

6

Phase Transformations in Single-Component Systems

Suppose water always froze as ice-one on Earth because it never had a seed to form...ice-nine—a crystal as hard as this desk—with...a melting point of one (hundred and)-thirty degrees.

Kurt Vonnegut, *Cat's Cradle*

Phase transformations are treated by the thermodynamics of open systems. Using the chemical potential, the equations for the (differential) changes of U , H , A , G , and S are generalized to the case of a variable amount of material. At equilibrium, the chemical potential is equal in coexisting phases. The variation of pressure with temperature required to maintain this equality is given by the Clapeyron or Clausius–Clapeyron equations. First-order, second-order, and lambda transitions are discussed. Activity and fugacity are used to deal with nonideal substances. The presence of an inert gas affects vapor pressure. Condensed phase equilibria, including triple points, are considered. Phase diagrams of CO_2 and H_2O are compared. Liquid crystals, glasses and some polymeric materials illustrate mesomorphic behavior.

6.1 Thermodynamics of Open Systems

In order to discuss phase transformations in this chapter and chemical reactions in the next chapter, we will need to develop the thermodynamics of open systems. In open systems, the number of moles of the various components of the system can change and the thermodynamic functions depend on the numbers of moles of these components, as well as on thermodynamic variables. For example, the natural variables for U become $U(S, V, n_i)$, where the index i ranges over the components of the system.

Mathematically, we can write for U , which is a state function of these variables,

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}} dn_i \quad (1)$$

In the derivatives with respect to the number of moles of each component of the system, the numbers of moles of all other components ($j \neq i$) are held constant. To simplify the notation while keeping it useful for treating phase transformation processes, the same species in different phases will be designated by different subscripts. We first apply this equation to a system with a constant number of moles (all $dn_i = 0$). With the number of moles of all components (including the same component in different phases) constant, material equilibrium is not an issue and we can use Eq. (20) of [Chapter 4](#):

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_i} = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{S, n_i} = -P \quad (2)$$

We define μ_i , the *chemical potential* of component i , as

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}} \quad (3)$$

giving

$$dU = T dS - P dV + \sum_i \mu_i dn_i \quad (4)$$

The use of T , P , and μ_i in Eq. (1) implies that these three quantities are uniform throughout the system and, therefore, that it is at thermal, mechanical and material equilibrium. Compared to Eq. (20) of Chapter 4, it is no longer

necessary to explicitly indicate material equilibrium when writing the equation. Using the definitions of the other thermodynamic function, we can write

$$dH = d(U + PV) = T dS + V dP + \sum_i \mu_i dn_i \quad (5)$$

$$dA = d(U - TS) = -S dT - P dV + \sum_i \mu_i dn_i \quad (6)$$

$$dG = d(H - TS) = -S dT + V dP + \sum_i \mu_i dn_i \quad (7)$$

Equations (4)–(7), yield four equivalent definitions for the chemical potential of component i :

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}} = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (8)$$

From its form, the chemical potential is obviously an intensive property and therefore must be a function only of other intensive variables and independent of the size of the system. We can write it as $\mu_i(T, P, c_j)$, where c_j is some measure of concentration of component j .

Consider the following process: Starting with a small amount of a system with concentrations c_j at T and P , we add components to the system, at constant T and P , in the proper ratio to keep the concentrations constant. We can integrate Eq. (7) for the Gibbs free-energy change for this process:

$$G_2 - G_1 \stackrel{\text{const}}{=} \int_1^2 \sum_i \mu_i dn_i \stackrel{\text{const}}{=} \sum_i \mu_i \int_1^2 dn_i = \sum_i \mu_i (n_{2,i} - n_{1,i}) \quad (9)$$

If the initial number of moles is vanishingly small, $n_{1,i} \rightarrow 0$, $G_1 = 0$. With the final number of moles equal to that in the system, $n_{2,i} = n_i$,

$$G = \sum_i \mu_i n_i \quad (10)$$

For a single-component system, this becomes

$$G = \mu n, \quad \mu = \frac{G}{n} = G_m \quad (11)$$

showing that, for single-component systems, the chemical potential is just the molar Gibbs free energy. Note that of the five definitions of μ in Eq. (8), only in the one in terms of G are intensive variables kept constant as the size of the system is increased; thus, only this relationship can be integrated with constant μ . Our extended definition of enthalpy and Gibbs free energy [Eq. (24) of [Chapter 2](#)] allows this to hold even in cases in which there are work terms in addition to the work of expansion.

6.2 Entropy Change for Open Systems

From Eqs. (4) and (5), the following equations for dS are obtained:

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \left(\frac{1}{T}\right) \sum_i \mu_i dn_i \quad (12)$$

$$dS = \left(\frac{1}{T}\right) dH - \left(\frac{V}{T}\right) dP - \left(\frac{1}{T}\right) \sum_i \mu_i dn_i \quad (13)$$

These give

$$\mu_i = -T \left(\frac{\partial S}{\partial n_i} \right)_{U, V, n_{j \neq i}} = -T \left(\frac{\partial S}{\partial n_i} \right)_{H, P, n_{j \neq i}} \quad (14)$$

Following Eqs. (33) and (36) of [Chapter 4](#), if there are other work terms of the form $L_i dl_i$, Eqs. (12) and (13) become

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV - \left(\frac{1}{T}\right) \sum_i \mu_i dn_i - \left(\frac{1}{T}\right) \sum_i L_i dl_i \quad (15)$$

$$dS = \left(\frac{1}{T}\right) dH - \left(\frac{V}{T}\right) dP - \left(\frac{1}{T}\right) \sum_i \mu_i dn_i + \left(\frac{1}{T}\right) \sum_i l_i dL_i \quad (16)$$

In addition to Eqs. (12) and (13), which give entropy changes in terms of changes of other state functions of the system, we can also calculate entropy changes by considering the energy and material transported to the system during the process. The approach of [Chapter 3](#) must be modified to include the entropy content of the matter transported between the system and the surroundings. The surroundings can be idealized as a reservoir, which maintains constant intensive properties (T , P , and μ_i) as heat and matter is withdrawn. The change of entropy of the surroundings as heat δq and moles δn_i of the various components are transported to the system is

$$dS_{\text{sur}} = - \left(\frac{\delta q}{T} + \sum_i S_{m,i} \delta n_i \right) \quad (17)$$

where $S_{m,i}$ is the molar entropy of component i . We will see in [Chapter 8](#) that when the components of the system interact, *partial* molar entropies must be used in place of molar entropies. Note that δn_i is not the total differential of n_i , because components may also be created or destroyed by chemical reactions *within* the system. If the system is at equilibrium with the surroundings, the transfers are reversible and there can be no net entropy change of the universe. The entropy transport to the system is therefore

$$\partial S = \left(\frac{\delta q}{T} + \sum_i S_{m,i} \delta n_i \right)_{\text{rev}} \quad (18)$$

Because

$$S_m = \frac{H_m - G_m}{T} = \frac{H_m - \mu}{T}$$

we can write Eq. (18) as

$$\begin{aligned} \partial S = & \left(\frac{\delta q}{T} + \frac{1}{T} \sum_i H_{m,i} \delta n_i \right)_{\text{rev}} - \left(\frac{1}{T} \sum_i \mu_i \delta n_i \right)_{\text{rev}} = \left(\frac{\delta q_{\text{tot}}}{T} \right)_{\text{rev}} \\ & - \left(\frac{1}{T} \sum_i \mu_i \delta n_i \right)_{\text{rev}} \end{aligned} \quad (19)$$

where δq_{tot} , the total heat added to the system, includes the enthalpy of the added material. Because the reservoir and the system maintain constant pressure during the reversible transfer and δq_{tot} at constant pressure is the change of enthalpy, Eq. (19) is identical to Eq. (13). *Reversible* in these equations indicates that in using them, the surroundings must be at thermal and material equilibrium with the system.

6.3 Phases and Phase Transformations

A phase is a homogeneous region of matter (i.e., a region with uniform properties). The region does not have to be connected; droplets of water on a cold surface are a single phase. Phases of single substances are usually gases, liquids, or a particular arrangement of molecules in a solid. (Among the other types of region to which the term *phase* is sometimes applied are: *plasmas*, highly ionized *gases*, and *interfaces*, where properties vary from those of one adjoining phase to the other.) Phases that have properties between those of liquids and solids are called *mesomorphic* and will be discussed later in this chapter. In this chapter, we consider only systems in which all phases are composed of the same substance. The phase transitions that we will initially discuss are vaporization (liquid to gas, sometimes called evaporation), melting (solid to liquid, often called *fusion*), sublimation (solid to gas) and their reverse—condensation, freezing, and deposition, respectively.

The change of a property in a phase change will be written as (for the volume change of vaporization as an example), $\Delta_{\text{vap}} V$, or, in the general case, $\Delta_{\phi} X$. It will be assumed that these quantities are on a molar basis. Thus, for water, $\Delta_{\text{fus}} V$ is the volume of 1 mol of liquid water minus the volume of 1 mol of ice. $\Delta_{\text{fus}} V$ of water is negative, as anyone who has had a water-filled auto radiator freeze can testify. $\Delta_{\text{fus}} V$ is positive for most materials, including ethylene glycol, which is currently used in most auto radiators. Because molar volume is a state function, $\Delta_{\text{freezing}} V = -\Delta_{\text{fus}} V$.

Of particular interest are changes in enthalpy, such as the heat of fusion, $\Delta_{\text{fus}}H$, and the heat of vaporization, $\Delta_{\text{vap}}H$, as well as the corresponding changes of entropy. A useful observation, discussed in [Chapter 3](#), is Trouton's rule, that entropies of vaporization are often $\sim 85 \text{ J K mol}$.

6.4 General Criterion for Equilibrium in a Multiphase System

Equilibrium in a multiphase system implies thermal, mechanical, and material equilibrium. Thermal equilibrium requires uniformity of temperature throughout the system, and mechanical equilibrium requires uniformity of pressure. To find the criterion for material equilibrium, we treat a two-phase system and consider a transfer of dn moles from phase β to phase α . First, we regard each phase as a separate system. Because material enters or leaves these phases, they are open systems and we must use Eq. (4) to write their change in internal energy:

$$dU_{\alpha} = T dS_{\alpha} - P dV_{\alpha} + \mu_{\alpha} dn \quad (20)$$

$$dU_{\beta} = T dS_{\beta} - P dV_{\beta} - \mu_{\beta} dn \quad (21)$$

Adding these two equations and realizing that $dS_{\alpha} + dS_{\beta} = dS$ and $dV_{\alpha} + dV_{\beta} = dV$ (extensive quantities without subscripts refer to the combined system) gives

$$dU = T dS - P dV + (\mu_{\alpha} - \mu_{\beta}) dn \quad (22)$$

We may also consider as our system, however, the combined system consisting of the two phases, which is closed. If the phase transformation is at equilibrium, material equilibrium holds and Eq. (20) of [Chapter 4](#) is applicable:

$$dU \stackrel{\text{m.e.}}{=} T dS - P dV \quad (23)$$

In order for Eqs. (22) and (23) to be compatible, at material equilibrium (phase equilibrium) we must have

$$\mu_{\alpha} = \mu_{\beta} \quad (24)$$

which is a general principle for phase equilibrium in single-component systems at thermal and mechanical equilibrium.

6.4.1 Phase Transfer at Constant Temperature and Pressure

Consider a one-component, two-phase system held at constant temperature and pressure by means of a piston as in Fig. 1 of Chapter 2. The change in Gibbs free energy for the transfer of dn moles from phase β to phase α is, from Eq. (7),

$$dG = dG_{\alpha} + dG_{\beta} = \mu_{\alpha} dn - \mu_{\beta} dn = (\mu_{\alpha} - \mu_{\beta}) dn \quad (25)$$

Because the overall system is closed, the transfer will occur spontaneously if dG is negative (i.e., from phase β to phase α if $\mu_{\beta} > \mu_{\alpha}$). If the chemical potentials of the two phases are equal, the system will be at equilibrium for phase transfer (as is known from the general principle derived in the last section). Chemical substances are driven from regions of high chemical potential to regions of low chemical potential, much like charge is driven from regions of high electrical potential to regions of low electrical potential. The chemical potential is one measure of the *escaping tendency* of a substance.

The chemical potential of a homogeneous material (a phase) is a function of two intensive variables, usually chosen as temperature and pressure. We say that such a material has two *degrees of freedom* (i.e., we are free to set two intensive variables). (Note that only intensive variables count as degrees of freedom.) In addition to being able to specify a number of intensive variables equal to the number of degrees of freedom of a system, we are also at liberty to specify the size of the phase with one extensive variable. The chemical potential can be represented as a *surface* on a plot of μ versus P and T . The condition for equilibrium between phase α and phase β is, according to Eq. (24),

$$\mu_{\alpha}(T, P) = \mu_{\beta}(T, P) \quad \text{or} \quad G_{m,\alpha}(T, P) = G_{m,\beta}(T, P) \quad (26)$$

Equation (26) represents the intersection of two surfaces in $\mu(P, T)$ space. The intersection of two surfaces is a curve in the three-dimensional space. The projection of this curve on the PT plane is given by $P(T)$. Because P is a function of T , at equilibrium between two phases, the system has been reduced to one degree of freedom by the requirement of Eq. (26). If one of the phases is a gas, $P(T)$ is the *vapor pressure* curve of the condensed phase. If both phases are condensed, P is the externally applied pressure. Alternatively, we could consider $T(P)$, which gives the temperature at which two phases are at equilibrium as a function of pressure.

6.4.2 Phase Transfer at Constant Temperature and Volume

Consider two phases of a single component in a container of fixed volume and temperature. Using Eq. (6) and noting that $dT = 0$, $dn_{\alpha} = -dn_{\beta} = dn$, and

$dV_\alpha = -dV_\beta$, we can write the change of Helmholtz free energy for transfer of dn_α moles from phase β to phase α as

$$dA = dA_\alpha + dA_\beta = -PdV_\alpha + \mu_\alpha dn + PdV_\alpha - \mu_\beta dn = (\mu_\alpha - \mu_\beta)dn. \quad (27)$$

Because processes in closed systems at constant T and V are spontaneous if the Helmholtz free energy decreases, phase transfer from β to α is spontaneous if $\mu_\beta > \mu_\alpha$. If $\mu_\beta(T, P) = \mu_\alpha(T, P)$, the system is at equilibrium. This determines $P(T)$. However, because the chemical potential of a phase is not a function of its size, we can set *both* T and V for a system containing two phases at equilibrium. The system still has only a single degree of freedom, because V , being an extensive variable, does not count as a degree of freedom. This can be seen most clearly in cases in which one of the phases is a gas. Temperature will determine the vapor pressure of the condensed phase and the vapor will expand to fill the volume of the container, which can be varied maintaining phase equilibrium, as long as some liquid phase remains.

6.4.3 Regimes of Phase Stability

At 0 K, entropy does not contribute to chemical potential because

$$\mu = G_m = H_m - TS_m \quad (28)$$

The ordering of chemical potentials of phases at 0 K is the same as that of their H_m (or of U_m), namely solid < liquid < gas. The molar free energy of a phase varies as

$$d\mu = dG_m = V_m dP - S_m dT \quad (29)$$

and, therefore,

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m \quad (30)$$

From the third law, entropies are always positive, requiring that the chemical potential of all phases decrease with temperature. However, because entropy is a measure of randomness, $S_{m,\text{gas}} > S_{m,\text{liq}} > S_{m,\text{sol}}$, and the chemical potential falls most rapidly with temperature for the gas phase and least rapidly for the solid phase. In Fig. 1a (drawn for a particular value of pressure), as the temperature is increased, $\mu_{\text{liq}}(T)$ crosses $\mu_{\text{sol}}(T)$ at the melting point, and the liquid remains the most stable phase until $\mu_{\text{gas}}(T)$ crosses $\mu_{\text{liq}}(T)$ at the boiling point. In Fig. 1b (drawn for a different substance or at a different pressure), $\mu_{\text{gas}}(T)$ falls so rapidly with temperature that it crosses $\mu_{\text{sol}}(T)$ before $\mu_{\text{liq}}(T)$ does. As a result, liquid is never the most stable phase and, at the given pressure, the solid *sublimates* directly to gas.

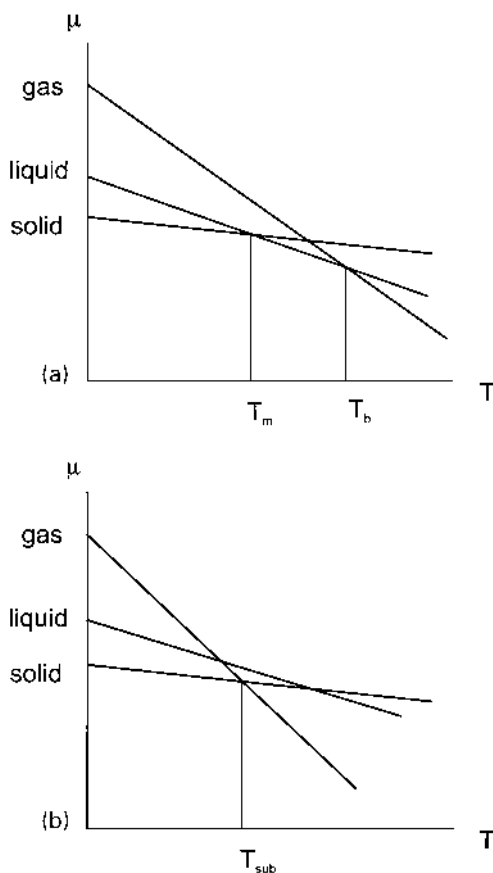


Figure 1 (a) Chemical potentials showing melting and boiling; (b) chemical potentials showing sublimation.

To discuss pressure regimes of phase stability, we use

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m \quad (31)$$

For condensed phases, we can take the molar volume as independent of pressure,

$$\mu \stackrel{cp}{=} \mu^\circ + V_m(P - P^\circ) \quad (32)$$

where μ° is the chemical potential at the standard pressure, P° , chosen as $1.0 \text{ bar} \approx 1.0 \text{ atm}$. Because the molar volume of solids and liquids are quite small, the pressure correction to their chemical potential is small and can sometimes be neglected.

For the gas phase, we can usually use the ideal gas expression, $V_m = RT/P$, giving

$$d\mu \stackrel{\text{i.g.}}{=} RT \frac{dP}{P} = RT d \ln P \quad (33)$$

$$\mu \stackrel{\text{i.g.}}{=} \mu^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \quad (34)$$

The chemical potential varies from $-\infty$ to $+\infty$ as the pressure of the gas varies from 0 to $+\infty$. As a result, there is always some gas pressure that will be at equilibrium with a condensed phase; this pressure is called the *vapor pressure* of the material at the given temperature. If all of the condensed phase does not evaporate (or sublime) before its vapor pressure is reached, equilibrium will be attained.

In Fig. 2, the chemical potential curves of Fig. 1a are shown for two different pressures. Because the molar volume of a gas is greater than that of condensed phases, the chemical potential of the gas is increased much more than those of liquid or solid by increasing pressure. The boiling point and sublimation point therefore increase with pressure. The molar volume of the liquid and solid are comparable, and either one may be larger. As a result, the melting point may either increase or decrease with pressure.

The phase transitions illustrated in Fig. 1 are examples of *first-order phase transitions*. These are characterized by discontinuities in the derivatives of the

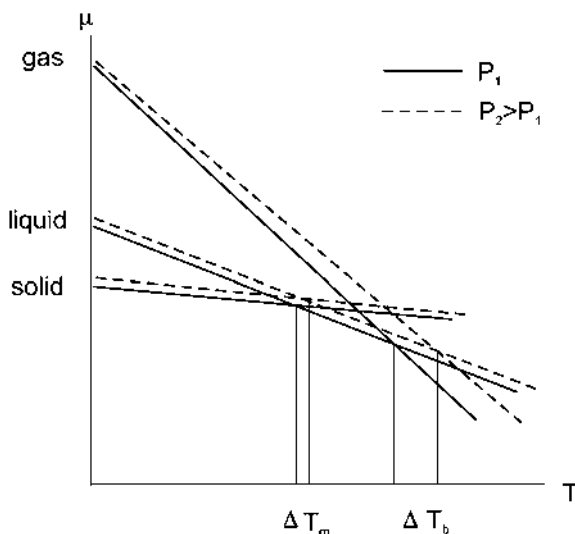


Figure 2 Chemical potentials at two pressures.

chemical potential at the phase transition. From Eq. (31), a discontinuity in $(\partial\mu/\partial P)_T$ requires a volume change for the transition. From Eq. (30), a discontinuity in $(\partial\mu/\partial T)_P$ results from an entropy change and an enthalpy change for the transition. In addition, because $C_P = (\partial H/\partial T)_P$, the heat capacity becomes infinite at a first-order phase transition. These changes are diagrammed in Fig. 3.

Second-order phase transitions, which are quite rare, involve a discontinuity in second derivatives at the transition point. They occur with zero enthalpy, entropy, and volume change. The transitions of certain metals (e.g., Hg and Sn) to a state in which they have no electrical resistance (superconductivity) are second-order phase transitions.

Another type of phase transition is called a lambda transition, because a graph of heat capacity versus temperature for this type of transition resembles the Greek letter λ , as shown in Fig. 4. This type of transition is usually associated with a change from an ordered state to a state with some disorder (order–disorder

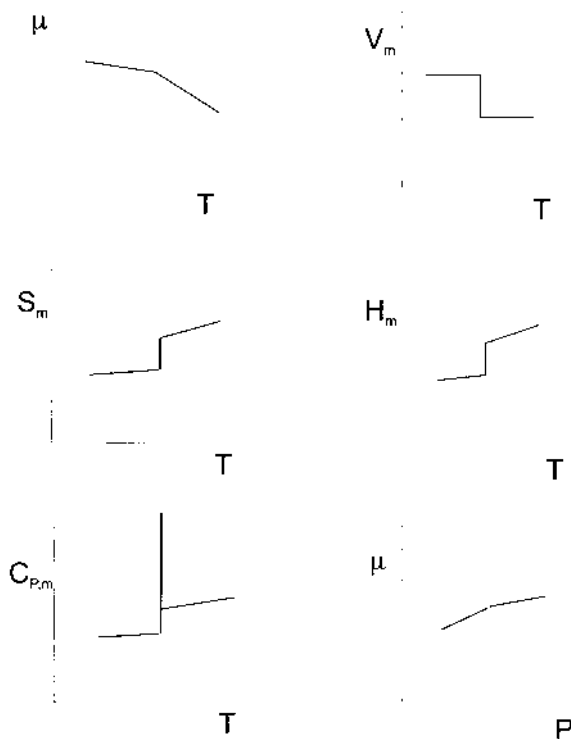


Figure 3 Changes at a first-order phase transition (drawn for the melting of ice).

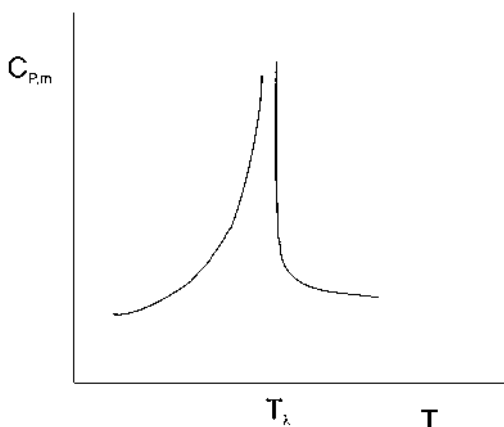


Figure 4 A lambda transition.

transition) as the temperature is raised. The transition occurs over a range of temperature, because it is cooperative—the first bits of disorder ease the way for additional disorder. At the transition temperature, all residual order disappears and the heat capacity goes to infinity. Throughout the transition, only a single phase is present. An example of a lambda transition occurs with an equimolar mixture of Cu and Zn (β brass) at 739 K. Below the lambda transition, each Cu atom is surrounded by four equidistant Zn atoms, whereas above the transition, Cu and Zn atoms are randomly arranged in the crystal.

6.5 Phase Equilibrium Conditions

The solution of Eq. (26) for the phase equilibrium condition gives $P(T)$ (e.g., vapor pressure as a function of temperature) or $T(P)$ (e.g., melting point as a function of pressure). A single point on one of these curves can be obtained by measurement or calculation.¹ We will now show how thermodynamics can be used to obtain the slope of these curves. Equation (26), $\mu_{\alpha} = \mu_{\beta}$, holds at phase equilibrium. If we change either P or T and the system remains at equilibrium, Eq. (26) must still hold:

$$\mu'_{\alpha} = \mu_{\alpha} + d\mu_{\alpha}^{\text{equil}} = \mu'_{\beta} = \mu_{\beta} + d\mu_{\beta} \quad (35)$$

Substituting Eq. (26) gives

$$d\mu_{\alpha} = dG_{m,\alpha} = d\mu_{\beta} = dG_{m,\beta} \quad (36)$$

Using Eq. (29),

$$dG_{m,\alpha} = V_{m,\alpha} dP - S_{m,\alpha} dT = dG_{m,\beta} = V_{m,\beta} dP - S_{m,\beta} dT \quad (37)$$

or

$$\frac{dP}{dT} = \frac{S_{m,\beta} - S_{m,\alpha}}{V_{m,\beta} - V_{m,\alpha}} = \frac{\Delta_\phi S}{\Delta_\phi V} \quad (38)$$

where $\Delta_\phi S$ and $\Delta_\phi V$ are the entropy and the volume change, respectively, for the phase change $\alpha \rightarrow \beta$. Because we are dealing with a system at equilibrium,

$$\Delta_\phi S = \frac{\Delta_\phi H}{T} \quad (39)$$

giving

$$\frac{dP}{dT} = \frac{\Delta_\phi H}{T \Delta_\phi V} \quad (40)$$

This is the *Clapeyron equation*, which applies to any type of phase equilibrium.

For equilibrium between a gas and a condensed phase, we can write (using vaporization as an example)

$$\mu_g = \mu_g^\circ + RT \ln\left(\frac{P}{P^\circ}\right) = \mu_l \approx \mu_l^\circ \quad (41)$$

(The chemical potentials of condensed phases are relatively pressure independent, due to their small molar volumes.) Rewriting,

$$\mu_g^\circ - \mu_l^\circ = \Delta_{\text{vap}} G^\circ = -RT \ln\left(\frac{P}{P^\circ}\right) \quad (42)$$

where $\Delta_{\text{vap}} G^\circ$ is the Gibbs free energy of vaporization when both liquid and vapor are in their standard (1.0 bar) states. Using Eq. (29) of [Chapter 4](#), the Gibbs–Helmholtz equation, we obtain

$$\Delta_{\text{vap}} H^\circ = \left(\frac{\partial(T^{-1} \Delta_{\text{vap}} G^\circ)}{\partial T^{-1}} \right)_P = \frac{d(T^{-1} \Delta_{\text{vap}} G^\circ)}{dT^{-1}} = -R \frac{d \ln(P/P^\circ)}{dT^{-1}} \quad (43)$$

The partial derivative can be converted into an ordinary derivative because $\Delta_{\text{vap}} G^\circ$ does not depend on pressure. Because P° does not depend on temperature, this becomes

$$\frac{d \ln P}{dT^{-1}} = -\frac{\Delta_{\text{vap}} H^\circ}{R} \quad (44)$$

which is known as the *Clausius–Clapeyron equation*. The same formula can be obtained from Eq. (40) by neglecting the molar volume of the condensed phase

and using the ideal gas law. The standard enthalpy change of vaporization (usually called the *heat of vaporization*) is given by

$$\Delta_{\text{vap}}H^\circ = H_{m,g}^\circ - H_{m,l}^\circ \quad (45)$$

The standard state of condensed phases, such as liquids, are chosen as the pure substance at 1.0 bar pressure at the temperature of interest. The standard state of an ideal gas is also at 1.0 bar. Over a moderate range of temperature, heats of vaporization and sublimation usually do not vary greatly and, as shown by Eq. (44), can be obtained from plots of the vapor pressure versus $1/T$. An example of this for ethyl acetate is shown in Fig. 5. Note the slight deviation of Fig. 5b from a straight line.

The integrated form of Eq. (44), assuming temperature-independent $\Delta_\phi H^\circ$,

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_\phi H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (46)$$

is useful for interpolating and extrapolation vapor pressure data.

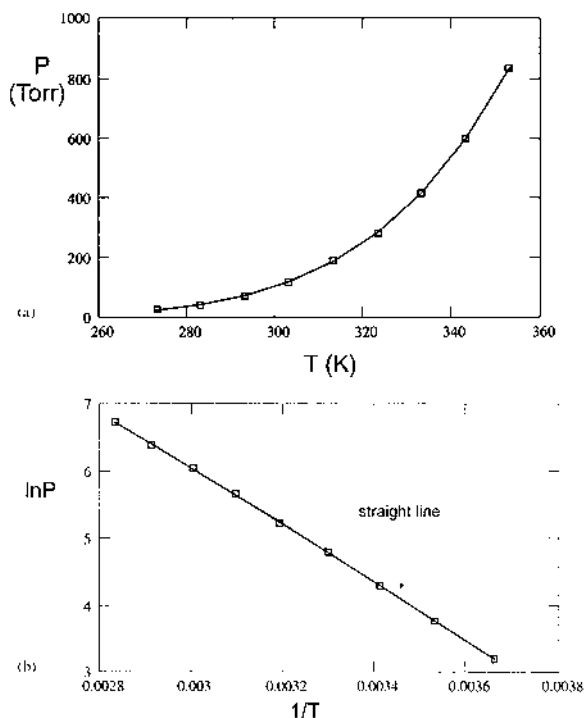


Figure 5 (a) Vapor pressure of ethyl acetate; (b) vapor pressure of ethyl acetate plotted according to Eq. (44).

Example 1. The normal boiling point of nonane is 150.8°C and its vapor pressure is 400 mm Hg at 128.2°C. What is the $\Delta_{\text{vap}}H^\circ$ of nonane? Compare $\Delta_{\text{vap}}S^\circ$ with the Trouton's law value, 85 J/K mol.

Solution:

$$\Delta_{\text{vap}}H^\circ = \frac{R \ln(P_2/P_1)}{(1/T_1 - 1/T_2)}$$

The temperature must be in Kelvin.

$$\Delta_{\text{vap}}H^\circ = 8.314 \frac{\text{J}}{\text{K mol}} \ln\left(\frac{760}{400}\right) \left[\left(\frac{1}{401.3} - \frac{1}{423.9}\right) \frac{1}{\text{K}}\right]^{-1}$$

$$= 40.1 \text{ mol/kJ}$$

$$\Delta_{\text{vap}}S^\circ = \frac{40,100 \text{ J}}{\text{mol}(423.9 \text{ K})} = 94.6 \text{ K mol/J}$$

This example illustrates how thermodynamic quantities, the determination of which we might expect would require calorimetric measurements, can often be much more easily obtained from calculations based on equilibrium conditions.

6.6 Vapor Pressure When a Gas Is Not Ideal

The form of Eq. (34) is so useful that we generalize it by defining for any substance, an *activity*, a , so that

$$\mu = \mu^\circ + RT \ln a \quad (47)$$

μ° is the chemical potential in the standard state, which must be defined for the substance. (Standard states were discussed in Section 4.7 of [Chapter 4](#).) From Eq. (47), the activity is given by

$$a = \exp\left(\frac{\mu - \mu^\circ}{RT}\right) \quad (48)$$

and depends on the choice of standard state. It is a dimensionless quantity. The activity is always 1.0 at the standard state. For condensed phases, the standard state is chosen to occur at 1.0 bar pressure, and the activity is 1.0 at this pressure. Because the molar volumes of condensed phases are very small, their activities remain close to 1.0 for moderate pressure deviations from 1.0 bar. (See Problem 3.)

From Eq. (34), for an ideal gas, the activity is P/P° , or just the numerical value of the pressure in bars. For an ideal gas, pressure is therefore

$$P \stackrel{\text{i.g.}}{=} aP^\circ \quad (49)$$

Because we would like to discuss the properties of real gases in terms of a variable analogous to pressure, we define the fugacity of a real gas as

$$f = aP^\circ \quad (50)$$

(For an ideal gas, $f = P$.) μ , a , and f are alternative measures of escaping tendency.

Using Eq. (50) in Eq. (47) gives

$$\mu = \mu^\circ + RT \ln\left(\frac{f}{P^\circ}\right) \quad (51)$$

We define the standard state of a real gas so that Eq. (51) is general (i.e., so that it also applies to ideal gases). For ideal gases, the standard state is at 1.0 bar pressure. For real gases, we also use a 1.0-bar ideal gas as the standard state. We find the standard state by the two-step process shown in Fig. 6. First we extrapolate the real gas to very low pressure, where $f \rightarrow P$ and the gas becomes ideal (Step I). We then convert the ideal gas to 1.0 bar (step II). The convenience of an ideal gas standard state is that it allows temperature conversions to be made with ideal gas heat capacities (which are pressure independent). Conversion to the real gas state is then made at the temperature of interest.

Some properties of an ideal gas, such as molar enthalpy, are independent of pressure, so that Step II is not necessary. The standard values for such properties

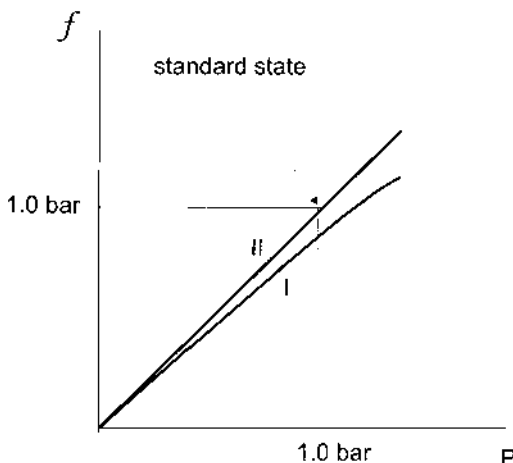


Figure 6 Correction of a real gas to its standard state.

are just obtained by extrapolating the measured values to zero pressure. Thus, for real gases, we get, instead of Eq. (44),

$$\frac{d \ln f}{dT^{-1}} = -\frac{\Delta_{\text{vap}}H^\circ}{R} \quad (52)$$

where $\Delta_{\text{vap}}H^\circ$ is the extrapolation of the heat of vaporization to zero pressure.

Although fugacity is theoretically and computationally significant, it is the pressure that we need for practical applications. To find the relation between f and P , we write, from Eqs. (31) and (51),

$$d\mu_T = V_m dP = RT d \ln f \quad (53)$$

Integrating this equation from $P = 0$, where f and P are equal,

$$\int_0^{P'} V_m dP = RT \int_0^{P'} d \ln f \quad (54)$$

Both of these integrands are infinite at their lower limit, and the integrals cannot be evaluated. To circumvent this difficulty, we define the *fugacity coefficient*, ϕ , so that

$$f = \phi P \quad (55)$$

with $\phi \rightarrow 1$ as $P \rightarrow 0$. Equation (54) then becomes

$$\int_0^{P'} V_m dP = RT \left(\int_0^{P'} d \ln \phi + \int_0^{P'} d \ln P \right) \quad (56)$$

or

$$\ln \phi(P') = \frac{1}{RT} \int_0^{P'} \left(V_m - \frac{RT}{P} \right) dP \quad (57)$$

The integrand of this integral goes to zero at the lower limit.

6.7 Equation of State for the Two-Phase Region

In [Chapter 1](#), we remarked on the oscillatory behavior of two-parameter equations of state, such as those of van der Waals, Berthelot, and Redlich-Kwong in the two-phase region. Usually, the parameters for these equations are determined from the critical point; therefore, the equations should have some validity slightly below the critical point in the two-phase region. Because these equations of states are cubic equations, with three real roots below the critical point, they give three values of V_m for any combination of P and T . Referring to [Fig. 7](#), V_{m1} and V_{m3} correspond to the liquid and gas, respectively, whereas V_{m2} , where

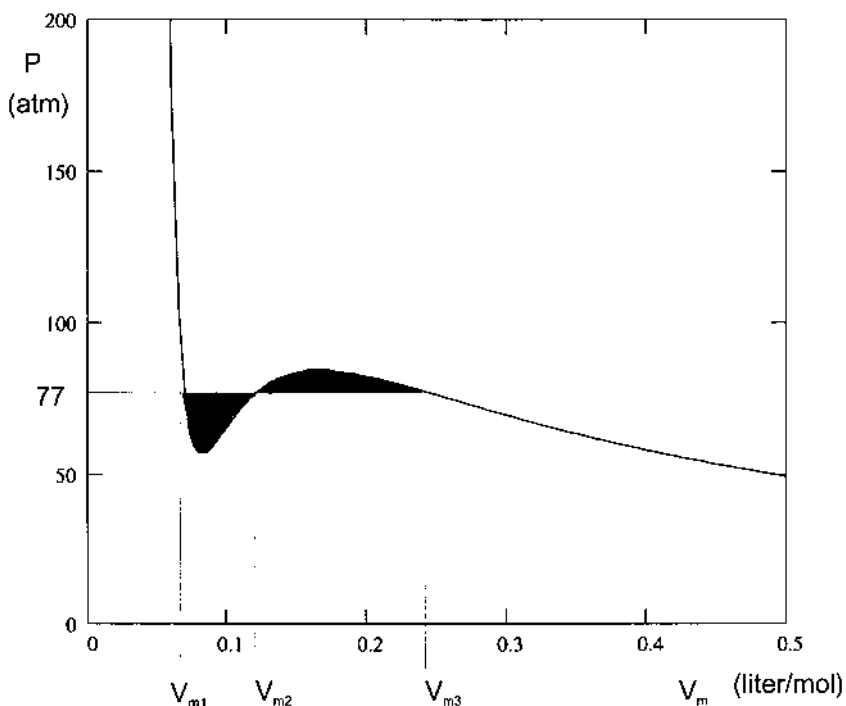


Figure 7 Vapor pressure of NH_3 at 370 K from the van der Waals equation.

$(\partial V_m / \partial P)_T > 0$ does not correspond to a real substance. However, we know that P and T are not independent in the two-phase region and we seek a criterion for finding $P(T)$ (i.e., the vapor pressure of the substance).

Because liquid and gas are at equilibrium in the two-phase region, the chemical potentials of the phases with V_{m1} and V_{m3} must be equal. Points 1 and 3 lie on the same isotherm; therefore, we can write

$$\mu_1 - \mu_3 = \int_1^3 V_m dP = 0 \quad (58)$$

Because we prefer to deal with an integral over V_m , integration by parts is used to give

$$V_{m,3}P - V_{m,1}P - \int_{V_{m,1}}^{V_{m,3}} P dV_m = 0 \quad (59)$$

which can be written as

$$\int_{V_{m,1}}^{V_{m,3}} P dV = P(V_{m,3} - V_{m,1}). \quad (60)$$

In other words, the pressure is chosen so that the area under the oscillating curve is the same as that under the straight line joining the end points. Estimates can be performed by shifting a transparent horizontal straight edge until the two shaded areas in Fig. 7 are visually equal, which occurs for the van der Waals equation for ammonia at 77 atm for 370 K. The measured vapor pressure is about 57 atm. Quantitative equalization of the areas can be done by trial and error, but is usually not worthwhile, because the major part of the inaccuracy is due to the poor fit of the equation in the two-phase regions. The Redlich–Kwong equation provides a better fit, and when used in a graphical procedure similar to that employed in Fig. 7, it gives a vapor pressure of 61 atm at 370 K.

6.8 Effect of Inert Gas on Phase Equilibria

In our consideration of phase equilibria at constant pressure, we imagined the overall system confined by a piston. However, when we talk about constant-pressure systems, we usually mean that the pressure is maintained by an inert gas (e.g., the atmosphere).² In some situations, much higher constant pressures of inert gases are applied to systems. If we take a gas-condensed phase equilibrium and apply an inert gas pressure to both phases, we get, from Eqs. (31) and (33),

$$d\mu_{\text{cond}} = V_m dP_{\text{inert}} = d\mu_{\text{gas}} = RT d \ln P \quad (61)$$

Note that μ of the gas depends only on the pressure of the gas at equilibrium, as we have assumed that it behaves ideally. On the other hand, in calculating change of μ of the condensed phase, we consider only the inert gas pressure. This pressure is much larger than the change in the vapor pressure of the active gas, and to the condensed phase, all types of pressure are the same. Integrating Eq. (61) from an inert gas pressure of zero at which the vapor pressure is P_0 to an inert gas pressure of P_{inert} gives

$$\ln\left(\frac{P}{P_0}\right) = \frac{V_m P_{\text{inert}}}{RT} \quad (62)$$

Example 2. The vapor pressure of water is 23.76 torr at 25°C. What is its vapor pressure in the presence of 1.0 atm of air considered an inert gas?... in the presence of 100 atm of air?

Solution: Since the density of water is 1.0 g/mL, its molar volume is 18 mL/mol.

At 1.0 atm;

$$\ln\left(\frac{P}{23.76}\right) = \frac{(18 \times 10^{-3} \text{ L})(1.0 \text{ atm})}{(\text{mol})(0.082 \text{ L atm/mol K})(298 \text{ K})} = 0.00074$$

$$\frac{P}{23.76} = \exp(0.00074) = 1.00074, \quad P = 23.78 \text{ torr}$$

At 100 atm;

$$\frac{P}{23.76} = \exp(0.074) = 1.0768, \quad P = 25.58 \text{ torr}$$

The example indicates that the inert gas effect would be difficult to measure at 1 atm, but becomes appreciable at very high pressures.

6.9 Condensed-Phase Equilibria

Condensed-phase equilibria are treated by Eq. (40), the Clapeyron equation. The most important type of condensed-phase equilibrium is that between solid and liquid. For melting, $\Delta_{\phi}H$ is always positive, because the solid is the lowest-energy (and enthalpy) arrangement of molecules. The direction of change of the melting temperature with pressure,

$$\left.\frac{dT}{dP}\right|_{\text{melt}} = \frac{T(\Delta_{\text{melt}}V)}{\Delta_{\text{melt}}H} = \frac{T(V_{m,\text{liq}} - V_{m,\text{sol}})}{\Delta_{\text{melt}}H} \quad (63)$$

is thus determined by the sign of $\Delta_{\text{melt}}V$. Usually, molar volumes of liquids are greater than those of solids and $\Delta_{\text{melt}}V$ is positive. In this case, the melting temperature increases with pressure. In water, however, the solid has a hydrogen-bonded configuration containing cavities and a larger molar volume than the liquid. As a result, freezing water expands (as in an automobile radiator unprotected by antifreeze) and the resulting ice is less dense and floats on the liquid. Equation (63) then tells us that the melting temperature of water decreases with increasing pressure. This is often offered as an explanation for the speed that can be achieved in ice skating. The narrow blades concentrate the skater's weight and produce a large pressure, at which the melting temperature of water is lowered below ambient temperature. The resulting film of liquid water provides low friction, which enhances the skater's speed. Because volume changes on melting are usually quite small, melting temperatures do not change very much with pressure.

Example 3. For water, the freezing point at 1 atm pressure is $0^{\circ}\text{C} = 273.15 \text{ K}$. The density of liquid water is 1.00 g/cm^3 and that

of ice is 0.92 g/cm^3 . The heat of fusion of water is 6.0 kJ/mol . What is the freezing point of water at 100 atm pressure?

Solution: Separating variables in Eq. (63) and integrating,

$$\begin{aligned}\ln\left(\frac{T_2}{T_1}\right) &= \frac{\Delta V_{\text{melt}}}{\Delta H_{\text{melt}}}(P_2 - P_1) \\ \Delta V_{\text{melt}} &= \left(\frac{\text{cm}^3}{1.0 \text{ g}} - \frac{\text{cm}^3}{0.92 \text{ g}}\right) \frac{18 \text{ g}}{\text{mol}} = -1.6 \frac{\text{cm}^3}{\text{mol}} \\ \ln\left(\frac{T_2}{273.15}\right) &= -\left(1.6 \frac{\text{cm}^3}{\text{mol}} \frac{\text{L}}{10^3 \text{ cm}^3}\right) \\ &\quad \times \left(6.0 \times 10^3 \frac{\text{J}}{\text{mol}} \frac{0.082 \text{ L atm}}{8.314 \text{ J}}\right)^{-1} (100 - 1) \text{ atm} \\ &= -0.0027\end{aligned}$$

Two different values for the gas constant were used to convert from Joule to liter atm:

$$T_2 = 273.15 \exp(-0.0027) = 272.41 \text{ K} = -0.75^\circ\text{C}$$

6.10 Equilibrium Between Three Phases

If a mixture of ice and water at 1 atm pressure and 0°C is placed in an insulated container and all of the air is pumped away and the container sealed, what will happen? As was shown in the previous section, at pressures lower than 1 atm , the melting point of ice is above 0°C . Water will, therefore, be solid at 0°C and reduced pressure. However, when some liquid water freezes, its latent heat is released and the temperature of the system is slightly increased. Equilibrium is reestablished at the higher temperature and reduced pressure. The pressure in the system is the vapor pressure of both liquid and solid water slightly above 0 K . The new equilibrium point of the system is called the *triple point* of water and is at 0.0098°C and 611 Pa . Three phases—solid, liquid, and gas—coexist at the triple point, and the chemical potential of water in each of the phases must be equal:

$$\mu_{\text{solid}} = \mu_{\text{liq}} = \mu_{\text{vap}} \quad (64)$$

This introduces two independent equations that must be satisfied and reduces the number of degrees of freedom of the system to zero. The triple point of a single-component system is invariant and provides a convenient temperature reference. Because vapor pressure, as well as chemical potential, is a measure of escaping tendency from a condensed phase, the vapor pressures of the solid and liquid are equal at the triple point.

6.11 Phase Diagrams

Regions of phase stability and equilibrium between phases are often presented by means of *phase diagrams*, which represent the properties of substances as a function of pressure and temperature. For a one-component system, on such a diagram, regions where a single phase exists are represented as areas (two degrees of freedom), regions where two phases exist at equilibrium are represented as curves (one degree of freedom), and where three phases exist at equilibrium as points (the triple point). In Fig. 8, the phase diagram of water is shown at low pressures. (As can be seen, the diagram is not drawn to scale.) The solid phase is represented by the area at high pressure and low temperature and the vapor phase by the area at low pressure. The liquid phase is represented by an intermediate area, with the curve separating the liquid and vapor ending at the critical point (220 atm and 374°C). Above the critical temperature, there is no observable phase transition between liquid and vapor and the material is called a *supercritical fluid*.

Water, of course, makes transitions from solid ice to liquid water (at 0°C) to water vapor (at 100°C) as it is heated at 1.0 atm pressure. Because at the pressure of the triple-point, the transformation is directly from solid to gas, the triple point pressure must be below 1.0 atm. Because $\Delta_{\text{melt}}V$ for water is negative, by Eq. (38), the solid–liquid equilibrium line has negative slope, and the triple point must be above 0°C. Considering the steepness of the line, the difference is very small and the measured triple point of water is 0.0098°C and 611 Pa (~4.6 torr).

A substance that can exist in more than one crystalline form is said to exhibit *allotropy*, and the different forms are called *allotropes*. Figure 9 is the high-pressure part of the phase diagram of water and shows that water has a number of allotropes. The crystalline forms of water in the allotropes that melt are

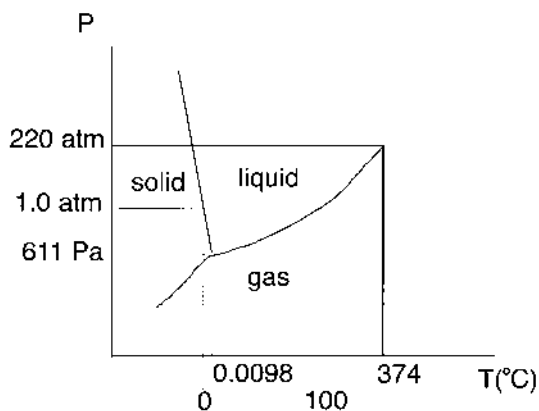


Figure 8 Phase diagram for water (not to scale).

denser than liquid water, as can be deduced from the positive slopes of their liquid–solid equilibrium lines. The allotropes of water result in a number of triple points, where three solid phases, or two solid phases and liquid water are at equilibrium. The phases are numbered in order of their discovery, from I through IX. There is no ice IV, because what was originally given that designation was later found to be *metastable*, converting to other phases over time. Conversion of one solid phase to another is often very slow. Assuring that equilibrium has been achieved is a major difficulty in studying high-pressure phase diagrams.

The ice IX shown in Fig. 9 is not that postulated in Vonnegut’s science fiction book, *Cat’s Cradle*, that is quoted at the beginning of this chapter. That ice-nine is the stable form of water at ambient conditions, never previously discovered, due to lack of a nucleation crystal. When the mad scientist in Vonnegut’s book synthesizes ice-nine and a crystal finds its way into the ocean, great calamities ensue.

The low-pressure phase diagram of carbon dioxide, shown in Fig. 10, is different from that of water in a number of respects. Carbon dioxide sublimates at 1.0 atm, leading to solid CO₂ being called “dry ice.” The triple point is at 5.1 atm

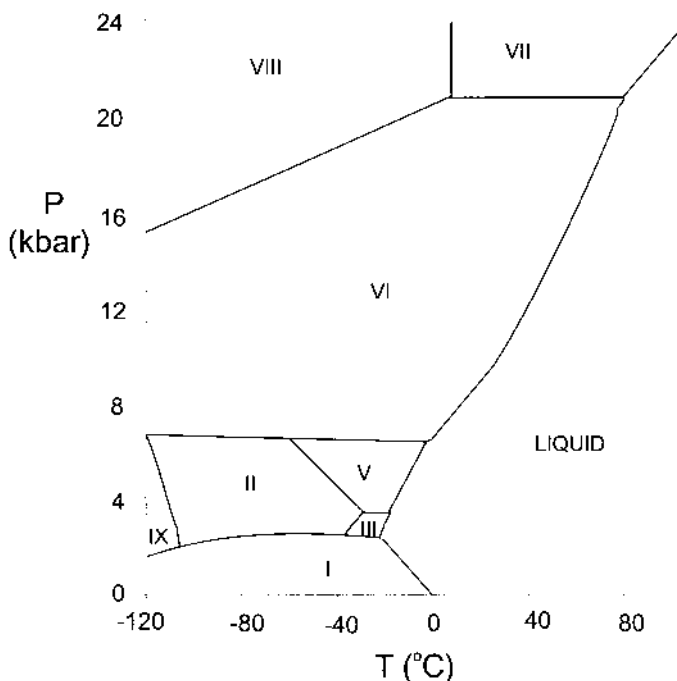


Figure 9 High-pressure phase diagram of water.

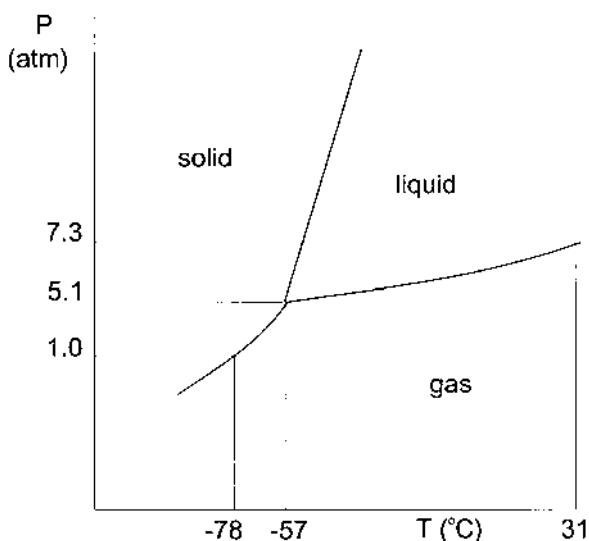


Figure 10 Phase diagram of carbon dioxide (not to scale).

and -57°C , and the solid is denser than the liquid (by far, the more common occurrence), leading to a positive slope of the solid–liquid equilibrium line. The critical point is at 73 atm and 31°C , conditions that are easily accessible with commercial high-pressure pumping equipment. As a result, supercritical carbon dioxide has found extensive use as a solvent in industrial processes. One of these is a method of removing caffeine from coffee that avoids using chlorinated solvents. Like many supercritical fluids, supercritical carbon dioxide is an excellent solvent. After the fluid CO_2 is passed through the coffee, dissolving the caffeine, the external pressure is released, and the carbon dioxide becomes gaseous and releases the caffeine. The carbon dioxide can be reused, by recompressing it, and no solvent residue is left in the coffee, because carbon dioxide is gaseous at ambient conditions.

6.12 Mesomorphic Phases

Mesomorphic phases have properties between those of solids and liquids. For example, rod-shaped or disk-shaped molecules often melt to form *liquid crystals*, which are fluid, but contain some order. One form of liquid crystals formed from rod-shaped molecules, called a *nematic* liquid crystal, is shown in Fig. 11. The molecules in the nematic phase are partially ordered in one dimension, with an orientation angle that can vary from one domain to another in the fluid. The forces

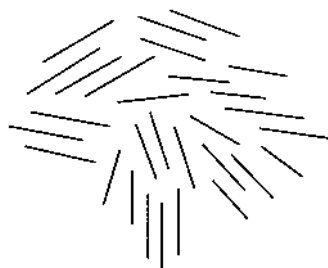


Figure 11 A nematic liquid crystal.

orienting the molecules are quite weak and the heat required to melt this type of liquid crystal is usually quite small. Small electric fields can be used to orient domains in liquid crystals, changing the way they scatter light. This is the basis for many of the displays used in digital watches, calculators, and laptop computers.

Glasses, which are rigid but noncrystalline (*amorphous*), are also mesomorphic. They undergo a *glass transition* at temperature T_g , above which they show fluid or elastomeric behavior. The glass transition occurs over a range of temperatures, rather than at a single, well-defined temperature characteristic of the melting of a crystalline material. Even at temperatures considerably below T_g , glasses are not totally rigid. This can be verified by accurately comparing the thickness of the top and the bottom of a pane of very old window glass. Some flow under the long-time influence of gravity can usually be noted. T_g depends on the heating rate, indicating that the glass transition is a kinetic as well as an equilibrium phenomenon.

Polymeric materials are often composed of crystalline regions imbedded in an amorphous matrix. As shown in Fig. 12, such a material undergoes several

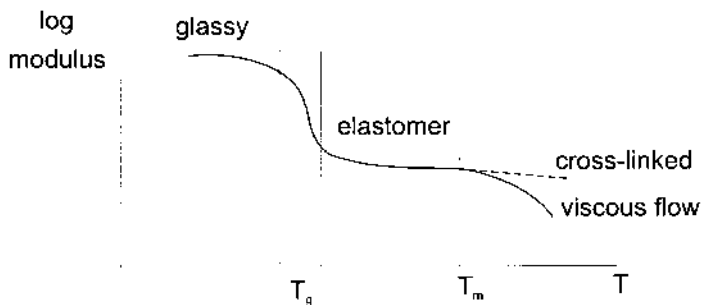


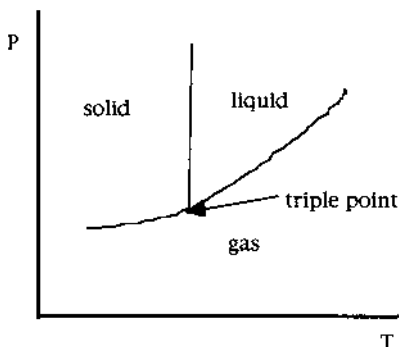
Figure 12 Phase transformations of a polymer.

changes of state as it is heated. At very low temperatures, thermal motion is insufficient to overcome attractions in both the crystalline and amorphous regions. Motions are limited to vibrations and the modulus is very high. The polymer is very brittle in this region and is easily fractured, as indicated by what happens when a rubber band is cooled to liquid-nitrogen temperature. At the glass transition temperature, T_g , the amorphous regions of the polymer become fluid, but the crystalline regions serve as cross-linking junctions, which produce the elastomeric behavior discussed in [Chapter 5](#). Actually, the glass transition occurs over a temperature range (the transition is not first order), as thermal motion becomes sufficient to overcome the disparate attractive interaction in various amorphous regions. Elastomeric behavior persists up to a considerably higher temperature, T_m (the melting temperature). At T_m , the stronger interactions in the crystalline regions become disturbed and (highly viscous) flow of the polymer becomes possible. For polyethylene, T_g is around -125°C and T_m is 140°C . For polymers in which chains are held together by chemical cross-links, viscous flow is not possible and no melting temperature is observed.

Questions

1. Comment on the sign of each of the following: $\Delta_{\text{vap}}H$, $\Delta_{\text{cond}}H$, $\Delta_{\text{fus}}S$, $\Delta_{\text{fus}}V$, and $\Delta_{\text{vap}}G$ (for $T > T_b$).
2. An ice cube is dropped into a glass of room-temperature water. An instant after the last of the ice melts, is the system a single phase?
3. Does Eq. (8) imply that for a single-component system, the chemical potential is the molar internal energy as well as the molar Gibbs free energy?
4. What is the difference between δn_i and dn_i ?
5. On [Fig. 1b](#), draw $\mu(T)$ for a gas and solid at a higher pressure and show how the sublimation temperature is affected by the pressure increase.
6. It is desired to determine the heat of vaporization of a substance. However, the normal boiling point of the substance is inconveniently high for laboratory measurement. How could the heat of vaporization of the substance be determined at a lower temperature?
7. Why do we not choose as the standard state for a real gas the state where $f \rightarrow P \rightarrow 0$. (Hint: What would be the values of the chemical potentials that we would tabulate at the standard state?)
8. At the triple point of water, is the system's volume invariant? Explain your answer.
9. In [Fig. 2](#), why is the separation for the curves at two different pressures relatively independent of temperature for the liquid and solid phases while it approaches zero for the gaseous phase as $T \rightarrow 0$?

10. According to our analysis, does the effect of an inert gas on the vapor pressure of a liquid result from a change in the escaping tendency from the liquid or from the gas, or from both. What is the direction of the change(s) in escaping tendency? Explain your answer.
11. What is wrong with the following phase diagram (drawn for an arbitrary substance)?



12. What would happen if a crystal of Vonnegut's ice IX was thrown into a glass of water. Include discussion of energy flows as well as phase changes.
13. Sketch a diagram analogous to Figs. 1a and 1b at the pressure at which a gas–liquid–solid triple point occurs.
14. Redraw Fig. 2 for water.
15. Redraw Fig. 3 for the boiling of water.
16. Why is solid CO_2 called “dry ice”?
17. The Earth's core is thought to be mainly iron, and seismic data indicate that the inner core is solid and the outer core is liquid. The pressure at the center of the Earth is 3.6×10^{11} Pa, and at this pressure, iron melts at 6350 K. From this information, what can you infer about the solid–liquid equilibrium boundary in the iron high-pressure phase diagram? (Pressure and temperature both increase toward the Earth's center.)

Problems

1. How much heat must be added to 1.0 kg of water at 25°C to convert it into steam at 300°C ? The C_p of liquid may be taken as $1 \text{ cal/gK} = 4.18 \text{ J/gK}$ (this is the definition of the calorie.). The heat of vaporization may be obtained from Table 1 of Chapter 3 and gaseous heat capacity data from Table 1 of Chapter 2.
2. The enthalpy of vaporization of water is 40.66 kJ/mol ; what is the boiling point of water in Denver, Colorado at an elevation of 1.0 mile? (See Chapter 5, Problem 17.)

3. The standard state of a condensed phase is taken at 1.0 bar pressure. Show that the activity of incompressible condensed matter at pressure P is from Eq. (47), $a = \exp[V_m(P - 1)/RT]$. Apply this formula to find the activity of liquid octane, with density 0.7 g/cm³ at 25°C and 100 atm pressure. How much does the chemical potential of liquid octane change between 1 and 100 atm?
4. Show that for a gas that is described by the first two terms in the virial expansion given by Eq. (27) in Chapter 1, the fugacity is given by $f = P \exp(B'P/RT)$. Show that for a van der Waals gas, the fugacity equals $P \exp(bP/RT) \exp(-aP/R^2T^2)$. (See Example 4 in Chapter 1.)
5. Using the results of Problem 4, for NH₃, at what pressure at 250 K is there a 10% difference between pressure and fugacity?
- 6.* What is the vapor pressure of water at 500°C? Use Eq. (52), with $\Delta H_{\text{vap}}^\circ(298) = 40.66 \text{ kJ/mol}$ and average heat capacities $C_p(\text{gas}) = 34 \text{ J K mol}$ and $C_p(\text{liq}) = 75 \text{ J K mol}$. The results of Problem 4 can be used to convert fugacity to pressure.
7. The vapor pressure of water is 634 mm Hg at 95°C and 1074 mm Hg at 110°C. Estimate the standard heat of vaporization of water using the Clapeyron equation and the Clausius–Clapeyron equation.
8. Determine the heat of vaporization of water from its triple point and normal boiling point.
- 9.^M Use graphical equalization of areas with the van der Waals and Redlich–Kwong equations to estimate the vapor pressure of water at 600 K. Compare these with the literature value of 122 atm.
10. Using expression (38) of Chapter 5 for its partition function and $U_0 = 0$, find a formula for the chemical potential of an ideal monatomic gas. Show that $(\partial\mu/\partial P)_T = V_m$.
11. Show that the requirement that second derivatives of μ are discontinuous at a second-order phase transition also requires that C_p be discontinuous at the transition.
12. Give a mathematical statement of the first law appropriate for open systems.
13. Derive the Clausius–Clapeyron equation [Eq. (44)] from Eq. (40) by neglecting the volume of the condensed phase and using the ideal gas law for the vapor.
14. Dry ice has a vapor pressure of 1.0 atm at -72.2°C and 2.0 atm at -69.1°C . Calculate the $\Delta_{\text{sub}}H^\circ$ of CO₂ and the vapor pressure of dry ice at -50°C .
15. The density of liquid CO₂ is greater than that of liquid water. It has been suggested that to ameliorate the greenhouse effect caused by atmospheric CO₂, CO₂ from power plants could be pumped deep enough under the ocean so that liquid CO₂, being heavier than the surrounding water, would sink to the ocean bottom. Using the data in Fig. 10, estimate the depth in the ocean to which CO₂ would have to be pumped so that it is a liquid.

16. From the data in [Appendix B](#), graphite is seen to be the stable form of carbon at 298 K and atmospheric pressure. The densities of graphite and diamond are 2.25 g/cm^3 and 3.52 g/cm^3 , respectively. Calculate the pressure to which graphite must be raised at 298 K in order for a diamond to become the stable form of carbon. Is this a viable method for converting graphite to diamond? Explain your answer.
17. Calculate the vapor pressure of water at 298 K, given that $\Delta G_f(298)$ is -237.129 kJ/mol for liquid water and -228.572 kJ/mol for gaseous water.
18. The normal boiling point of CS_2 is 46.3°C . Use Trouton's rule to estimate the vapor pressure of CS_2 at 25°C .
19. An auto radiator has a vent valve that releases at 3 atm pressure. If the radiator is filled with water in summer, what is the maximum temperature that the water can reach before the valve vents? The $\Delta_{\text{vap}}H^\circ$ of water is 40.6 kJ/mol at the boiling point.

Notes

1. *Ab initio* (from first principles) calculations are difficult to do with reasonable accuracy, due to the difficulty in calculating the energy of liquids.
2. The atmosphere is not completely inert. N_2 and O_2 have some solubility in most solutions. We will see in [Chapter 8](#) that dissolving gases in liquids lowers the vapor pressure of the liquid. Also, in a system open to the atmosphere, complete equilibrium will not be established because material will continually be transported to the ambient environment. In practice, however, a small opening will be sufficient to maintain the pressure of the atmosphere while allowing neglect of the loss of gaseous material by diffusion or convection.