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.
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.\(^1\)

\[
S(U + \Delta U, V, N) + S(U - \Delta U, V, N) \leq 2S(U, V, N) \quad \text{(for all } \Delta)\]  

(8.1)

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

\[
\left( \frac{\partial^2 S}{\partial U^2} \right)_{V, N} \leq 0
\]  

(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

\[
S(U, V + \Delta V, N) + S(U, V - \Delta V, N) \leq 2S(U, V, N) \quad (8.3)
\]

or in differential form

\[
\left( \frac{\partial^2 S}{\partial V^2} \right)_{U, N} \leq 0
\]  

(8.4)

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


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 \(S(U, V, \ldots)\) lie everywhere below its tangent planes. That is, for arbitrary \(\Delta U\) and \(\Delta V\)

\[
S(U + \Delta U, V + \Delta V, N) + S(U - \Delta U, V - \Delta V, N) \leq 2S(U, V, N)
\]  

(8.5)

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

$$\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} - \left( \frac{\partial^2 S}{\partial U \partial V} \right)^2 \geq 0 \quad (8.6)$$

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 \(\left[ (\partial^2 S/\partial U^2)(\partial^2 S/\partial V^2) \right] - \left( \frac{\partial^2 S}{\partial U \partial V} \right)^2 \) must be positive. The condition \(\partial^2 S/\partial U^2 \leq 0\) 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

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

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.

---

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 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 $T_c$ is the "critical temperature," and the transition at $T_c$ 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 minima 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 $X_f$ 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. Occasion-

![Thermodynamic potential with multiple minima.](image)

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
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 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 $(u, f, h, e.c.)$ 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 9.4**
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 $T_5$ is the transition temperature. The high density phase is stable below the transition temperature.

**Figure 9.5**
Minima of the Gibbs potential as a function of $T$.

**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. 9.1a. 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

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)

\[
P = \frac{RT}{(v - b)} - \frac{a}{v^2}
\]  

(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 semieprirical 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.
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

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

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

$$d\mu = -s \, dT + v \, dP \quad (9.15)$$

whence, integrating at constant temperature

$$\mu = \int v \, dP + \phi(T) \quad (9.16)$$

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

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

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

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.
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. 9.9a 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."
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

\[
\int_D^F v \, dP + \int_K^F v \, dP + \int_M^K v \, dP + \int_M^O v \, dP = 0 \tag{9.19}
\]

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 \( 1 \) 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.

\[
\Delta s = s_D - s_O = \frac{1}{T} \int \Delta P \, dv = \frac{1}{T} \cdot \text{(shaded area)}
\]

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9.13}
\caption{The discontinuity in molar entropy. The area between adjacent isotherms is related to the entropy discontinuity and thence to the latent heat.}
\end{figure}

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 \( \Delta Q = T \Delta s \). 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 \( v_r \) 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 \( x_r \) and \( x_g \) are the mole fractions of the two phases

\[
V = N v = N x_r v_r + N x_g v_g \tag{9.25}
\]

from which one easily finds

\[
x_r = \frac{v_g - v}{v_g - v_r} \tag{9.26}
\]
Solution

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

\[
\left( \frac{\partial^2 P}{\partial v^2} \right)_{T_c} = 0.
\]

(Why?) Solving these two simultaneous equations gives

\[
v_{cr} = 3b \quad P_{cr} = \frac{a}{27b^2}, \quad RT_{cr} = \frac{8a}{27b}
\]

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 \(\tilde{v}_r\). The equal area construction corresponding to equations 9.20 and 9.21 is

\[
\int_{v_g}^{v_r} \tilde{P} \, d\tilde{v} = \tilde{P}_r (\tilde{v}_g - \tilde{v}_r)
\]

where \(\tilde{P}_r = \tilde{P}_s\) 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

\[
\ln(3\tilde{v}_g - 1) + \frac{9}{4\tilde{T}} \frac{1}{\tilde{v}_g} - \frac{1}{3\tilde{v}_g - 1} = \ln(3\tilde{v}_r - 1) + \frac{9}{4\tilde{T}} \frac{1}{\tilde{v}_r} - \frac{1}{3\tilde{v}_r - 1}
\]

Simultaneous solution of this equation and of the van der Waals equations for \(\tilde{v}_g(\tilde{P}, \tilde{T})\) and \(\tilde{v}_r(\tilde{P}, \tilde{T})\) gives \(\tilde{v}_g, \tilde{v}_r\) 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 \(\Delta \tilde{v} = -\tilde{P} \Delta \tilde{f}\).

9.4-2. Derive the expressions for \(v_{cr}, P_r\), and \(T_c\) given in Example 1.