8.1: Phase Equilibria

8.1.1 Equilibrium conditions

If the state of an isolated system is an equilibrium state, this state does not change over time (Sec. 2.4.4). We expect an isolated system that is *not* in an equilibrium state to undergo a spontaneous, irreversible process and eventually to reach an equilibrium state. Just how rapidly this process occurs is a matter of kinetics, not thermodynamics. During this irreversible adiabatic process, the entropy increases until it reaches a maximum in the equilibrium state.

A general procedure will now be introduced for finding conditions for equilibrium with given constraints. The procedure is applied to phase equilibria of single-substance, multiphase systems in the next section, to transfer equilibria in multicomponent, multiphase systems in Sec. 9.2.7, and to reaction equilibria in Sec. 11.7.3.

The procedure has five steps:

1. In this section we consider a system of a single substance in two or more uniform phases with distinctly different intensive properties. For instance, one phase might be a liquid and another a gas. We assume the phases are not separated by internal partitions, so that there is no constraint preventing the transfer of matter and energy among the phases. (A tall column of gas in a gravitational field is a different kind of system in which intensive properties of an equilibrium state vary continuously with elevation; this case will be discussed in Sec. 8.1.4.)

   Phase α' will be the reference phase. Since internal energy is extensive, we can write $U = U^{\alpha'} + \sum_{\alpha \neq \alpha'} U^{\alpha}$ and $dU = dU^{\alpha'} + \sum_{\alpha \neq \alpha'} dU^{\alpha}$. We assume any changes are slow enough to allow each phase to be practically uniform at all times. Treating each phase as an open subsystem with expansion work only, we use the relation $dU = T\,dS - p\,dV + \mu\,dn$ (Eq. 5.2.5) to replace each dU^{α} term:

$$dU = (T^{\alpha'}\,dS^{\alpha'} - p^{\alpha'}\,dV^{\alpha'} + \mu^{\alpha'}\,dn^{\alpha'}) + \sum_{\alpha \neq \alpha'}(T^{\alpha}\,dS^{\alpha} - p^{\alpha}\,dV^{\alpha} + \mu^{\alpha}\,dn^{\alpha}) \tag{8.1.1}$$

   This is an expression for the total differential of U when there are no constraints.

   In an isolated system, an equilibrium state cannot change spontaneously to a different state. Once the isolated system has reached an equilibrium state, an imagined finite change of any of the independent variables consistent with the constraints (a so-called *virtual displacement*) corresponds to an impossible process with an entropy decrease. Thus, the equilibrium state has the *maximum* entropy that is possible for the isolated system. In order for S to be a maximum, dS must be zero for an infinitesimal change of any of the independent variables of the isolated system.

   This requirement is satisfied in the case of the multiphase system only if the coefficient of each term in the sums on the right side of Eq. 8.1.6 is zero. Therefore, in an equilibrium state the temperature of each phase is equal to the temperature $T^{\alpha'}$ of the reference phase, the pressure of each phase is equal to $p^{\alpha'}$, and the chemical potential in each phase is equal to $\mu^{\alpha'}$. That is, at equilibrium the temperature, pressure, and chemical potential are uniform throughout the system. These are, respectively, the conditions described in Sec. 2.4.4 of *thermal equilibrium*, *mechanical equilibrium*, and *transfer equilibrium*. These conditions must hold in order for a multiphase system of a pure substance without internal partitions to be in an equilibrium state, regardless of the process by which the system attains that state.

8.1.3 Simple derivation of equilibrium conditions

Here is a simpler, less formal derivation of the three equilibrium conditions in a multiphase system of a single substance.

It is intuitively obvious that, unless there are special constraints (such as internal partitions), an equilibrium state must have thermal and mechanical equilibrium. A temperature difference between two phases would cause a spontaneous transfer of heat from the warmer to the cooler phase; a pressure difference would cause spontaneous flow of matter.

When some of the substance is transferred from one phase to another under conditions of constant T and p, the intensive properties of each phase remains the same including the chemical potential. The chemical potential of a pure phase is the Gibbs energy per amount of substance in the phase. We know that in a closed system of constant T and p with expansion work only, the total Gibbs energy decreases during a spontaneous process and is constant during a reversible process (Eq. 5.8.6). The Gibbs energy will decrease only if there is a transfer of substance from a phase of higher chemical potential to a phase of lower

chemical potential, and this will be a spontaneous change. No spontaneous transfer is possible if both phases have the same chemical potential, so this is a condition for an equilibrium state.

8.1.4 Tall column of gas in a gravitational field

The earth's gravitational field is an example of an external force field that acts on a system placed in it. Usually we ignore its effects on the state of the system. If, however, the system's vertical extent is considerable we must take the presence of the field into account to explain, for example, why gas pressure varies with elevation in an equilibrium state.

A tall column of gas whose intensive properties are a function of elevation may be treated as an infinite number of uniform phases, each of infinitesimal vertical height. We can approximate this system with a vertical stack of many slab-shaped gas phases, each thin enough to be practically uniform in its intensive properties, as depicted in Fig. 8.1. The system can be isolated from the surroundings by confining the gas in a rigid adiabatic container. In order to be able to associate each of the thin slab-shaped phases with a definite constant elevation, we specify that the volume of each phase is constant so that in the rigid container the vertical thickness of a phase cannot change.

We can use the phase of lowest elevation as the reference phase α', as indicated in the figure. We repeat the derivation of Sec. 8.1.2 with one change: for each phase α the volume change dV^α is set equal to zero. Then the second sum on the right side of Eq. 8.1.6, with terms proportional to dV^α, drops out and we are left with

$$dS = \sum_{\alpha \neq \alpha'} \frac{T^{\alpha'} - T^\alpha}{T^{\alpha'}} \, dS^\alpha + \sum_{\alpha \neq \alpha'} \frac{\mu^{\alpha'} - \mu^\alpha}{T^{\alpha'}} \, dn^\alpha \qquad (8.1.7)$$

In the equilibrium state of the isolated system, dS is equal to zero for an infinitesimal change of any of the independent variables. In this state, therefore, the coefficient of each term in the sums on the right side of Eq. 8.1.7 must be zero. We conclude that in an equilibrium state of a tall column of a pure gas, *the temperature and chemical potential are uniform throughout*. The equation, however, gives us no information about pressure.

We will use this result to derive an expression for the dependence of the fugacity f on elevation in an equilibrium state. We pick an arbitrary position such as the earth's surface for a reference elevation at which h is zero, and define the standard chemical potential $\mu^\circ(g)$ as the chemical potential of the gas under standard state conditions at this reference elevation. At $h=0$, the chemical potential and fugacity are related by Eq. 7.8.7 which we write in the following form, indicating the elevation in parentheses:

$$\mu(0) = \mu^\circ(g) + RT \ln \frac{f(0)}{p^\circ} \qquad (8.1.8)$$

Imagine a small sample of gas of mass m that is initially at elevation $h=0$. The vertical extent of this sample should be small enough for the variation of the gravitational force field within the sample to be negligible. The gravitational work needed to raise the gas to an arbitrary elevation h is $w' = mgh$ (Sec. 3.6). We assume this process is carried out reversibly at constant volume and without heat, so that there is no change in T, p, V, S, or f. The internal energy U of the gas must increase by $mgh = nMgh$, where M is the molar mass. Then, because the Gibbs energy G depends on U according to $G = U - TS + pV$, G must also increase by $nMgh$.

The chemical potential μ is the molar Gibbs energy G/n. During the elevation process, f remains the same and μ increases by Mgh:

$$\mu(h) = \mu(0) + Mgh \qquad \begin{array}{l} (8.1.9) \\ (f(h) = f(0)\,) \end{array}$$

From Eqs. 8.1.8 and 8.1.9, we can deduce the following general relation between chemical potential, fugacity, and elevation:

$$\mu(h) = \mu^\circ(g) + RT \ln \frac{f(h)}{p^\circ} + Mgh \qquad \begin{array}{l} (8.1.10) \\ (\text{pure gas in} \\ \text{gravitational field}) \end{array}$$

Compare this relation with the equation that defines the fugacity when the effect of a gravitational field is negligible: $\mu = \mu^\circ(g) + RT \ln(f/p^\circ)$ (Eq. 7.8.7). The additional term Mgh is needed when the vertical extent of the gas is considerable.

Some thermodynamicists call the expression on the right side of Eq. 8.1.10 the "total chemical potential" or "gravitochemical potential" and reserve the term "chemical potential" for the function $\mu°(g) + RT \ln(f/p°)$. With these definitions, in an equilibrium state the "total chemical potential" is the same at all elevations and the "chemical potential" decreases with increasing elevation.

This e-book instead defines the chemical potential μ of a pure substance at any elevation as the molar Gibbs energy at that elevation, as recommended in a 2001 IUPAC technical report (Robert A. Alberty, *Pure Appl. Chem.*, **73**, 1349–1380, 2001). When the chemical potential is defined in this way, it has the same value at all elevations in an equilibrium state.

We know that in the equilibrium state of the gas column, the chemical potential $\mu(h)$ has the same value at each elevation h. Equation 8.1.10 shows that in order for this to be possible, the fugacity must decrease with increasing elevation. By equating expressions from Eq. 8.1.10 for $\mu(h)$ at an arbitrary elevation h, and for $\mu(0)$ at the reference elevation, we obtain

$$\mu°(g) + RT \ln \frac{f(h)}{p°} + Mgh = \mu°(g) + RT \ln \frac{f(0)}{p°} \tag{8.1.11}$$

Solving for $f(h)$ gives

$$f(h) = f(0)e^{-Mgh/RT} \tag{8.1.12}$$
(pure gas at equilibrium
in gravitational field)

If we treat the gas as ideal, so that the fugacity equals the pressure, this equation becomes

$$p(h) = p(0)e^{-Mgh/RT} \tag{8.1.13}$$
(pure ideal gas at equilibrium
in gravitational field)

Equation 8.1.13 is the *barometric formula* for a pure ideal gas. It shows that in the equilibrium state of a tall column of an ideal gas, the pressure decreases exponentially with increasing elevation.

This derivation of the barometric formula has introduced a method that will be used in Sec. 9.8.1 for dealing with *mixtures* in a gravitational field. There is, however, a shorter derivation based on Newton's second law and not involving the chemical potential. Consider one of the thin slab-shaped phases of Fig. 8.1. Let the density of the phase be ρ, the area of each horizontal face be A_s, and the thickness of the slab be δh. The mass of the phase is then $m = \rho A_s \delta h$. The pressure difference between the top and bottom of the phase is δp. Three vertical forces act on the phase: an upward force pA_s at its lower face, a downward force $-(p + \delta p)A_s$ at its upper face, and a downward gravitational force $-mg = -\rho A_s g \delta h$. If the phase is at rest, the net vertical force is zero: $pA_s - (p + \delta p)A_s - \rho A_s g \delta h = 0$, or $\delta p = -\rho g \delta h$. In the limit as the number of phases becomes infinite and δh and δp become infinitesimal, this becomes

$$dp = -\rho g \, dh \tag{8.1.14}$$
(fluid at equilibrium
in gravitational field)

Equation 8.1.14 is a general relation between changes in elevation and hydrostatic pressure in *any* fluid. To apply it to an ideal gas, we replace the density by $\rho = nM/V = M/V_m = Mp/RT$ and rearrange to $dp/p = -(gM/RT)\,dh$. Treating g and T as constants, we integrate from $h=0$ to an arbitrary elevation h and obtain the same result as Eq. 8.1.13.

8.1.5 The pressure in a liquid droplet

The equilibrium shape of a small liquid droplet surrounded by vapor of the same substance, when the effects of gravity and other external forces are negligible, is spherical. This is the result of the surface tension of the liquid–gas interface which acts to minimize the ratio of surface to volume. The interface acts somewhat like the stretched membrane of an inflated balloon, resulting in a greater pressure inside the droplet than the pressure of the vapor in equilibrium with it.

We can derive the pressure difference by considering a closed system containing a spherical liquid droplet and surrounding vapor. We treat both phases as open subsystems. An infinitesimal change dU of the internal energy is the sum of contributions from the liquid and gas phases and from the surface work $\gamma \, dA_s$, where γ is the surface tension of the liquid–gas interface and A_s is the surface area of the droplet (Sec. 5.7):

$$dU = dU^l + dU^g + \gamma\,dA_s = T^l\,dS^l - p^l\,dV^l + \mu^l\,dn^l + T^g\,dS^g - p^g\,dV^g + \mu^g\,dn^g + \gamma\,dA_s \qquad (8.1.15)$$

Note that Eq. 8.1.15 is not an expression for the total differential of U, because V^l and A_s are not independent variables. A derivation by a procedure similar to the one used in Sec. 8.1.2 shows that at equilibrium the liquid and gas have equal temperatures and equal chemical potentials, and the pressure in the droplet is greater than the gas pressure by an amount that depends on r:

$$p^l = p^g + \frac{2\gamma}{r} \qquad (8.1.16)$$

Equation 8.1.16 is the *Laplace equation*. The pressure difference is significant if r is small, and decreases as r increases. The limit $r \to \infty$ represents the flat surface of bulk liquid with p^l equal to p^g.

The derivation of Eq. 8.1.16 is left as an exercise (Prob. 8.1). The Laplace equation is valid also for a liquid droplet in which the liquid and the surrounding gas may both be mixtures (Prob. 9.3).

The Laplace equation can also be applied to the pressure in a gas *bubble* surrounded by liquid. In this case the liquid and gas phases switch roles, and the equation becomes $p^g = p^l + 2\gamma/r$.

8.1.6 The number of independent variables

From this point on in this e-book, unless stated otherwise, the discussions of multiphase systems will implicitly assume the existence of thermal, mechanical, and transfer equilibrium. Equations will not explicitly show these equilibria as a condition of validity.

In the rest of this chapter, we shall assume the state of each phase can be described by the usual variables: temperature, pressure, and amount. That is, variables such as elevation in a gravitational field, interface surface area, and extent of stretching of a solid, are not relevant.

How many of the usual variables of an open multiphase one-substance equilibrium system are independent? To find out, we go through the following argument. In the absence of any kind of equilibrium, we could treat phase α as having the three independent variables T^α, p^α, and n^α, and likewise for every other phase. A system of P phases without thermal, mechanical, or transfer equilibrium would then have $3P$ independent variables.

> We must decide how to count the number of phases. It is usually of no thermodynamic significance whether a phase, with particular values of its intensive properties, is contiguous. For instance, splitting a crystal into several pieces is not usually considered to change the number of phases or the state of the system, provided the increased surface area makes no significant contribution to properties such as internal energy. Thus, the number of phases P refers to the number of different *kinds* of phases.

Each independent relation resulting from equilibrium imposes a restriction on the system and reduces the number of independent variables by one. A two-phase system with thermal equilibrium has the single relation $T^\beta = T^\alpha$. For a three-phase system, there are two such relations that are independent, for instance $T^\beta = T^\alpha$ and $T^\gamma = T^\alpha$. (The additional relation $T^\gamma = T^\beta$ is not independent since we may deduce it from the other two.) In general, thermal equilibrium gives $P-1$ independent relations among temperatures.

By the same reasoning, mechanical equilibrium involves $P-1$ independent relations among pressures, and transfer equilibrium involves $P-1$ independent relations among chemical potentials.

The total number of independent relations for equilibrium is $3(P-1)$, which we subtract from $3P$ (the number of independent variables in the absence of equilibrium) to obtain the number of independent variables in the equilibrium system: $3P - 3(P-1) = 3$. Thus, *an open single-substance system with any number of phases has at equilibrium three independent variables*. For example, in equilibrium states of a two-phase system we may vary T, n^α, and n^β independently, in which case p is a dependent variable; for a given value of T, the value of p is the one that allows both phases to have the same chemical potential.

8.1.7 The Gibbs phase rule for a pure substance

The complete description of the state of a system must include the value of an *extensive* variable of each phase (e.g., the volume, mass, or amount) in order to specify how much of the phase is present. For an equilibrium system of P phases with a

total of 3 independent variables, we may choose the remaining $3 - P$ variables to be *intensive*. The number of these intensive independent variables is called the **number of degrees of freedom** or **variance**, F, of the system:

$$F = 3 - P$$

<div align="right">(8.1.17)
(pure substance)</div>

The application of the phase rule to multicomponent systems will be taken up in Sec. 13.1. Equation 8.1.17 is a special case, for $C = 1$, of the more general Gibbs phase rule $F = C - P + 2$.

We may interpret the variance F in either of two ways:

- A system with two degrees of freedom is called *bivariant*, one with one degree of freedom is *univariant*, and one with no degrees of freedom is *invariant*. For a system of a pure substance, these three cases correspond to one, two, and three phases respectively. For instance, a system of liquid and gaseous H_2O (and no other substances) is univariant ($F = 3 - P = 3 - 2 = 1$); we are able to independently vary only one intensive property, such as T, while the liquid and gas remain in equilibrium.