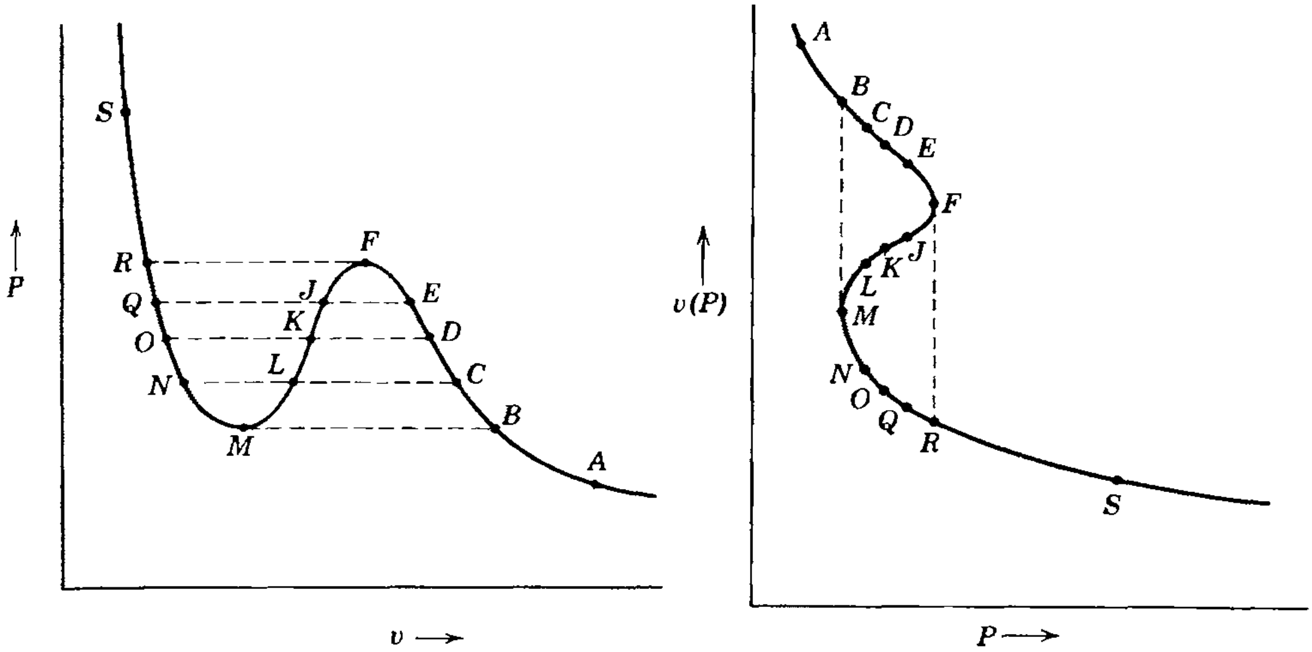

FIGURE 9.9
A particular isotherm of the van der Waals shape.

abscissa and $v$ as ordinate. By arbitrarily assigning a value to the chemical potential at the point $A$, we can now compute the value of $\mu$ at any other point on the same isotherm, such as $B$, for from equation 9.16

$$\mu_B - \mu_A = \int_A^B v(P)\,dP \tag{9.17}$$

In this way we obtain Fig. 9.10. This figure, representing $\mu$ versus $P$, can be considered as a plane section of a three-dimensional representation of $\mu$ versus $P$ and $T$, as shown in Fig. 9.11. Four different constant-temperature sections of the $\mu$-surface, corresponding to four isotherms, are shown. It is also noted that the closed loop of the $\mu$ versus $P$ curves, which results from the fact that $v(P)$ is triple valued in $P$ (see Fig. 9.9), disappears for high temperatures in accordance with Fig. 9.8.

Finally, we note that the relation $\mu = \mu(T, P)$ constitutes a fundamental relation for one mole of the material, as the chemical potential $\mu$ is the Gibbs function per mole. It would then appear from Fig. 9.11 that we have almost succeeded in the construction of a fundamental equation from a single given equation of state, but it should be recalled that although each of the traces of the $\mu$-surface (in the various constant temperature planes of Fig. 9.11) has the proper form, each contains an additive "constant" $\phi(T)$, which varies from one temperature plane to another. Consequently, we do not know the complete form of the $\mu(T, P)$-surface, although we certainly are able to form a rather good mental picture of its essential topological properties.

With this qualitative picture of the fundamental relation implied by the van der Waals equation, we return to the question of stability.

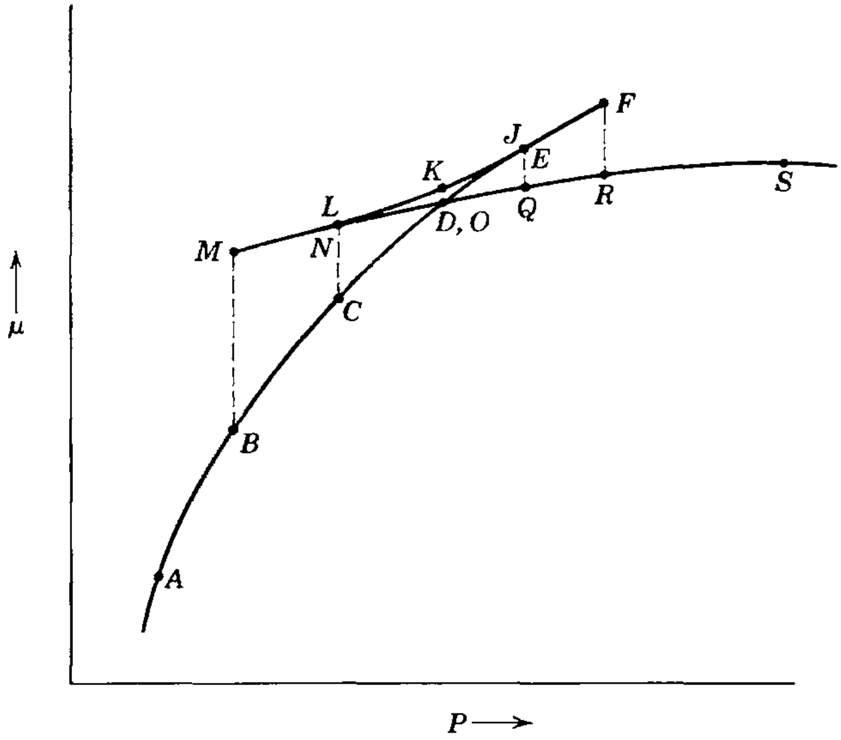

FIGURE 9.10
Isothermal dependence of the molar Gibbs potential on pressure.

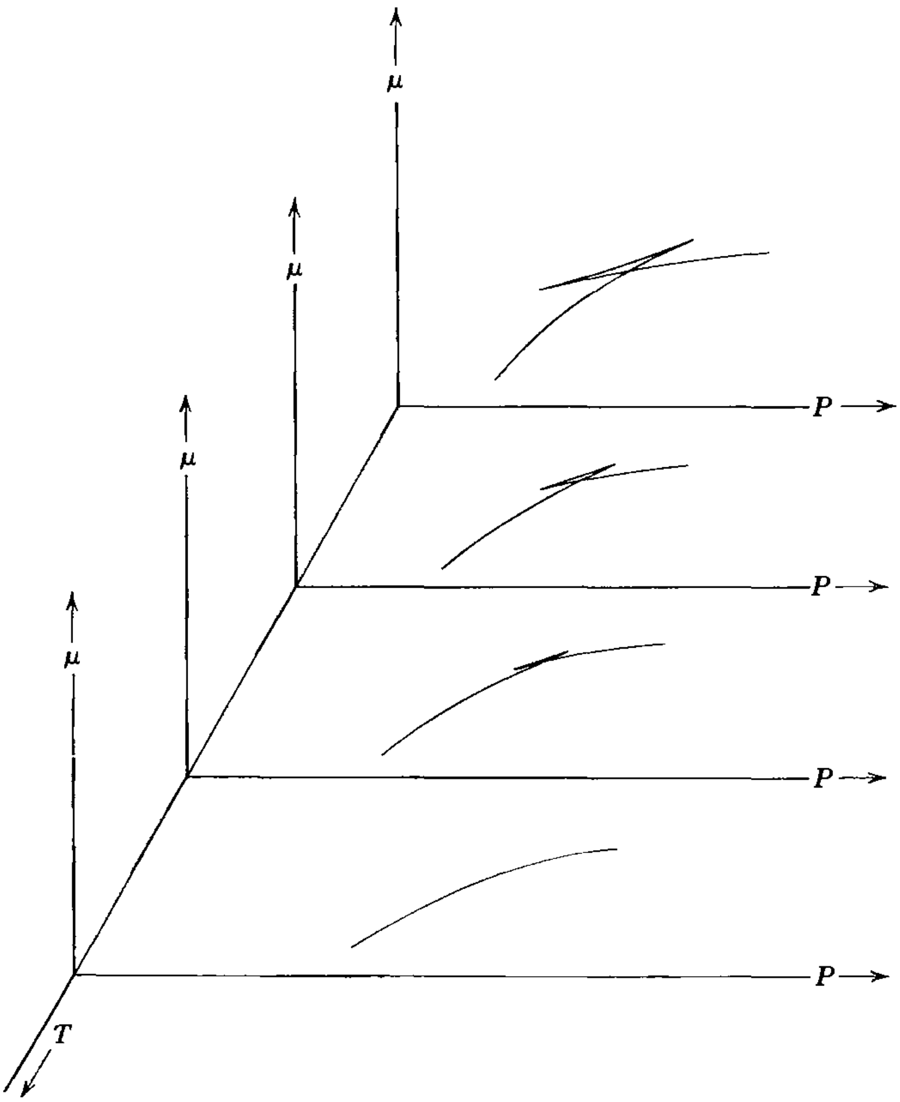

FIGURE 9.11

Consider a system in the state $A$ of Fig. 9.9 and in contact with thermal and pressure reservoirs. Suppose the pressure of the reservoir to be increased quasi-statically, maintaining the temperature constant. The system proceeds along the isotherm in Fig. 9.9 from the point $A$ in the direction of point $B$. For pressures less than $P_B$ we see that the volume of the system (for given pressure and temperature) is single valued and unique. As the pressure increases above $P_B$, however, three states of equal $P$ and $T$ become available to the system, as, for example, the states designated by $C$, $L$, and $N$. Of these three states $L$ is unstable, but at both $C$ and $N$ the Gibbs potential is a (local) minimum. These two local minimum values of the Gibbs potential (or of $\mu$) are indicated by the points $C$ and $N$ in Fig. 9.10. Whether the system actually selects the state $C$ or the state $N$ depends upon which of these two local minima of the Gibbs potential is the lower, or absolute, minimum. It is clear from Fig. 9.10 that the state $C$ is the true physical state for this value of the pressure and temperature.

As the pressure is further slowly increased, the unique point $D$ is reached. At this point the $\mu$-surface intersects itself, as shown in Fig. 9.10, and the absolute minimum of $\mu$ or $G$ thereafter comes from the other branch of the curve. Thus at the pressure $P_E = P_Q$, which is greater than $P_D$, the physical state is $Q$. Below $P_D$ the right-hand branch of the isotherm in Fig. 9.9*a* is the physically significant branch, whereas above $P_D$ the left-hand branch is physically significant. *The physical isotherm thus deduced from the hypothetical isotherm of Fig. 9.9 is therefore shown in Fig. 9.12.*

The isotherm of Fig. 9.9 belongs to an "underlying fundamental relation"; that of Fig. 9.12 belongs to the stable "thermodynamic fundamental relation."

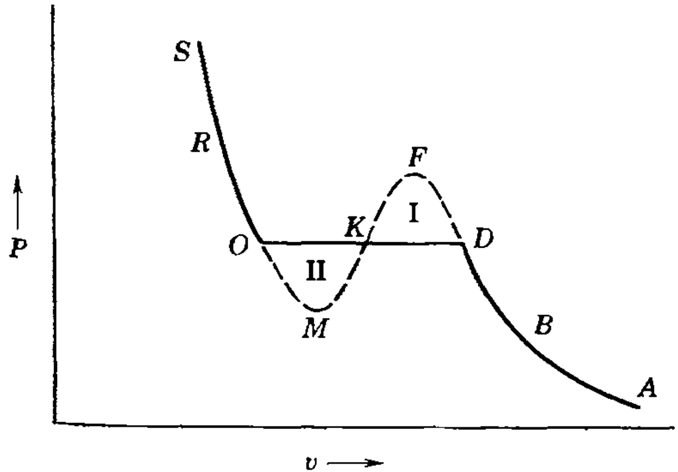

FIGURE 9.12
The physical van der Waals isotherm. The "underlying" isotherm is $SOMKFDA$, but the equal-area construction converts it to the physical isotherm $SOKDA$.

The points $D$ and $O$ are determined by the condition that $\mu_D = \mu_O$ or, from equation 9.17

$$\int_D^O v(P)\,dP = 0 \tag{9.18}$$

where the integral is taken along the hypothetical isotherm. Referring to Fig. 9.9, we see that this condition can be given a direct graphical interpretation by breaking the integral into several portions

$$\int_D^F v\,dP + \int_F^K v\,dP + \int_K^M v\,dP + \int_M^O v\,dP = 0 \tag{9.19}$$

and rearranging as follows

$$\int_D^F v\,dP - \int_K^F v\,dP = \int_M^K v\,dP - \int_M^O v\,dP \tag{9.20}$$

Now the integral $\int_D^F v\,dP$ is the area under the arc $DF$ in Fig. 9.12 and the integral $\int_K^F v\,dP$ is the area under the arc $KF$. The difference in these integrals is the area in the closed region $DFKD$, or the area marked I in Fig. 9.12. Similarly, the right-hand side of equation 9.20 represents the area II in Fig. 9.12, and the unique points $O$ and $D$ are therefore determined by the graphical condition

$$\text{area I} = \text{area II} \tag{9.21}$$

*It is only after the nominal (non-monotonic) isotherm has been truncated by this equal area construction that it represents a true physical isotherm.*

Not only is there a nonzero change in the molar volume at the phase transition, but there are associated nonzero changes in the molar energy and the molar entropy as well. The change in the entropy can be computed by integrating the quantity

$$ds = \left(\frac{\partial s}{\partial v}\right)_T dv \tag{9.22}$$

along the hypothetical isotherm $OMKFD$. Alternatively, by the thermodynamic mnemonic diagram, we can write

$$\Delta s = s_D - s_O = \int_{OMKFD} \left(\frac{\partial P}{\partial T}\right)_v dv \tag{9.23}$$

A geometrical interpretation of this entropy difference, in terms of the area between neighboring isotherms, is shown in Fig. 9.13.

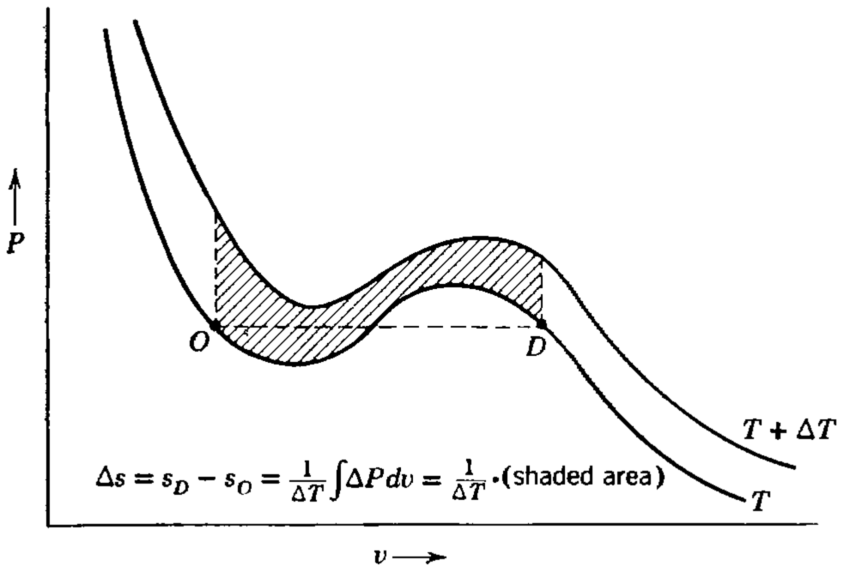

FIGURE 9.13
The discontinuity in molar entropy. The area between adjacent isotherms is related to the entropy discontinuity and thence to the latent heat.

As the system is transformed at fixed temperature and pressure from the pure phase $O$ to the pure phase $D$, it absorbs an amount of heat per mole equal to $l_{DO} = T\Delta s$. The volume change per mole is $\Delta v = v_D - v_O$, and this is associated with a transfer of work equal to $P\Delta v$. Consequently, the total change in the molar energy is

$$\Delta u = u_D - u_O = T\Delta s - P\Delta v \tag{9.24}$$

Each isotherm, such as that of Fig. 9.12, has now been classified into three regions. The region $SO$ is in the liquid phase. The region $DA$ is in the gaseous phase. The flat region $OKD$ corresponds to a mixture of the two phases. Thereby the entire $P$–$v$ plane is classified as to phase, as shown in Fig. 9.14. The mixed liquid-plus-gas region is bounded by the inverted parabola-like curve joining the extremities of the flat regions of each isotherm.

Within the two-phase region any given point denotes a mixture of the two phases at the extremities of the flat portion of the isotherm passing through that point. The fraction of the system that exists in each of the two phases is governed by the "lever rule." Let us suppose that the molar volumes at the two extremities of the flat region of the isotherm are $v_\ell$ and $v_g$ (suggesting but not requiring that the two phases are liquid and gas, for definiteness). Let the molar volume of the mixed system be $v = V/N$. Then if $x_\ell$ and $x_g$ are the mole fractions of the two phases

$$V = Nv = Nx_\ell v_\ell + Nx_g v_g \tag{9.25}$$

from which one easily finds

$$x_\ell = \frac{v_g - v}{v_g - v_\ell} \tag{9.26}$$

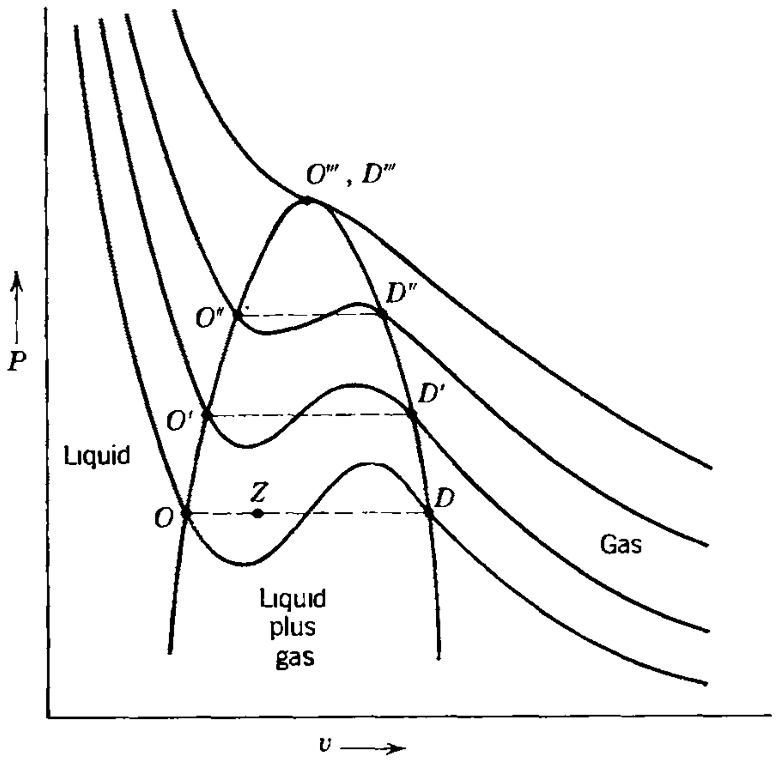

FIGURE 9 14
Phase classification of the $P - v$ plane.

and

$$x_g = \frac{v - v_\ell}{v_g - v_\ell} \tag{9.27}$$

That is, an intermediate point on the flat portion of the isotherm implies a mole fraction of each phase that is equal to the fractional distance of the point from the *opposite* end of the flat region. Thus the point $Z$ in Fig 9.14 denotes a mixed liquid–gas system with a mole fraction of liquid phase equal to the "length" $ZD$ divided by the "length" $OD$. This is the very convenient and pictorial lever rule.

The vertex of the two-phase region, or the point at which $O''$ and $D''$ coincide in Fig. 9.14, corresponds to the *critical point*—the termination of the gas–liquid coexistence curve in Fig. 9.1*a*. For temperatures above the critical temperature the isotherms are monotonic (Fig. 9.14) and the molar Gibbs potential no longer is reentrant (Fig. 9.10).

Just as a $P$–$v$ diagram exhibits a two-phase region, associated with the discontinuity in the molar volume, so a $T$–$s$ diagram exhibits a two-phase region associated with the discontinuity in the molar entropy.

**Example 1**

Find the critical temperature $T_{cr}$ and critical pressure $P_{cr}$ for a system described by the van der Waals equation of state. Write the van der Waals equation of state in terms of the reduced variables $\tilde{T} \equiv T/T_{cr}$, $\tilde{P} \equiv P/P_{cr}$ and $\tilde{v} \equiv v/v_{cr}$.

### Solution

The critical state coincides with a point of horizontal inflection of the isotherm, or

$$\left(\frac{\partial P}{\partial v}\right)_{T_{cr}} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_{cr}} = 0.$$

(Why?) Solving these two simultaneous equations gives

$$v_{cr} = 3b \qquad P_{cr} = \frac{a}{27b^2}, \qquad RT_{cr} = \frac{8a}{27b}$$

from which we can write the van der Waals equation in reduced variables:

$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2}$$

### Example 2

Calculate the functional form of the boundary of the two-phase region in the $P$–$T$ plane for a system described by the van der Waals equation of state.

### Solution

We work in reduced variables, as defined in the preceding example. We consider a fixed temperature and we carry out a Gibbs equal area construction on the corresponding isotherm. Let the extremities of the two-phase region, corresponding to the reduced temperature $\tilde{T}$, be $\tilde{v}_g$ and $\tilde{v}_\ell$. The equal area construction corresponding to equations 9.20 and 9.21 is

$$\int_{v_\ell}^{v_g} \tilde{P}\, d\tilde{v} = \tilde{P}_\ell(\tilde{v}_g - \tilde{v}_\ell)$$

where $\tilde{P}_\ell = \tilde{P}_g$ is the reduced pressure at which the phase transition occurs (at the given reduced temperature $\tilde{T}$). The reader should draw the isotherm, identify the significance of each side of the preceding equation, and reconcile this form of the statement with that in equations 9.20 and 9.21; he or she should also justify the use of reduced variables in the equation. Direct evaluation of the integral gives

$$\ln(3\tilde{v}_g - 1) + \frac{9}{4\tilde{T}}\frac{1}{\tilde{v}_g} - \frac{1}{3\tilde{v}_g - 1} = \ln(3\tilde{v}_\ell - 1) + \frac{9}{4\tilde{T}}\frac{1}{\tilde{v}_\ell} - \frac{1}{3\tilde{v}_\ell - 1}$$

Simultaneous solution of this equation and of the van der Waals equations for $\tilde{v}_g(\tilde{P}, \tilde{T})$ and $\tilde{v}_\ell(\tilde{P}, \tilde{T})$ gives $\tilde{v}_g$, $\tilde{v}_\ell$ and $\tilde{P}$ for each value of $\tilde{T}$.

## PROBLEMS

**9.4-1.** Show that the difference in molar volumes across a coexistence curve is given by $\Delta v = -P^{-1}\Delta f$.

**9.4-2.** Derive the expressions for $v_c$, $P_c$ and $T_c$ given in Example 1.

**9.4-3.** Using the van der Waals constants for $H_2O$, as given in Table 3.1, calculate the critical temperature and pressure of water. How does this compare with the observed value $T_c = 647.05$ K (Table 10.1)?

**9.4-4.** Show that for sufficiently low temperature the van der Waals isotherm intersects the $P = 0$ axis, predicting a region of negative pressure. Find the temperature below which the isotherm exhibits this unphysical behavior.

*Hint*: Let $\tilde{P} = 0$ in the reduced van der Waals equation and consider the condition that the resultant quadratic equation for the variable $\tilde{v}^{-1}$ have two real roots.

*Answer:*
$\tilde{T} = \frac{27}{32} \simeq 0.84$

**9.4-5.** Is the fundamental equation of an ideal van der Waals fluid, as given in Section 3.5, an "underlying fundamental relation" or a "thermodynamic fundamental relation?" Why?

**9.4-6.** Explicitly derive the relationship among $\tilde{v}_g$, $\tilde{v}_\ell$ and $\tilde{T}$, as given in Example 2.

**9.4-7.** A particular substance satisfies the van der Waals equation of state. The coexistence curve is plotted in the $\tilde{P}, \tilde{T}$ plane, so that the critical point is at (1, 1). Calculate the reduced pressure of the transition for $\tilde{T} = 0.95$. Calculate the reduced molar volumes for the corresponding gas and liquid phases.

*Answer:*

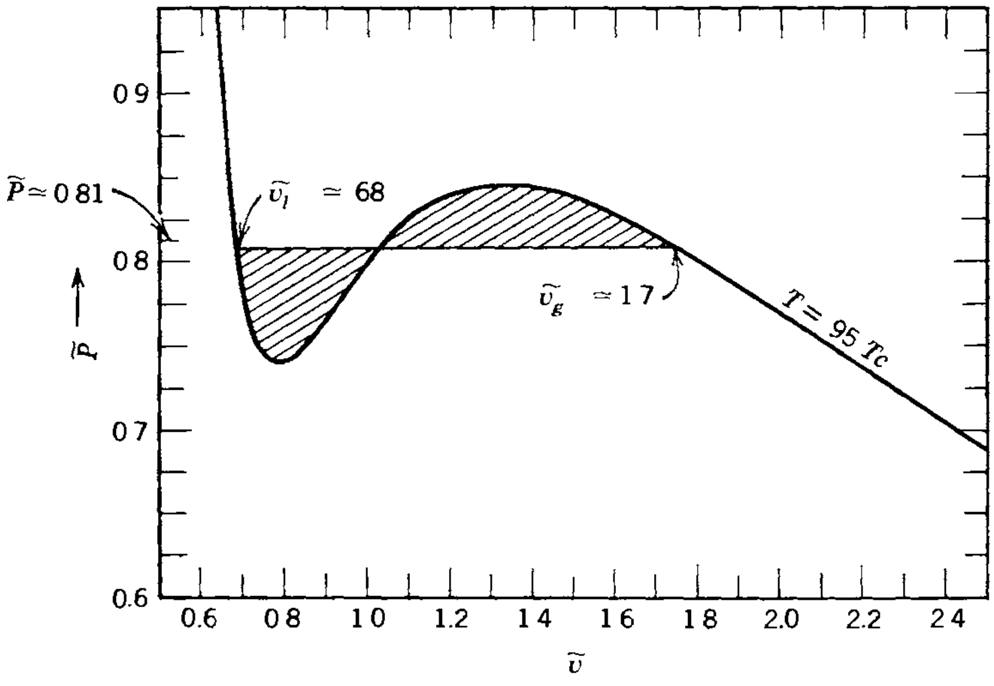

FIGURE 9 15
The $\tilde{T} = 0.95$ isotherm.

The $\tilde{T} = 0.95$ isotherm is shown in Fig. 9.15.
Counting squares permits the equal area construction

shown, giving the approximate roots indicated on the figure. Refinement of these roots by the analytic method of Example 2 yields $\tilde{P} = 0.814$, $\tilde{v}_g = 1.71$ and $\tilde{v}_\ell = 0.683$

**9.4-8.** Using the two points at $\tilde{T} = 0.95$ and $\tilde{T} = 1$ on the coexistence curve of a fluid obeying the van der Waals equation of state (Problem 9.4-7), calculate the average latent heat of vaporization over this range. Specifically apply this result to $H_2O$.

**9.4-9.** Plot the van der Waals isotherm, in reduced variables, for $T = 0.9T_c$. Make an equal area construction by counting squares on the graph paper. Corroborate and refine this estimate by the method of Example 2.

**9.4-10.** Repeat problem 9.4-8 in the range $0.90 \leq \tilde{T} \leq 0.95$, using the results of problems 9.4-7 and 9.4-9. Does the latent heat vary as the temperature approaches $T_c$? What is the expected value of the latent heat precisely at $T_c$? The latent heat of vaporization of water at atmospheric pressure is $\simeq 540$ calories per gram. Is this value qualitatively consistent with the trend suggested by your results?

**9.4-11.** Two moles of a van der Waals fluid are maintained at a temperature $T = 0.95T_c$ in a volume of 200 $\text{cm}^3$. Find the mole number and volume of each phase. Use the van der Waals constants of oxygen.

## 9-5 GENERAL ATTRIBUTES OF FIRST-ORDER PHASE TRANSITIONS

Our discussion of first-order transitions has been based on the general shape of realistic isotherms, of which the van der Waals isotherm is a characteristic representative. The problem can be viewed in a more general perspective based on the convexity or concavity of thermodynamic potentials.

Consider a general thermodynamic potential, $U[P_s, \ldots, P_t]$, that is a function of $S, X_1, X_2, \ldots, X_{s-1}, P_s, \ldots, P_t$. The criterion of stability is that $U[P_s, \ldots, P_t]$ must be a convex function of its extensive parameters and a concave function of its intensive parameters. Geometrically, the function must lie above its tangent hyperplanes in the $X_1, \ldots, X_{s-1}$ subspace and below its tangent hyperplanes in the $P_s, \ldots, P_t$ subspace.

Consider the function $U[P_s, \ldots, P_t]$ as a function of $X_j$, and suppose it to have the form shown in Fig. 9.16*a*. A tangent line *DO* is also shown. It will be noted that the function lies above this tangent line. It also lies above all tangent lines drawn at points to the left of *D* or to the right of *O*. The function does not lie above tangent lines drawn to points intermediate between *D* and *O*. The local curvature of the potential is positive for all points except those between points *F* and *M*. Nevertheless a phase

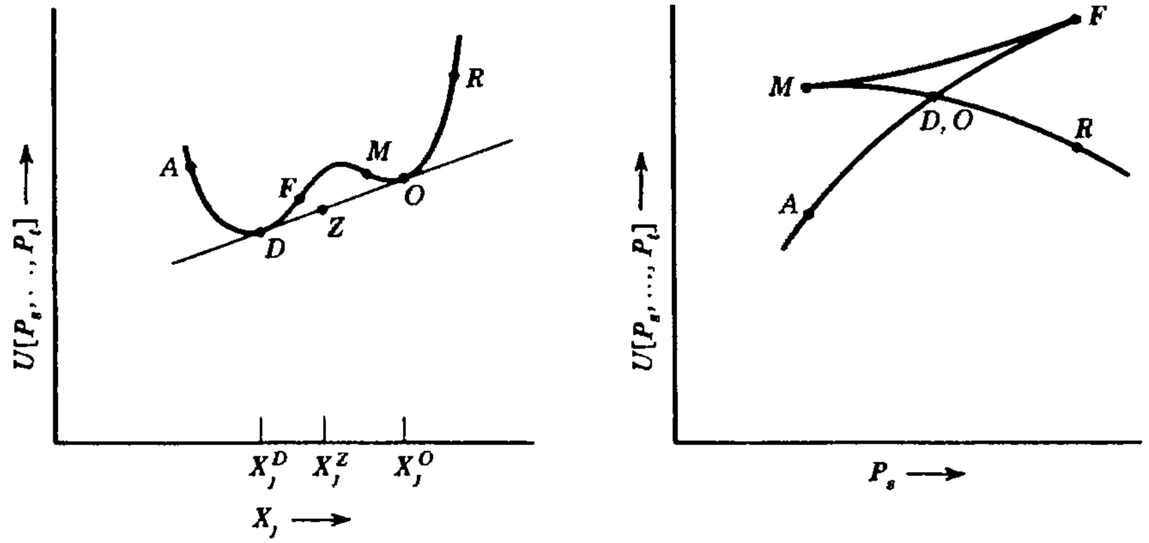

FIGURE 9.16
Stability reconstruction for a general potential.

transition occurs from the phase at $D$ to the phase at $O$. Global curvature fails (becomes negative) at $D$ before local curvature fails at $F$.

The "amended" thermodynamic potential $U[P_s, \ldots, P_t]$ consists of the segment $AD$ in Fig. 9.15*a*, the straight line two-phase segment $DO$, and the original segment $OR$.

An intermediate point on the straight line segment, such as $Z$, corresponds to a mixture of phases $D$ and $O$. The mole fraction of phase $D$ varies linearly from unity to zero as $Z$ moves from point $D$ to point $O$, from which it immediately follows that

$$X = \frac{\left(X_j^0 - X_j^Z\right)}{\left(X_j^0 - X_j^D\right)}$$

This is again the "lever rule."

The value of the thermodynamic potential $U[P_s, \ldots, P_t]$ in the mixed state (i.e., at $Z$) clearly is less than that in the pure state (on the initial curve corresponding to $X_j^z$). Thus the mixed state given by the straight line construction does minimize $U[P_s, \ldots, P_t]$ and does correspond to the physical equilibrium state of the system.

The dependence of $U[P_s, \ldots, P_t]$ on an *intensive* parameter $P_s$ is subject to similar considerations, which should now appear familiar. The Gibbs potential $U[T, P] = N\mu(T, P)$ is the particular example studied in the preceding section. The local curvature is negative except for the segment $MF$ (Fig. 9.16*b*). But the segment $MD$ lies above, rather than below, the tangent drawn to the segment $ADF$ at $D$. Only the curve $ADOR$ lies everywhere below the tangent lines, thereby satisfying the conditions of global stability.

Thus the particular results of the preceding section are of very general applicability to all thermodynamic potentials.