Chapter 17: Phase Transitions in Pure Substances

The standard boiling point of ethanol is 78.0°C and the standard enthalpy of vaporization is 38.56 kJ mol^{-1}. Calculate the vapor pressure at 25.0°C.

The sudden change in properties of a pure substance as it melts, boils, or sublimes is quite striking. Why do the density and entropy of a substance abruptly change at some fixed temperature? Why does the temperature remain constant while two phases are in contact at equilibrium? Why does the magnetic field of a ferromagnet drop to zero at a fixed temperature? Phase transitions have great value in helping to understand the physical structure of matter; phase transitions are a window into intermolecular forces. Gases would not liquefy if there were no intermolecular attractions. Strong intermolecular forces result in high melting points and boiling points. Phase equilibrium also has important practical implications.

Phase transitions are important in biogeochemical cycles. For example, the polar ice sheets are major reservoirs of pure water. Some chemical reactions in the troposphere occur on the surface of ice or on a thin surface layer of liquid water on ice particles.[1] Phase transitions also have important applications in thermal energy storage and energy transfer. Steam is the most commonly used thermal energy transfer medium. Finally, phase transitions have important technological applications in areas such as phase transfer data storage on compact disks.

17.1 The Chemical Potentials of the Phases are Equal at Equilibrium

Phase Transitions Minimize the Chemical Potential: The chemical potential of a pure substance is just the Gibbs energy per mole. The variation of the chemical potential with temperature and pressure for phase i is given by dG = – S dT + V dP in terms of molar quantities:

$$d\mu_i = -S_i\,dT + V_i\,dP \qquad \text{(pure substance)} \qquad 17.1.1$$

where S_i is the molar entropy and V_i is the molar volume for the pure substance in the particular phase. The slope of chemical potential versus temperature at constant pressure for each individual phase is given by the first term in Eq. 17.1.1:

$$\left(\frac{\partial\mu_i}{\partial T}\right)_P = -S_i \qquad \text{(pure substance)} \qquad 17.1.2$$

The molar entropy of a substance is always positive, making the chemical potential decrease with temperature, Figure 17.1.1. Since the molar entropy increases for each subsequent phase, $S_i(s) < S_i(l) << S_i(g)$, the slopes of the lines are steeper in progressing from solid to liquid to gas. The temperature dependence of the chemical potential is greatest for gases.

Follow the chemical potential curve for a solid starting at low temperature. As a solid is heated, the chemical potential decreases. At low temperature, the chemical potential for the liquid phase is higher than the solid, but the chemical potential for the liquid also decreases with temperature. The chemical potential curves for the solid and liquid cross at the melting point, where $\mu(s) = \mu(l)$. Above the melting point, the substance can lower its chemical potential by dropping from the solid curve to the liquid curve. In other words the chemical potential is minimized by melting. As we continue to heat the substance, beyond the boiling point the chemical potential for the vapor phase drops below the liquid phase and the substance minimizes the chemical potential by evaporating.

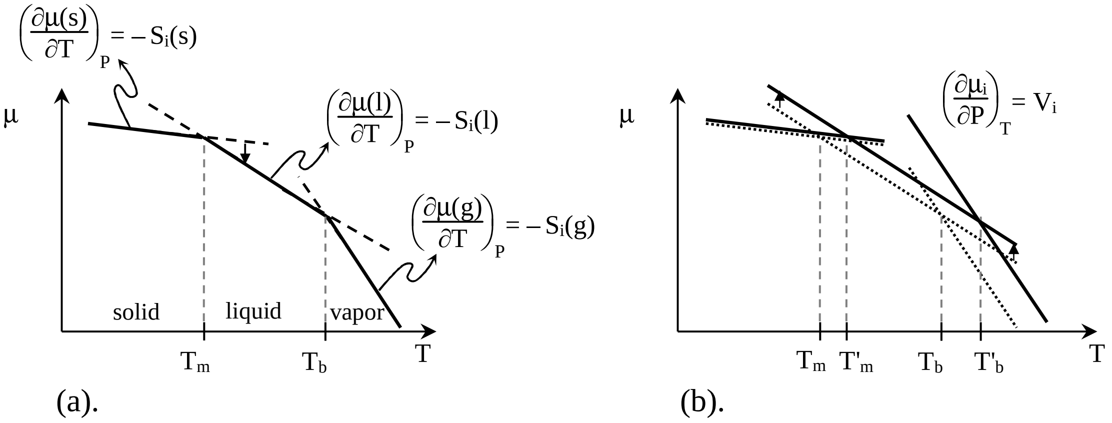


Figure 17.1.1: (a). The slope of the chemical potential versus temperature at constant pressure is the negative of the entropy for each individual phase. (b). An increase in pressure increases the chemical potential of each phase, proportional to the pure molar volume of the phase, resulting in an increase in melting and boiling points, assuming $V_i(s) < V_i(l)$.

As we proved in Eq. 15.2.25, the chemical potentials of the two phases are equal at equilibrium. If the chemical potentials are not equal, a spontaneous process results, increasing one phase at the expense of the other until one of the phases disappears. The temperature remains constant as long as two phases are in contact and at equilibrium. Energy transferred into the system converts one phase into the other instead of raising the temperature. Once one of the phases is exhausted, thermal energy input then increases the temperature of the one-phase system.

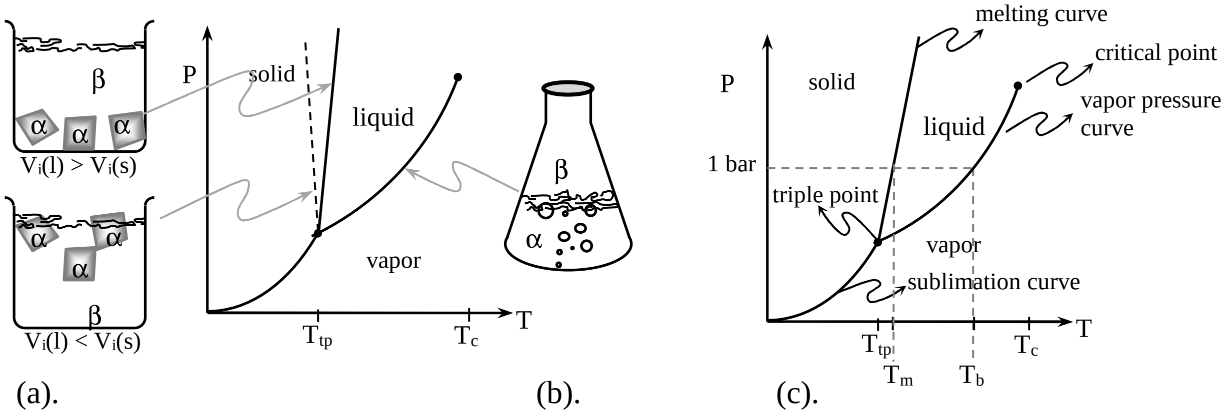
Consider the extensions of the chemical potential curves for the phases above or below the normal transition temperatures. These extensions are shown as dashed lines in Figure 17.1.1a. Can a solid continue along the solid phase chemical potential curve above the melting point? A solid can exist above its melting point, at least for short periods of time. Similarly, if cooled rapidly, a liquid can exist below its melting point. However, if a dust particle lands on the surface of the liquid or the container is bumped, the liquid quickly crystallizes into the solid phase. A solid or a liquid above its normal transition temperature is said to be **super-heated**, and a liquid or a vapor below its normal transition temperature is called **super-cooled**. Super-heated or super-cooled phases are metastable. Metastable phases are kinetically trapped in the higher chemical potential phase. The “bumping” phenomena during distillation is an example of the sudden vaporization of a liquid that is heated above its normal boiling point. Super-cooled liquids are commonly encountered during recrystallizations. Sometimes getting crystals to form from a melt is difficult; scratching the surface of the beaker with a stirring rod or adding a seed crystal initiates the formation of the solid by providing a nucleation site.

Phase transitions occur to minimize the chemical potential of a substance, but what does this tell us about the effects of intermolecular forces? Consider the balance of the enthalpy and entropy for a phase transition at a particular temperature: $\Delta_{tr}G = \Delta_{tr}H - T\,\Delta_{tr}S$. The enthalpy change for a phase transition, $\Delta_{tr}H$, is endothermic because of the energy necessary to overcome the intermolecular attractions. The forces include Van der Waals, electrostatic, and hydrogen-bonding interactions. Melting, sublimation, or vaporization weaken these attractions. At low temperature the enthalpy term dominates. The phase with the strongest intermolecular forces is the stable phase at low temperature. Intermolecular forces also have an effect on the entropy change for a phase transition, but the biggest contribution to the entropy change is the increased energy dispersal from forming a more mobile phase. At high temperature, the entropy term dominates and the higher entropy, more mobile phase, is the stable phase.

How does pressure effect phase transitions? The pressure dependence of the chemical potential for a phase is given by the molar volume of the phase, Eq. 16.6.16:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i \tag{17.1.3}$$

The chemical potential of a phase always increases with increasing pressure. For example, for the liquid phase in Figure 17.1.1b, the chemical potential curve at a higher pressure corresponds to moving each point on the liquid curve upward by approximately the same amount. The change is biggest for the gas phase, which has the highest molar volume. For most substances, $V_i(s) < V_i(l) << V_i(g)$ and the intersection of both the solid-liquid and the liquid-vapor chemical potential curves are at higher temperature for an increase in pressure. Therefore, the melting point for most substances and the boiling point increase with increasing pressure. A clearer way to diagram the pressure and temperature dependence for phase equilibria is to draw a phase diagram in the P-T plane, Figure 17.1.2.



(a). (b). (c).

Figure 17.1.2: Phase diagram for first order transitions. The α phase is the low temperature phase and the β phase is the high temperature phase: (a). melting or fusion, solid → liquid, (b). boiling, liquid → vapor. (c). The solid, liquid, and vapor regions of the phase diagram are separated by coexistence curves that fix the pressure at a given temperature if the phases are in contact at equilibrium. T_{tr} is the triple point, T_m is the standard melting point, T_b is the standard boiling point, and T_c is the critical point.

The solid, liquid, and vapor regions of the phase diagram are separated by coexistence curves that describe the P-T relationships when the phases are in contact at equilibrium. The properties of the system are constrained to lie along the coexistence curves if the corresponding phases are present and at equilibrium. The coexistence curve for the solid-liquid transition, the melting curve, plots the change in melting point with applied pressure. The coexistence curve for the liquid-vapor transition, the vapor pressure curve, plots the change in vapor pressure of the liquid with temperature. The coexistence curve for the solid-vapor transition, the sublimation curve, plots the sublimation pressure as a function of the temperature. The vapor pressure curve ends in the gas-liquid critical point. Compare Figure 17.1.2 with Figure 7.5.2. The vapor pressure curve in the P-T diagram corresponds to the "side view" of the two-phase region in the P-V diagram.

The molar volume of most all liquids is greater than the solid, and the corresponding melting curve has a positive slope; for most substances the melting point increases with pressure. Correspondingly, the density of the solid is greater than the liquid and the solid sinks in the melt. However, for water, bismuth, and antimony the molar volume of the liquid is less than the solid and the melting curve has a negative slope. The melting point of water, bismuth, and antimony decreases with increasing pressure, as indicated by the dashed curve in Figure 17.1.2a. Correspondingly, the liquid is denser than the solid phase and the solid floats in the melt.

The three coexistence curves meet at one point, the triple point. At the triple point the chemical potentials of all three phases are equal. The triple point occurs at one specific, fixed pressure and temperature. The phase diagram qualitatively describes the P-T relationships. We now need to derive the equations for the coexistence curves.

The Chemical Potentials of the Two Phases are Equal Along the Coexistence Curve: By convention, we write the phase transition in the direction from the low temperature phase to the high temperature phase: $\alpha \rightarrow \beta$. For example, for melting we assume the direction is $s \rightarrow l$ and for vaporization $l \rightarrow g$. At the equilibrium phase transition temperature for a given pressure P, the chemical potential of the two phases is equal, Eq. 15.2.25:

$$\mu_A(\text{phase } \alpha, P, T) = \mu_A(\text{phase } \beta, P, T) \qquad \text{(equilibrium)} \quad 17.1.4$$

This equality fixes the phase transition temperature for a given pressure. Consider the vapor pressure curve as an example. The system starts with the liquid and vapor at equilibrium at temperature T and pressure P. If the temperature is changed by an amount dT to the new temperature $T' = T + dT$, the change in pressure necessary to keep the two phases at equilibrium is dP with the corresponding new pressure $P' = P + dP$. The change in chemical potential for the two phases must be equal for the chemical potentials at the new conditions to remain equal:

$$d\mu_i(\alpha, P', T') = d\mu_i(\beta, P', T') \qquad \text{(equilibrium)} \quad 17.1.5$$

Using Eq. 17.1.1 for each phase gives the changes:

$$-S_i(\alpha)\, dT + V_i(\alpha)\, dP = -S_i(\beta)\, dT + V_i(\beta)\, dP \qquad \text{(equilibrium)} \quad 17.1.6$$

Solving for the change in pressure necessary to remain at equilibrium for a change in temperature gives:

$$\frac{dP}{dT} = \frac{S_i(\beta) - S_i(\alpha)}{V_i(\beta) - V_i(\alpha)} = \frac{\Delta_{tr}S_i}{\Delta_{tr}V_i} \qquad \text{(equilibrium)} \quad 17.1.7$$

using the definitions: $\Delta_{tr}S_i \equiv S_i(\beta) - S_i(\alpha)$ and $\Delta_{tr}V_i \equiv V_i(\beta) - V_i(\alpha)$. For the phase transition at the equilibrium temperature, the entropy is given by Eq. 13.3.2:

$$\Delta_{tr}S_i = \frac{\Delta_{tr}H_i}{T} \qquad \text{(equilibrium)} \ (13.3.2)$$

Substituting this last equation for the entropy change into Eq. 17.1.7 gives:

$$\frac{dP}{dT} = \frac{\Delta_{tr}H_i}{T\,\Delta_{tr}V_i} \qquad \text{(equilibrium)} \quad 17.1.8$$

This expression is called the **Clapeyron** equation, which holds for any equilibrium phase transition that has non-zero $\Delta_{tr}H_i$ and $\Delta_{tr}V_i$. The pressure derivative is not a partial derivative because the requirement of equal chemical potentials constrains the system to lie on the coexistence curve. We can make useful approximations to the Clapeyron equation to determine the equations of the three coexistence curves.

The Change in Vapor Pressure with Temperature Depends on the Enthalpy Change: The coexistence curve for the liquid-vapor transition is the vapor pressure curve. For liquid-vapor equilibrium, the molar volume of the vapor is much greater than the liquid, $V_i(\text{vapor}) >> V_i(\text{liquid})$. The change in molar volume for the transition is then to a good approximation given by just the volume of the vapor, $\Delta_{tr}V_i = V_i(\text{vapor})$. If we treat the vapor as an ideal gas, the change in molar volume for the transition is:

$$\Delta_{tr}V_i \approx V_i(\text{vapor}) = \frac{RT}{P} \qquad \text{(equilibrium, ideal gas)} \quad 17.1.9°$$

Substituting this last approximation into the Clapeyron equation gives:

$$\frac{dP}{dT} = \frac{\Delta_{tr}H_i\,P}{R\,T^2} \qquad \text{(equilibrium, ideal gas)} \quad 17.1.10°$$

We need to integrate this derivative to find the vapor pressure curve. Separating variables gives:

$$\frac{dP}{P} = \frac{\Delta_{tr}H_i}{R\,T^2}\,dT \qquad \text{(equilibrium, ideal gas)} \quad 17.1.11°$$

This expression is called the **Clausius-Clapeyron** equation. For predicting the vapor pressure of a liquid as a function of temperature, $\Delta_{tr}H_i = \Delta_{vap}H_i$ and T is the temperature of the vapor and liquid at equilibrium. The approximations used in deriving the Clausius-Clapeyron equation also hold for sublimation, where $\Delta_{tr}H_i = \Delta_{sub}H_i$. Integrating Eq. 17.1.11° between the equilibrium vapor pressures P_1 and P_2 at the corresponding temperatures T_1 and T_2 and assuming the transition enthalpy is constant over the temperature range gives:

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta_{tr}H_i}{R\,T^2}\,dT \qquad \text{(equilibrium, ideal gas)} \quad 17.1.12°$$

$$\ln\!\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{(equilibrium, ideal gas, cst. } \Delta_{tr}H_i\text{)} \quad 17.1.13°$$

Exponentiating both sides of the last equation and solving for P_2 in terms of P_1 gives:

$$P_2 = P_1\, e^{-\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad \text{(equilibrium, ideal gas, cst. } \Delta_{tr}H_i\text{)} \quad 17.1.14°$$

These last two results are examples of the exponential temperature dependence discussed in *General Pattern* ***℘4***. The integrals can also be done as indefinite integrals:

$$\ln P + c = -\frac{\Delta_{tr}H_i}{RT} + c' \qquad \text{(equilibrium, ideal gas, cst. } \Delta_{tr}H_i\text{)} \quad 17.1.15°$$

The integration constants can be combined and renamed as ln C = (c' – c) to give:

$$\ln P = -\frac{\Delta_{tr}H_i}{RT} + \ln C \qquad \text{(equilibrium, ideal gas, cst. } \Delta_{tr}H_i\text{)} \quad 17.1.16°$$

This relationship shows that a plot of ln P versus 1/T gives a straight line with slope = – $\Delta_{tr}Hi_m/R$. Exponentiating both sides of this last equation again shows the general form of the exponential temperature dependence in *General Pattern* ***℘4***:

$$P = C\, e^{-\frac{\Delta_{tr}H_i}{RT}} \qquad \text{(equilibrium, ideal gas, cst. } \Delta_{tr}H_i\text{)} \quad 17.1.17°$$

The plot of the vapor pressure of a liquid or the sublimation pressure of a solid as a function of the temperature follows the general exponential shape in Figure 3.5.1. The form of Eq. 17.1.13° is used if only two data points are known. The plot of ln P versus 1/T or a non-linear plot fit directly to Eq. 17.1.17° is used if multiple experimental values are available. These integrated forms of the Clausius-Clapeyron equation can be used to predict the vapor pressure of a substance as a function of temperature, predict the boiling point of a substance as a function of applied pressure, or determine the enthalpy of vaporization or sublimation of a substance.

Example 17.1.1:

The standard boiling point of ethanol is 78.0°C and the standard enthalpy of vaporization is 38.56 kJ mol^{-1}. Calculate the vapor pressure at 25.0°C.

Answer: The standard boiling point corresponds to the temperature for which the vapor pressure equals 1 bar. Given $\Delta_{vap}H° = 38.56 \text{ kJ mol}^{-1} = 3.856\text{x}10^4 \text{ J mol}^{-1}$ and Eq. 17.1.13°:

$$\ln\left(\frac{P_2}{1.00 \text{ bar}}\right) = -\frac{3.856 \text{ x}10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{298.15 \text{ K}} - \frac{1}{351.15 \text{ K}}\right) = -2.3477$$

$$P_2 = 0.09559 \text{ bar} = 0.09434 \text{ atm} = 71.7 \text{ torr}$$

Example 17.1.2:

Organic chemists often use reduced pressure distillations to limit thermal degradation during the purification of a substance. The normal boiling point of cyclohexane is 80.7°C. Use Trouton's rule to estimate the standard enthalpy of vaporization. Calculate the boiling point of cyclohexane if the applied pressure is 200. torr.

Answer: The normal boiling point corresponds to the temperature for which the vapor pressure equals 1 atm. Don't forget to convert to absolute temperatures: 80.7°C = 353.85 K. From

Sec. 13.3, $\Delta_{vap}S° = \Delta_{vap}H°/T_b \approx 10.5\ R$ from Trouton's rule for unassociated liquids. Solving for $\Delta_{vap}H°$:

$$\Delta_{vap}H° = T_b\,\Delta_{vap}S° \approx 353.85\ \text{K}(87.3\ \text{J K}^{-1}\ \text{mol}^{-1}) \approx 30.9\ \text{kJ mol}^{-1}$$

Using Eq. 17.1.13°:

$$\ln\left(\frac{200.\ \text{torr}}{760.\ \text{torr}}\right) = -\frac{3.09\text{x}10^4\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{T_2} - \frac{1}{353.85\ \text{K}}\right) = -1.335$$

$$T_2 = 314.\ \text{K} = 42.°\text{C}$$

Notice that you can use any pressure units, since the pressure enters the calculation as a ratio. You can check that there are three significant figures in 314. K, assuming two significant figures in $\Delta_{vap}H°$, by repeating the calculation with $\Delta_{vap}H° \approx 32.\ \text{kJ mol}^{-1}$ and noting the change. The literature value for the enthalpy of vaporization of cyclohexane is 29.97 kJ mol^{-1}.

Example 17.1.3:
The vapor pressure of water at 20.00°C is 23.38 mbar. The standard boiling point of water is 99.61°C. Calculate the enthalpy of vaporization of water, assuming a constant enthalpy over the temperature range.

Answer: The standard boiling point corresponds to the temperature for which the vapor pressure equals 1 bar. Don't forget to convert to absolute temperatures: 20.00°C = 293.15 K and 99.61°C = 372.76 K. Using Eq. 17.1.13°:

$$\ln\left(\frac{23.38\ \text{mbar}}{1000\ \text{mbar}}\right) = -\frac{\Delta_{vap}H°}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{293.15\ \text{K}} - \frac{1}{372.76\ \text{K}}\right)$$

$$-3.7559 = -\frac{\Delta_{vap}H°}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\,(7.2853\text{x}10^{-4}\ \text{K}^{-1})$$

$$\Delta_{vap}H° = 42.86\ \text{kJ mol}^{-1}$$

This value differs from the literature value, $\Delta_{vap}H° = 42.00\ \text{kJ mol}^{-1}$, because we didn't take into account the non-ideality of the vapor and the temperature dependence of the enthalpy of vaporization. See Problems 10 and 13 for the more exact expressions.

℘9

General Pattern 9: Exponential Temperature Dependence $d\ln P/dT = \Delta_r H/RT^2$: Eq. 17.1.10° is a commonly occurring form of exponential temperature dependence. An alternate way of writing the Clausius-Clapeyron equation in differential form is based on the identity:

$$\frac{dP}{P} = d\ln P \qquad \text{since} \quad \int \frac{dP}{P} = \int d\ln P = \ln P + c \qquad 17.1.18$$

Substitution of this identity into Eq. 17.1.11° results in:

$$d \ln P = \frac{\Delta_{tr}H_i}{RT^2}\,dT \qquad \text{or} \qquad \frac{d \ln P}{dT} = \frac{\Delta_{tr}H_i}{RT^2} \qquad \text{(equilibrium, ideal gas)} \qquad 17.1.19^\circ$$

This last equation is in the same form as the Arrhenius expression for the temperature dependence of the rate constant, Sec. 4.4:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \qquad \text{(cst. V)} \qquad (4.4.25)$$

We will show in Chap. 20 that the temperature dependence of the equilibrium constant also has the same form:

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \qquad \text{(equilibrium)} \qquad (20.1.26)$$

These expressions integrate to:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\left(\frac{k_{T2}}{k_{T1}}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\frac{K_{p,T_2}}{K_{p,T_1}} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\text{(cst. } \Delta_{tr}H_i,\ E_a,\ \Delta_r H^\circ\text{)} \qquad 17.1.20$$

This last expression is discussed in many General Chemistry texts. In addition we can note that:

$$\frac{dT}{T^2} = -\,d\left(\frac{1}{T}\right) \qquad \text{since} \qquad \int \frac{dT}{T^2} = -\int d\left(\frac{1}{T}\right) = -\frac{1}{T} + c \qquad 17.1.21$$

Substitution of this identity into Eqs. 17.1.19°, 4.4.25, and 20.1.26 gives:

$$d \ln P = -\frac{\Delta_{tr}H_i}{R}\,d\left(\frac{1}{T}\right) \qquad d \ln k = -\frac{E_a}{R}\,d\left(\frac{1}{T}\right) \qquad d \ln K_p = -\frac{\Delta_r H^\circ}{R}\,d\left(\frac{1}{T}\right) \qquad 17.1.22$$

Eqs. 17.1.13°, 17.1.16°, 17.1.20, and 17.1.22 show that a plot of ln P, ln k, or ln K_p versus 1/T gives a straight line with slope $-\,\Delta_{tr}H_i/R$, $-E_a/R$, and $-\Delta_r H^\circ/R$, respectively. This general type of temperature dependence leads to *General Pattern* ***℘4***, which shows how to manipulate the general integrated form.

℘9

The Melting Point can Increase or Decrease with Pressure: The coexistence curve for the solid-liquid transition is the melting curve. The melting curve determines the change in melting point with applied pressure. For solid-liquid equilibrium, the change in molar volume for melting is a weak function of pressure. So $\Delta_{fus}V_m$ can be taken as a constant over a moderate range of pressures. The change in melting point is small, even for very large applied pressures. Therefore, to an excellent approximation, the transition enthalpy is also constant, except for extreme geological circumstances. Using these two approximations, the right-hand side of the Clapeyron equation, Eq. 17.1.8, for melting transitions for small changes in melting point is a constant. The infinitesimals in dP and dT can then be immediately integrated to give:

$$\frac{\Delta P}{\Delta T} = \frac{\Delta_{fus}H_i}{T_m\,\Delta_{fus}V_i} \qquad \text{(equilibrium, moderate } \Delta P\text{)} \qquad 17.1.23$$

with T_m the melting point of the solid. Solving for the change in melting point gives:

$$\Delta T = \frac{T_m\, \Delta_{fus}V_i}{\Delta_{fus}H_i}\, \Delta P \qquad \text{(equilibrium, moderate } \Delta P) \qquad 17.1.24$$

Now we see why the melting curve in Figure 17.1.1 has a positive slope for most substances; for most substances the liquid has a higher molar volume than the solid, giving $\Delta_{fus}V_i = V_i(l) - V_i(s) > 0$. The phase transition is endothermic, so all the constant terms on the right of Eqs. 17.1.8 and 17.1.24 are positive. However, for water, bismuth, and antimony, the liquid has a smaller molar volume than the solid, $\Delta_{fus}V_i < 0$ and the melting curve then has a negative slope. The unusual change in molar volume for water is a reflection of the extensive hydrogen bonding network in ice that increases the distance between the molecules. When ice melts, this hydrogen bonding network partially collapses, decreasing the molar volume.

The decrease of the melting point for ice with pressure makes ice skating possible. The skate blade has a very small contact area with the ice, creating a large applied pressure. The increase in pressure lowers the melting point, which melts some of the ice to provide a lubricating surface.

Example 17.1.4:
Calculate the contact area that is necessary to lower the melting point of ice initially at 1.000 bar by 2.00°C for a 70.0 kg skater. The densities of water and ice at 0.00ºC are 1.000 g cm^{-3} and 0.9168 g cm^{-3}, respectively. The enthalpy of fusion is 6.008 kJ mol^{-1} at 273.15 K.

Answer: The change in molar volume is

$$\Delta_{fus}V_i = V_i(l) - V_i(s) = 18.02 \text{ g mol}^{-1} (1/1.000 \text{ g cm}^{-3} - 1/0.9168 \text{ g cm}^{-3})$$
$$= -0.7278 \text{ cm}^3 \text{ mol}^{-1} = -7.278\text{x}10^{-7} \text{ m}^3 \text{ mol}^{-1}$$

Using Eq. 17.1.24:

$$\Delta T = \frac{T_m\, \Delta_{fus}V_i}{\Delta_{fus}H_i}\, \Delta P = \frac{273.15 \text{ K} (-7.278\text{x}10^{-7} \text{ m}^3 \text{ mol}^{-1})}{6.008\text{x}10^3 \text{ J mol}^{-1}}\, \Delta P$$

$$\Delta T = -3.309\text{x}10^{-8} \text{ K Pa}^{-1}\, \Delta P = -2.00 \text{ K}$$

$$\Delta P = 604.4\text{x}10^5 \text{ Pa}$$

The applied pressure is given by the force per unit area:

$$\Delta P = f/A = mg/A = 70.0 \text{ kg}(9.807 \text{ m s}^{-2})/A = 604.4\text{x}10^5 \text{ Pa}$$
$$A = 1.136\text{x}10^{-5} \text{ m}^2 = 1.136\text{x}10^{-5} \text{ m}^2 (1000 \text{ cm}/1 \text{ m})^2 = 11.36 \text{ mm}^2$$

which is why skate blades have a gentle curve from front to back and are hollow ground (“⊔”).

The decrease in molar volume upon melting of ice certainly plays an important role in the distribution of aquatic life in temperate regions. If ice was denser than liquid water, lakes would freeze from the bottom up, which would force any aquatic organisms to the surface and subsequent exposure to harsh winter temperatures and desiccation.

The Vapor Pressure of a Liquid Increases with Increasing Total Applied Pressure: The Clausius-Clapeyron equation applies to a liquid under its own pure vapor pressure. Is the vapor pressure of a substance the same when the vapor is in the presence of other gases? In particular, is the vapor pressure the same when the system is open to the atmosphere? Consider the vapor pressure of a substance, P_β, with a total applied pressure of P. Assume that the other components of the gas phase (e.g., nitrogen and oxygen) do not dissolve in the liquid. If the mole fraction of the substance in the vapor is y_β, then the partial vapor pressure is given by Dalton's Law of partial pressures, $P_\beta = y_\beta P$. As the applied pressure is increased, y_β and P_β both increase. With a change in applied pressure from P to P', the change in chemical potential of the vapor and the liquid must be equal for the system to remain at equilibrium, Eq. 17.1.5:[2]

$$d\mu_i(\alpha,P',T') = d\mu_i(\beta,P',T') \qquad \text{(equilibrium, cst. T)} \qquad 17.1.25$$

The chemical potential of the liquid is changed by the change in total pressure, dP. At constant temperature, from Eq. 17.1.6:

$$V_i(\alpha)\, dP = d\mu_i(\beta,P',T') \qquad \text{(equilibrium, cst. T)} \qquad 17.1.26$$

where $V_i(\alpha)$ is the molar volume of the liquid. The chemical potential of the ideal vapor is dependent on the partial vapor pressure above the liquid, Eq. 16.6.20°:

$$\mu_i\,(g) = \mu_i°(g) + RT \ln P_\beta/P° \qquad \text{(ideal vapor)} \qquad 17.1.27°$$

The change in chemical potential is given as:

$$d\mu_i\,(g) = RT\, d \ln P_\beta \qquad \text{(ideal vapor)} \qquad 17.1.28°$$

Substitution of this last equation into Eq. 17.1.26 gives the dependence of the partial vapor pressure on applied pressure:

$$RT\, d \ln P_\beta = V_i(\alpha)\, dP \qquad \text{(equilibrium, ideal vapor, cst. T)} \qquad 17.1.29°$$

Integration of this last equation from the initial vapor pressure $P_{\beta,1}$ and applied pressure P_1 to the final vapor pressure $P_{\beta,2}$ and applied pressure P_2, assuming that the molar volume of the liquid is constant, gives:

$$\ln \frac{P_{\beta,2}}{P_{\beta,1}} = \frac{V_i(\alpha)}{RT}\,(P_2 - P_1) \qquad \text{(equilibrium, ideal vapor, cst. T)} \qquad 17.1.30°$$

As the applied pressure increases, the vapor pressure increases. In effect, increasing applied pressure "squeezes" molecules into the vapor phase. However, the effect is not large. The molar volume of liquid water at 25°C is 18.0 $cm^3\ mol^{-1}$ or $1.80x10^{-5}\ m^3\ mol^{-1}$. The vapor pressure of water at 25°C is 3.168 kPa, or 23.76 torr, Table 2.1.1. For water under its own pure vapor pressure, in Eq. 17.1.31° the initial pressures are $P_1 = P_{\beta,1} = 3.168x10^3$ Pa. For water open to the atmosphere at $P_2 = 1\ bar = 1.00x10^5$ Pa, the saturated vapor pressure of water increases to 3.170 kPa, or 23.78 torr. The pure vapor pressure of a liquid in a closed container is essentially identical to the saturated partial vapor pressure at atmospheric pressure in air. Significant changes in vapor pressure occur only at high applied pressures.

17.2 Second Order Transitions Have a Discontinuity in the Heat Capacity with Temperature

The phase transitions that we have been discussing are called **first-order phase transitions** because they have a finite transition enthalpy and change in molar volume. The Clapeyron equation holds for all first-order phase transitions. However, many types of phase transitions occur without a transition enthalpy. How do we characterize these "**higher-order**" phase transitions?

Consider a first-order phase transition. The presence of two phases is often discovered by observing a reflection from the interface between the two phases. The reflection occurs because the index of refraction of light in the two phases is different. When light passes from one medium to another with a different index of refraction, some of the light is reflected. The two phases have a different index of refraction because of the difference in density. The difference in density corresponds to a difference in molar volume, $d = \mathfrak{M}/V_m$. The change in molar volume between the phases corresponds to a discontinuity, or a sudden change, in the properties of the two phases. In other words, some property of the substance must have a discontinuous change for a phase transition to occur.

First-Order Phase Transitions Have a Change in Enthalpy and Entropy: The phase transition temperature corresponds to a discontinuous change in the slope of the chemical potential curve, Figure 17.1.1. The slopes for the two phases at a transition, from Eq. 17.1.2, are:

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -S_i(\alpha) \qquad \text{and} \qquad \left(\frac{\partial \mu_\beta}{\partial T}\right)_P = -S_i(\beta) \qquad 17.2.1$$

For the equilibrium phase transition, then, the difference in slope of the chemical potential curves at the equilibrium temperature is given by:

$$\left(\frac{\partial \Delta_{tr}\mu}{\partial T}\right)_P = \left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P \qquad 17.2.2$$

Substitution of Eqs. 17.2.1 into Eq. 17.2.2 gives the change in entropy for the phase transition as:

$$\Delta_{tr}S_i = -\left(\frac{\partial \Delta_{tr}\mu}{\partial T}\right)_P \qquad \text{(equilibrium)} \quad 17.2.3$$

From the entropy change for a phase transition, Eq. 13.3.2, the corresponding change in enthalpy for the transition is given by:

$$\Delta_{tr}H_i = T_{tr}\,\Delta_{tr}S_i \qquad \text{(equilibrium)} \quad 17.2.4$$

The enthalpy change for the phase transition is also called the **latent heat**. The change in molar volume for the transition is similarly related to the change in slope of the chemical potential with respect to pressure:

$$\Delta_{tr}V_i = \left(\frac{\partial \Delta_{tr}\mu}{\partial P}\right)_T = \left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T \qquad \text{(equilibrium)} \quad 17.2.5$$

The change in molar volume produces a discontinuous change in the density.

The Ehrenfest Criteria: Some phase transitions occur without a discontinuous change in enthalpy or molar volume. Transitions in this category are called **higher-order** or **second-order** transitions, depending on the details of the process. Examples include the gas-liquid critical point and super-conducting, ferroelectric, and ferromagnetic transitions. What property of the substance changes discontinuously for these transitions? The temperature dependence of the chemical potential for a first-order transition and a second-order transition are shown schematically in Figure 17.2.1. The entropy versus temperature curve is given by Eq. 17.2.1 as the negative of the derivative of the chemical potential versus temperature. The result for a first-order transition is a sudden increase in entropy for the phase transition. For a second-order transition, the chemical potential changes smoothly with temperature, with the result that the entropy curve shows a sudden change in slope at the transition temperature, but not a discontinuity.

The heat capacity is also related to a temperature derivative of the entropy and chemical potential. Using Eq. 12.2.32 and solving for the heat capacity gives:

$$dS = \frac{C_p}{T}\,dT \qquad C_{p,i} = T\left(\frac{\partial S}{\partial T}\right)_P = -\,T\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P \qquad \text{(cst. P)} \qquad 17.2.6$$

The last equality results from substitution of Eq. 17.1.2 for the entropy. Consider a first-order transition, Figure 17.2.1. The slope of the entropy versus temperature curve is roughly constant before and after the transition giving $(\partial S/\partial T)_P$ as a relatively constant value and a correspondingly slowly varying heat capacity before and after the transition. Just at the transition, the slope is infinite giving rise to an infinite heat capacity at the transition temperature. An infinite heat capacity seems surprising at first. However, for a phase transition, heat transfer into the system occurs without a change in temperature, so $C_P = đq_P/dT \rightarrow \infty$. For a second-order phase transition, the slope of the entropy versus temperature curve increases as the transition is approached, which in turn results in an increasing heat capacity with temperature. At the transition temperature, the entropy versus temperature curve has a sudden change in slope, resulting in a discontinuous heat capacity. Summarizing then, to detect a phase transition, some property of the substance must exhibit a discontinuity with temperature. For a first-order transition, the first derivative of the chemical potential curve is discontinuous, leading to a transition entropy and enthalpy. For a second-order transition, the second derivative of the chemical potential with temperature is discontinuous, leading to a discontinuity in the heat capacity. Since the second derivative is discontinuous, the resulting transition is called a second-order transition. These expectations for the appearance of discontinuities are called the **Ehrenfest criteria**.

The Ehrenfest criteria are idealized requirements that are probably only met exactly by superconducting transitions in metallic systems. For most higher-order transitions, the heat capacity curve appears as a **lambda-transition**, as shown schematically in Figure 17.2.1. This type of phase transition gets its name because of the similarity of the shape of the heat capacity curve with the Greek letter lambda, λ. The distinguishing characteristic is the strong temperature dependence of the heat capacity as the substance approaches the transition. The heat capacity may approach a finite limiting value at the transition temperature or diverge to infinity. Experimental determination of the type of divergence is difficult. The phase transition temperature in second-order or lambda-type transitions is called the **critical temperature**, and phase transitions with second-order or lambda-type transitions are called **critical phenomena**.

Examples of lambda-transitions include the gas-liquid critical point, smectic liquid crystals (LCD displays), superfluid helium, binary mixture solubility (e.g., nitroethane, 3-methylpentane), ferromagnets (permanent magnets), ferroelectrics (microphone and acoustic guitar transducers), and other order-disorder transitions (thermochromic substances, which are used in color changing drinking straws). Lamda-transitions result from long-range cooperativity near the critical temperature.

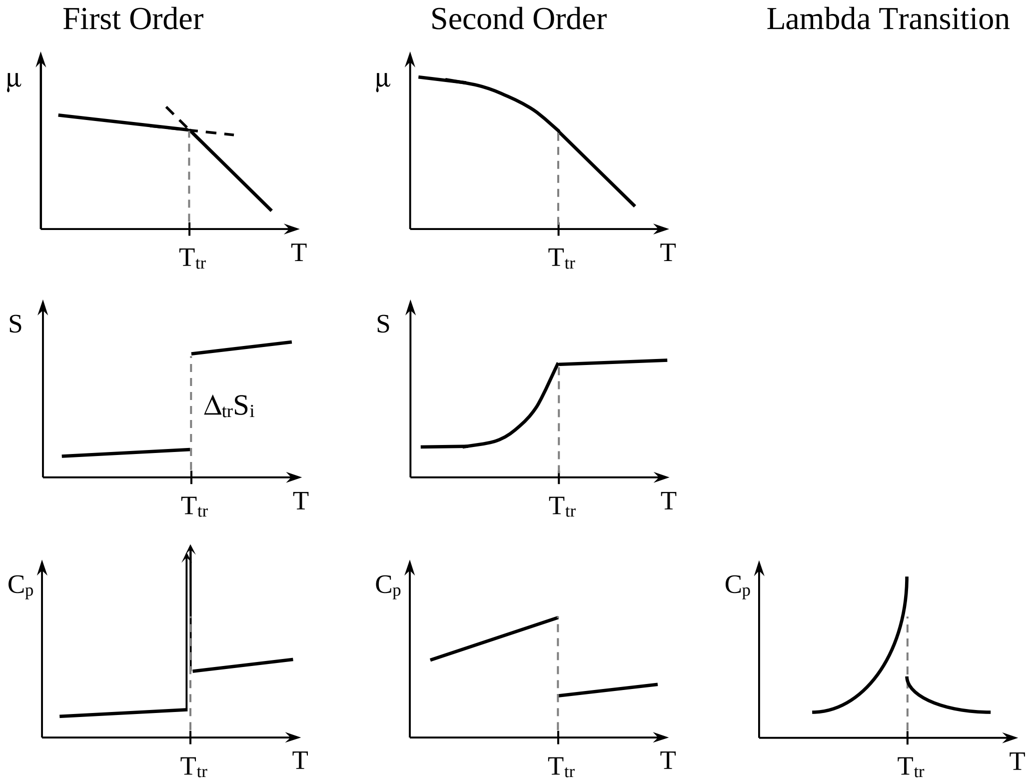


Figure 17.2.1: First-order transitions show a discontinuity in the first derivative of the chemical potential with respect to temperature or pressure. Second-order transitions show a discontinuity in the second derivative of the chemical potential with respect to temperature or pressure, but the heat capacity varies gradually near the transition temperature. Lambda transitions show a divergent heat capacity near the transition temperature (which may or may not go to infinity).

Second-Order Transitions Show Pre-Transition Effects: First-order phase transitions are completely **cooperative**. The molecules cooperate with each other in gaining new motional freedom; when one molecule gains motional energy then other nearby molecules find it easier to add motional energy. The motions of the molecules are correlated throughout the phase at the phase transition temperature. In a first-order phase transition all the molecules undergo the phase transition together, subject only to the availability of thermal energy. A pure first-order transition has an infinitely sharp transition. In second-order phase transitions, the formation of cooperative, correlated motions has a limited range. In approaching the transition temperature from below, the molecules begin to reorganize and to move in concert with each other. As the temperature approaches the critical temperature, the distance range of this cooperation increases. This distance range is called the **correlation length**. Near the phase transition temperature, islands of molecules in the more mobile phase intermix with the less mobile phase. These islands of disorder are called **domains**. The domains anticipate the transition or “start the transition” early, which broadens the transition by **pre-transition effects**. The number of molecules on average in these disordered domains is called the **cooperative unit**, C.U. The larger the cooperative unit and correlation length, the narrower the phase transition temperature range. In the limit of infinite correlation length, the transition becomes first order.

The gas-liquid critical point is a typical example of a cooperative phase transition. The approach to the critical point and the corresponding increase in correlation length can be measured by laser light scattering, as well as by increases in the heat capacity. The formation of correlated domains near the critical temperature causes local changes in the index of refraction. Light scattering results when the correlation length approaches the wavelength of the light. The phase appears cloudy as the critical temperature is approached.

The Nematic to Isotropic Phase Transition in Liquid Crystals is Mixed First and Second Order: **Liquid crystalline** phases are liquid-like phases that exist between the normal isotropic-liquid phase and the normal crystalline solid phase. Liquid crystalline phases are liquid-like because they can be poured like a liquid, but they also have long-range correlated motions of the molecules. Liquid crystals are formed from long rod-like molecules. In liquid crystalline phases, the molecules tend to align along their long axes. The same effect is seen if you put pencils in a box in random orientations, and then shake the box. Several types of liquid crystalline phases exist, depending on the degrees of freedom that are limited, Figure 17.5.1. In the normal liquid phase, the molecular orientations and diffusion rates are isotropic (independent of direction). In the **nematic** phase the molecules tend to orient along their long axis and diffusion rates differ in the direction parallel and perpendicular to the long axes of the molecules. In the **smectic-A** phase the molecules align in sheets and diffusion within the sheets is much faster than between the sheets. In the **smectic-C** phase, the molecules have a net tilt within the sheets. The liquid crystalline phases show significant light scattering, caused by long-range correlation of the molecular motions.

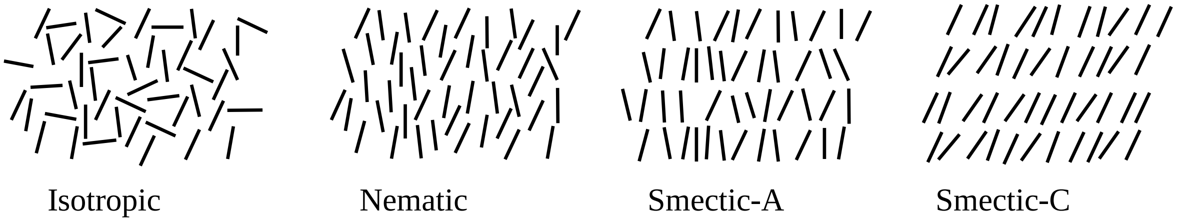
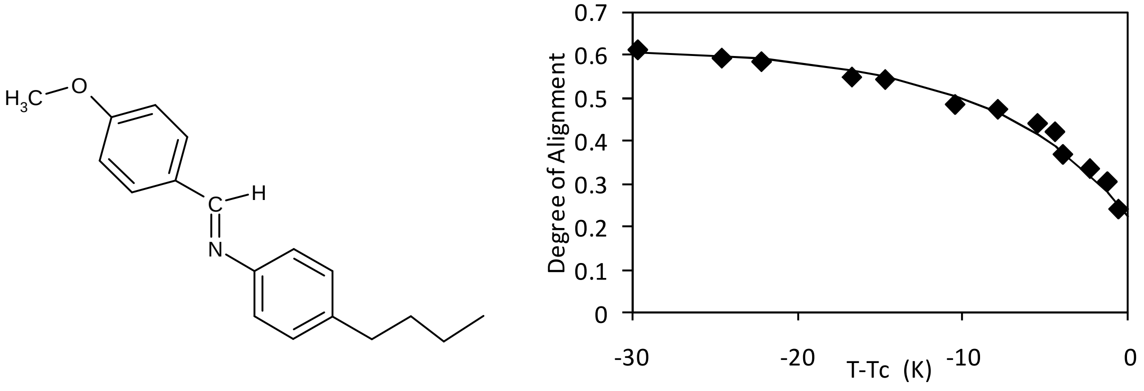

Isotropic Nematic Smectic-A Smectic-C

Figure 17.5.1: Liquid Crystalline Phases. Motional degrees of freedom are lost in progressing from the high temperature, high entropy, isotropic liquid phase to the lower temperature phases. Not all liquid crystals display each phase. More ordered phases are also possible.

The nematic to isotropic phase transition shows pre-transition effects, caused by the long-range correlations, and a small transition enthalpy, Figure 17.5.2. Such phase transitions are said to be mixed first and second order.[3,4] Liquid crystalline displays for consumer electronics are made from a thin film of a chiral liquid crystal in the smectic-C phase held between two plastic sheets. One of the plastic sheets is made from a polarizing material.



(a). (b).

Figure 17.5.2: (a). *p*-Methoxybenzylidene-*p'*-*n*-butylaniline, MBBA, is in the nematic phase at room temperature. (b). The nematic to isotropic-liquid phase transition for MBBA is mixed first and second order. The transition shows pre-transition effects and a discontinuity at the critical temperature.^{3}

Transitions in Phospholipid Bilayers are Cooperative: The gel to liquid-crystalline phase transition of phospholipid bilayers is another example of a cooperative transition. The gel to liquid-crystalline phase transition is also mixed first and second order. Phospholipids have hydrophilic headgroups and hydrophobic acyl-tails. Phospholipids spontaneously assemble into bilayer structures in aqueous solution in which the headgroups are on the surfaces exposed to water and the hydrophilic tails are directed inwards, Figure 17.5.3. Dipalmitoyl phosphatidylcholine is a typical phospholipid. The assembly of the bilayer is entropy driven due to the release of water molecules from the solvation shell of the phospholipids, as the lipids aggregate into the bilayer. Liposomes are produced when the phospholipid bilayer forms around an aqueous cavity. Liposomes are a good model system for the cell membrane. Cell membranes, however, also contain embedded proteins and other lipids, such as cholesterol. Liposomes are useful in their own right, as aids in pharmaceutical delivery and in cosmetic preparations.

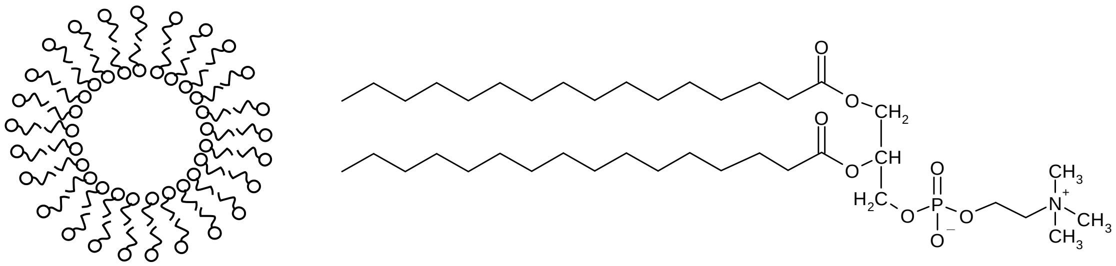


Figure 17.5.3. Liposome formed from a phospholipid bilayer. Dipalmitoyl phosphatidylcholine (DPPC, 16:0 PC, dipalmitoyl lecithin).

The phospholipids in the lower temperature gel state are tightly packed by Van der Waals forces. At the onset of the phase transition, the phospholipids cooperatively melt, Figure 17.5.4.[5] In the resulting liquid-crystalline state, the phospholipids are more loosely associated, owing to weakened van der Waals forces between the acyl chains, weakened polar interactions of the phospholipid headgroups, and a lateral expansion of the acyl chains.[5-7] Much of the added energy is in increased chain torsional vibrations. In the DSC of synthetic phospholipids, a small peak at a lower temperature than the main melting peak is also seen.[5-8] This small initial peak is a gel state to gel state molecule packing reorganization.

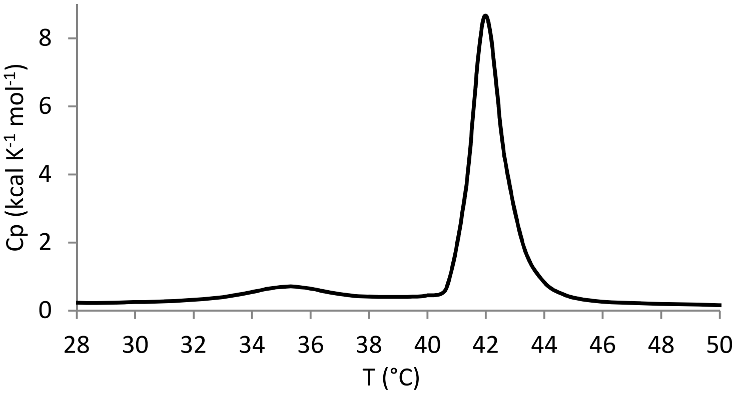


Figure 17.5.4: Differential scanning calorimetry thermogram of DPPC showing pre-transition broadening of the gel to liquid crystalline phase transition.

Phase-Change Data Storage Uses a First-Order Transition from Crystalline to Amorphous Forms: Rewritable computer storage media, CD-RW and DVD-RW, store information by converting a chalcogenide between crystalline and amorphous forms by heating. The crystalline and amorphous forms have markedly different indexes of refraction, which can be sensed by scanning a laser over the recording surface. AgInSbTe is an example of a chalcogenide used in data storage. The chalcogenide forms a meta-stable amorphous phase when heated above the melting point and then rapidly cooled. Then heating the amorphous chalcogenide above a characteristic temperature called the crystallization point, but below the melting point, forms an ordered crystalline state. A pulsed, tightly focused, infrared laser produces the heating. The amorphous state might represent digital “1’s” and the crystalline state digital “0’s”. Amorphous phases are super-cooled liquids and are often called glasses. Window glass is amorphous silica with added calcium and sodium oxide. Phase-change chalcogenide glasses, such as $Ge_2Sb_2Te_5$, are also used in non-volatile computer memory, which is designated PC-RAM or chalcogenide-RAM. $Ge_2Sb_2Te_5$ has markedly different electrical conductivity in its amorphous and crystalline forms.[9] PC-RAM has lower energy requirements and is more durable than flash memory.

17.3 Summary–Looking Ahead

Phase transitions minimize the chemical potential of the substance. At equilibrium, the chemical potential is everywhere equal. At a given pressure, the constraint of equal chemical potentials for two phases in contact at equilibrium fixes the phase transition temperature. Phase transitions result in a discontinuity in some property of the substance. First-order phase transitions have a discontinuity in the entropy and molar volume. The entropy change for the phase transition results in an enthalpy change for the transition, $\Delta_{tr}S = \Delta_{tr}H/T_{tr}$. The boiling points and melting points of substances have a direct relationship to the intermolecular forces.

We need to understand phase equilibrium in pure substances before we consider the theory of solutions and phase transitions in multi-component systems. For example, the variation of vapor pressure with temperature is central in understanding distillations. The activities of the solvent and solute in a solution can be determined by boiling point elevation or freezing point depression. For another example, as we saw in Chapter 5, the interface between phases can act as a site of adsorption and heterogeneous catalysis. The phase transitions of water among solid ice, liquid water, and water vapor are the underlying phenomena determining the biogeochemical cycle for water. The unusual properties of water play a role in the evolution of biological diversity in temperate climates. In the next three chapters we consider the theory of multi-component systems, the formation of solutions, and chemical equilibrium.

Chapter Summary

1. The chemical potential of a pure substance is expressed in terms of molar quantities:

$$d\mu_i = -S_i\,dT + V_i\,dP$$

2. The variation of the chemical potential for a pure substance, i, with T and P are:

$$\left(\frac{\partial\mu_i}{\partial T}\right)_P = -S_i \qquad \left(\frac{\partial\mu_i}{\partial P}\right)_T = V_i$$

3. The slopes of the chemical potential are discontinuous at the equilibrium phase transition temperature for a first order phase transition:

$$\left(\frac{\partial\Delta_{tr}\mu}{\partial T}\right)_P = \left(\frac{\partial\mu_\beta}{\partial T}\right)_P - \left(\frac{\partial\mu_\alpha}{\partial T}\right)_P \qquad \Delta_{tr}S_i = -\left(\frac{\partial\Delta_{tr}\mu}{\partial T}\right)_P \qquad \Delta_{tr}V_i = \left(\frac{\partial\Delta_{tr}\mu}{\partial P}\right)_T$$

4. At the equilibrium phase transition temperature, the chemical potentials of the two phases are equal: $\mu_A(\text{phase }\alpha,P,T) = \mu_A(\text{phase }\beta,P,T)$, which fixes the phase transition temperature for a given pressure.

5. For first-order phase transitions at equilibrium, the Clapeyron equation determines the coexistence curves:

$$\frac{dP}{dT} = \frac{\Delta_{tr}H_i}{T\,\Delta_{tr}V_i}$$

5. For vaporization and sublimation at equilibrium and treating the vapor as an ideal gas, the Clausius-Clapeyron equation is:

$$\frac{dP}{P} = \frac{\Delta_{tr}H_i}{R\,T^2}\,dT \qquad \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad P_2 = P_1\,e^{-\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

$$d\ln P = -\frac{\Delta_{tr}H_i}{R}\,d\left(\frac{1}{T}\right) \qquad \ln P = -\frac{\Delta_{tr}H_i}{RT} + \ln C \qquad P = C\,e^{-\frac{\Delta_{tr}H_i}{RT}}$$

6. The change in melting point for moderate changes in pressure is:

$$\Delta T = \frac{T_m\,\Delta_{fus}V_i}{\Delta_{fus}H_i}\,\Delta P$$

7. The vapor pressure of a liquid increases with increasing total applied pressure:

$$\ln \frac{P_{\beta,2}}{P_{\beta,1}} = \frac{V_i(\alpha)}{RT}(P_2 - P_1)$$

where the initial vapor pressure is $P_{\beta,1}$ at applied pressure P_1 and the final vapor pressure is $P_{\beta,2}$ at applied pressure P_2, and assuming the vapor is ideal and the molar volume of the liquid, $V_i(\alpha)$, is constant.
8. The heat capacity is given by the second derivative of the chemical potential versus temperature:

$$C_{p,i} = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P$$

9. Ehrenfest criteria for phase transitions specify that, for a first-order transition, the first derivative of the chemical potential curve is discontinuous, leading to a transition entropy and enthalpy. For a second-order transition, the second derivative of the chemical potential with temperature is discontinuous, leading to a discontinuity in the heat capacity.
10. For most higher-order transitions, the heat capacity curve appears as a lambda-transition, giving a strong temperature dependence of the heat capacity as the substance approaches the transition.
11. The phase transition temperature in second-order or lambda-type transitions is called the critical temperature, and phase transitions with second-order or lambda-type behavior are called critical phenomena.
12. First-order phase transitions are completely cooperative. In second-order phase transitions, the formation of cooperative, correlated motions has a limited range. The distance range for the correlation is called the correlation length.
13. Near the phase transition temperature, domains in the more mobile phase intermix with the less mobile phase. The domains anticipate the transition, which broadens the transition by pre-transition effects. The size of the domains is given by the correlation length.
14. The lambda transition at the gas-liquid critical point is studied using laser light scattering.
15. Liquid crystalline phases are liquid-like phases that exist between the normal isotropic-liquid phase and the crystalline solid phase and have long-range correlated motions of the molecules. Cheese is a liquid crystalline material.
16. The nematic to isotropic-liquid transition in liquid crystals and the gel to liquid crystal transitions in phospholipid bilayers are mixed first and second order.

General Pattern 9: Exponential Temperature Dependence $d\ln P/dT = \Delta_r H/RT^2$: Using the alternate forms for the differentials:

$$\frac{dP}{P} = d\ln P \qquad \frac{dT}{T^2} = -d\left(\frac{1}{T}\right)$$

the temperature dependence of the vapor pressure, the sublimation pressure, the rate constant in chemical kinetics and the thermodynamic equilibrium constant have the same general form:

$$\frac{d\ln P}{dT} = \frac{\Delta_{tr}H_i}{RT^2} \qquad \frac{d\ln k}{dT} = \frac{E_a}{RT^2} \qquad \frac{d\ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \qquad \text{(equilibrium)}$$

$$d \ln P = -\frac{\Delta_{tr}H_i}{R}\, d\left(\frac{1}{T}\right) \qquad d \ln k = -\frac{E_a}{R}\, d\left(\frac{1}{T}\right) \qquad d \ln K_p = -\frac{\Delta_r H^\circ}{R}\, d\left(\frac{1}{T}\right)$$

These expressions integrate for constant $\Delta_{tr}H_m$, E_a, and $\Delta_r H^\circ$ to:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\left(\frac{k_{T2}}{k_{T1}}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\frac{K_{p,T_2}}{K_{p,T_1}} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

General Pattern ***℘4*** is a continuation of this general pattern.

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Problems: Phase Transitions in Pure Substances

1. Prove that the dependence of the freezing point on the pressure for a pure substance for large changes in pressure is given by:

$$T = T_m\, e^{\Delta P\, \Delta_{fus}V_i / \Delta_{fus}H_i}$$

2. Calculate the change in the melting point for water ice for an increase in pressure of 10.00 bar starting from the melting point at 1.00 bar. The densities of water and ice at 0.00ºC are 1.000 g cm^{-3} and 0.917 g cm^{-3}, respectively. The enthalpy of fusion is 6.008 kJ mol^{-1} at 273.15 K.

3. The vapor pressure of acetone is 0.377 bar at 30.0°C and 0.817 bar at 50.0°C. Calculate (a) the enthalpy of vaporization of acetone and (b) the normal boiling point.

4. The normal boiling point of methanol is 64.05°C. The vapor pressure of methanol at 20.00°C is 0.1530 bar. Calculate the enthalpy of vaporization of methanol.

5. The vapor pressure of solid CsI at several temperatures is given in the following table. Calculate the enthalpy of sublimation of CsI.

T (K)	767.2	801.8	816.3	830.3	846.8
P/10^{-6} (bar)	2.03	7.45	12.5	20.5	36.4

6. The vapor pressure of ethanol as a function of temperature is given in the table below. Determine the enthalpy of vaporization of ethanol. Calculate the standard boiling point of ethanol.

T (°C)	-2.3	19.0	34.9	63.5	78.4
P_{vap} (mbar)	13.3	53.3	133.3	533.3	1013.
P_{vap} (mm Hg)	10.0	40.0	100.0	400.0	760.0

7. The vapor pressure of benzoic acid is 0.133 bar at 186.2°C and 0.533 bar at 227.0°C. Calculate the standard boiling point.

8. For methanol, the enthalpy of fusion is 3.215 kJ mol^{-1} and the volume change on melting is 2.75 mL mol^{-1} at the standard melting point of 175.59 K.[1] The enthalpy of vaporization is 35.21 kJ mol^{-1} at the standard boiling point of 337.8 K. Estimate the triple point temperature and pressure for methanol. Assume constant transition enthalpies over the temperature range. [Hint: you may use the Goal Seek option in Excel.]

9. The sublimation pressure versus temperature of ammonia is ln P = 23.03 – 3754./T. The vapor pressure of liquid ammonia is ln P = 19.49 – 3063./T. (a) Find the enthalpy of sublimation and the enthalpy of vaporization. (b). Calculate the triple point for ammonia. (c). Find the enthalpy of fusion at the triple point.[2]

10. Integrate the differential form of the Clausius-Clapeyron equation:

$$d\ \ln P = \frac{\Delta_{tr}H_i}{RT^2}\, dT$$

from an initial temperature of T_o to a final temperature of T. In this equation T is the equilibrium phase transition temperature at the given pressure. Assume the phase transition has a molar enthalpy change given by:

$$\Delta_{tr}H_{i,T} = \Delta_{tr}H_{i,T_o} + \Delta_{tr}C_{p,i}\,(T - T_o)$$

where $\Delta_{tr}C_{p,m}$ is the change in heat capacity for the phase transition, which is assumed to be a constant. Show that the result is:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{\Delta_{tr}H_{i,T_o}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}}{R}\ln\left(\frac{T}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}T_o}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

11. Reference handbooks sometimes list the vapor pressure of liquids in the form:

$$\ln P = A - \frac{B}{T} - C \ln T + D\, T$$

Show that the result from the last problem can be rewritten in this form. Use *General Pattern ℘4: Exponential Temperature Dependence* as a guide.

12. Long’s Peak in the Colorado Rocky Mountains is 3962. m high. What is the boiling point of water at this altitude? Assume a constant temperature of 20.0°C (see Problem 1.15) and the pressure at sea level is 1.00 atm. The enthalpy of vaporization of water is 42.00 kJ mol^{-1}.

13. For non-ideal gases, from Eq. 7.5.2, PV = z nRT. Find the corresponding integrated form of the Clausius-Clapeyron equation for liquid-vapor or solid-vapor equilibrium. In other words, correct Eq. 17.1.13° for vapor non-ideality. Assume z and $\Delta_{tr}H_m$ are constant over the temperature range for the integration.

14. Calculate the vapor pressure of methanol at 20.0°C under a total ambient pressure of 10.0 bar of air. The vapor pressure of methanol at 20.00°C is 0.1530 bar, under its own vapor pressure.

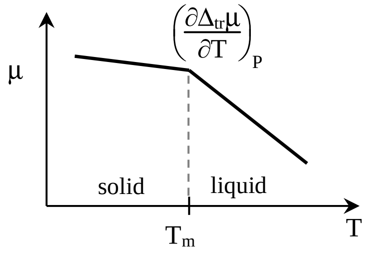
15. Particulates released from volcanic eruptions can be a significant source of heavy metals in the environment. The magma under a volcano is at high temperature and total pressure. Under these circumstances, normally non-volatile substances can have a significant vapor pressure. NaCl and heavy metal chlorides are found in the vapor phase at high total pressure as volatile molecular species. The concentration of Pb in the minerals formed from the vapor phase in a volcano is much higher than in the original magma. At high pressure, the vapor above a magma is non-ideal and the fugacity must be used. Eq. 17.1.30 assumes the vapor behaves as an ideal gas. Let $P_{\beta,o}$ be the vapor pressure of the pure liquid under its pure vapor pressure. Assume the pure vapor pressure at the given temperature is sufficiently small that the pure vapor is ideal, giving $f_{\beta,o} = P_{\beta,o}$. Show that the fugacity of the vapor, f_β, in equilibrium with the pure liquid at the elevated total pressure, P, is then:

$$\ln \frac{f_\beta}{P_{\beta,o}} = \frac{V_i(\alpha)}{RT}\,(P - P_{\beta,o})$$

16. Redraw Figure 17.1.1 for water.

17. Some property needs to be discontinuous to observe a phase transition. What property is discontinuous in a pure Ehrenfest second-order phase transition?

18. Find the difference in slope across the melting transition for the chemical potential versus temperature curve, $(\partial \Delta_{tr}\mu/\partial T)_P$, at standard pressure.



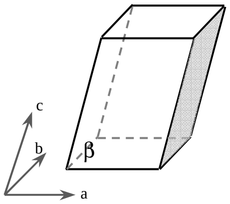
19. Draw the chemical potential versus pressure curves for the solid, liquid, and vapor phases of a pure substance, at constant temperature. Assume that $V_i(s) < V_i(l)$. Describe the process that occurs at the intersection of the chemical potential curves.

20. (a). Sketch the chemical potential curves versus temperature for the solid, liquid, and vapor phases of substance at a constant pressure below the triple point and (b) for a substance at the triple point pressure.

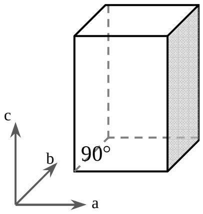
21. If first-order phase transitions are “completely cooperative,” how can two-phase systems exist at equilibrium? For example, how can ice and liquid water coexist at equilibrium at the equilibrium phase transition temperature?

22. Use the concept of correlation length and domain size to explain why the heat capacity of a substance increases as the temperature increases to the critical point.

23. The monoclinic and orthorhombic unit cells are illustrated, below. The unit cell lengths for both unit cells are all different, a ≠ b ≠ c. The orthorhombic unit cell has all 90° angles between the unit cell directions, $\alpha = \beta = \gamma = 90°$. The monoclinic unit cell has one angle not equal to 90°, $\alpha = \gamma = 90°$, β.



Monoclinic



Orthorhombic

Methanol crystallizes into long hydrogen-bonded chains. There are two crystalline forms. Crystal II has a monoclinic unit cell and is the low temperature form. Crystal I has an orthorhombic unit cell and is the high temperature form. The difference is a small displacement of the hydrogen-bonded chains in the direction perpendicular to the direction of the chains. The solid-solid phase transition temperature is 157.4 K at 1 atm. The transition was reported to be second-order. Carlson and Westrum redetermined the heat capacity of very pure methanol samples to determine the thermodynamic parameters for the phase transition, Figure P17.1.[1] Crystal I readily super-cools, so heat capacity data for this phase is available below the equilibrium phase transition temperature. Is the transition first or second order?

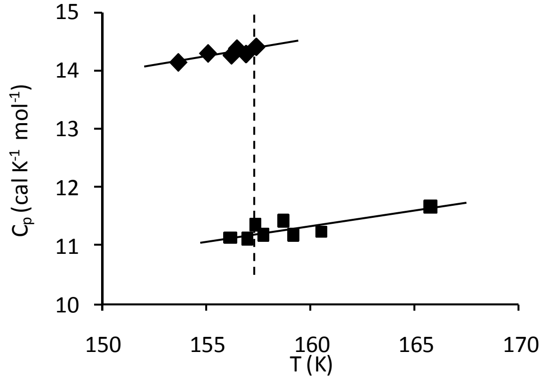
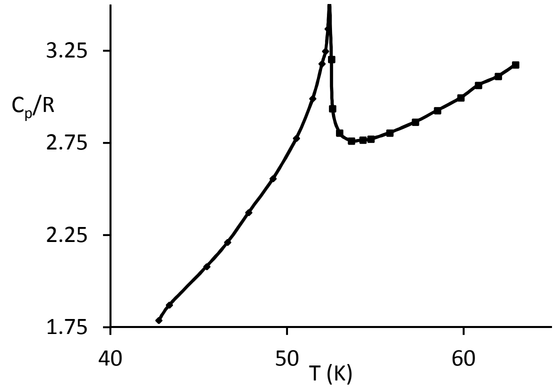


Figure P17.1: Heat capacity data for 99.98 mol% methanol near the solid-solid phase transition at 157.4 K.

24. $NiCl_2$ has a solid-state magnetic phase transition at 52 K. The low temperature phase is anti-ferromagnetic, and the high temperature phase is paramagnetic. Antiferromagnetic phases are an ordered lattice of unpaired electrons that alternate spin-up and spin-down. In the absence of an external magnetic field, paramagnetic phases also have an equal, or nearly equal, number of electrons spin-up and spin-down, distributed at random. The paramagnetic phase is at higher entropy at a given finite temperature. A plot of the heat capacity as a function of temperature is shown below.[3] Characterize this solid-state phase transition.



antiferromagnetic: ↑↓↑↓↑↓↑↓↑↓↑↓↑↓

ferromagnetic: ↑↑↑↑↑↓↑↑↑↑↑↑↑↑

paramagnetic: ↑↓↑↑↑↓↓↑↓↓↑↓↑↓

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1. H. G. Carlson, E. F. Westrum, Jr., “Methanol: heat capacity, enthalpies of transition and melting, and thermodynamic properties from 5-300K,” *J. Chem. Phys.*, **1971**, *54*, 1464-1471.
2. F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971. Problem 25.13.
3. R. H. Busey, W. F. Giauque, “The Heat Capacity of Anhydrous $NiCl_2$ from 15 to 300 K. The Antiferromagnetic Anomaly near 52 K. Entropy and Free Energy,” *J. Am. Chem. Soc.*, **1953**, *75*, 4443.