The molar volume of some solid is 0.142 L mol\(^{-1}\) at 1.00 atm at its normal melting temperature of 427.15 K. The molar volume of the corresponding liquid at this temperature and pressure is 0.1526 L mol\(^{-1}\). At a pressure of 11.8 atm the melting temperature increases to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

**Solution**

The Clapeyron equation describes the slope of the phase boundary on a \(P\) vs. \(T\) phase diagram in terms of the entropy change and molar volume change between the two phases:

\[
\frac{dP}{dT} = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V}
\]

integrate:

\[
\int_{P_1}^{P_2} dP = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V} \int_{T_1}^{T_2} dT
\]

if we regard \(\Delta_{\text{fus}}S\) and \(\Delta_{\text{fus}}V\) as independent of \(T\),

\[
\Delta P = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V} \Delta T
\]

Solve for \(\Delta_{\text{fus}}V\):

\[
\Delta_{\text{fus}}V = \frac{\Delta P \Delta_{\text{fus}}V}{\Delta T}
\]

where

\[
\Delta_{\text{fus}}V = V_m(l) - V_m(s)\]

fusion is solid \(\rightarrow\) liquid; therefore \(\Delta_{\text{fus}}V\) is the liquid molar volume minus the solid molar volume

\[
= 0.1526\text{L mol}^{-1} - 0.142\text{L mol}^{-1} = 0.0106\text{L mol}^{-1}
\]

\(\Delta P\) and \(\Delta T\) are:

\[
\Delta P = P_2 - P_1 = 11.8\text{atm} - 1\text{atm}\quad\text{and}\quad\Delta T = T_2 - T_1 = 429.26\text{K} - 427.15\text{K} = 2.11\text{K}
\]

Substituting these into the expression for \(\Delta_{\text{fus}}S\) gives

\[
\Delta_{\text{fus}}S = \frac{(10.8\text{atm})(0.0106\text{L mol}^{-1})}{2.11\text{K}} \times 101.325\text{J L}^{-1}\text{atm}^{-1} \quad\text{always convert your final answer to appropriate units}
\]

\[
= 5.50\text{JK}^{-1}\text{mol}^{-1}
\]

To find the enthalpy, you might be tempted to use,

\[
\Delta_{\text{fus}}H' = T_{\text{fus}} \Delta_{\text{fus}}S
\]

but what would you use for \(T_{\text{fus}}\)? In this case, either would appear to give an acceptable solution, but this is only because \(\Delta T\) is small. A more rigorous approach would be to write the Clapeyron equation in terms of the enthalpy, integrate it, then solve for \(\Delta_{\text{fus}}H'\):

\[
\frac{dP}{dT} = \frac{\Delta_{\text{fus}}H'}{T_{\text{fus}}V} \Rightarrow \int_{P_1}^{P_2} dP = \frac{\Delta_{\text{fus}}H'}{T_{\text{fus}}V} \int_{T_1}^{T_2} dT
\]

integrate:

\[
\Delta P = \frac{\Delta_{\text{fus}}H'}{\Delta_{\text{fus}}V} \ln \frac{T_2}{T_1}
\]

Solve for \(\Delta_{\text{fus}}H'\):

\[
\Delta_{\text{fus}}H' = \frac{\Delta P \Delta_{\text{fus}}V}{\ln \left(\frac{T_2}{T_1}\right)} = \frac{(10.8\text{atm})(0.0106\text{L mol}^{-1})}{\ln \left(\frac{429.26\text{K}}{427.15\text{K}}\right)} \times 0.101325\text{kJ L}^{-1}\text{atm}^{-1}
\]

\[
= 2.35\text{kJ mol}^{-1}
\]

8.2 Calculate the freezing point of water at an elevation of 7000 feet where the atmospheric pressure is 0.772 atm. At this pressure and at 273 K, the density of water is 1.00 g mL\(^{-1}\) and the density of ice is 0.92 g mL\(^{-1}\). The enthalpy of fusion is 6.00 kJ mol\(^{-1}\).
**Solution**

We can use the integrated Clapeyron equation,

$$
\Delta P = \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T_2}{T_1}
$$

and solve it for $T_2$:

$$
\ln T_2 = \ln T_1 + \frac{\Delta P \Delta_{fus} V}{\Delta_{fus} H} \Rightarrow T_2 = T_1 \exp \left( \frac{\Delta P \Delta_{fus} V}{\Delta_{fus} H} \right)
$$

For $T_1$ we use 273 K and $\Delta P = P_2 - P_1 = 0.772 \text{ atm} - 1 \text{ atm} = -0.228 \text{ atm}$

$\Delta_{fus} V$ is the molar volume of the liquid minus that of the solid where the molar volumes are calculated from the densities:

$$
\Delta_{fus} V = V_m(l) - V_m(s) = \frac{M_{H_2O}}{\rho(l)} - \frac{M_{H_2O}}{\rho(s)} = 18 \text{ g mol}^{-1} \left( \frac{1}{1.00 \text{ g mL}^{-1}} - \frac{1}{0.92 \text{ g mL}^{-1}} \right) = -0.157 \text{ mL mol}^{-1}
$$

$$
= -1.57 \times 10^{-3} \text{ L mol}^{-1}
$$

Now we have all the quantities we need:

$$
T_2 = (273 \text{ K}) \exp \left[ \frac{(-0.228 \text{ atm})(-1.57 \times 10^{-3} \text{ L mol}^{-1})}{6.00 \text{ kJ mol}^{-1}} \times 0.101325 \text{ kJ L atm}^{-1} \right]
$$

$$
= 273.002 \text{ K}
$$

Such a small difference in freezing point is expected because the slope of the solid-liquid phase boundary is so steep (i.e., even for a large $\Delta P$, $\Delta T$ is small).

8.3 Use the phase diagram for water shown in Figure 8.6b, to determine which phase (solid, liquid, or gas; you do not have to distinguish between different solids) has the lowest chemical potential at the following combinations of temperature and pressure: (a) 298 K and 1 bar, (b) 298 K and 0.13 mbar, (c) 373 K and 500 bar, (d) 373 K and 10 bar, (e) 373 K and 100 mbar.

**Solution**

(a) liquid, (b) gas, (c) liquid, (d) liquid, (e) gas.

8.4 $\Delta_{vap} H$ for water is 40.67 kJ mol$^{-1}$ at the normal boiling point. Many bacteria can survive at 373 K by forming spores. However, most spores die at 393 K. Hence, autoclaves used to sterilize medical and laboratory equipment are pressurized to raise the boiling point of water to 393 K. (a) At what pressure does water boil at 373 K? (b) What is the boiling temperature of water at the top of Pike’s Peak (elevation 14,100 ft), where the atmospheric pressure is ~0.587 atm?

**Solution**

Here, we are interested in the transition from a liquid (a condensed phase) to a vapor so we can use the Clausius-Clapeyron equation which is easily integrated if we regard $\Delta_{vap} H$ as independent of temperature:

$$
\frac{d \ln P}{dT} = \frac{\Delta_{vap} H}{R} \Rightarrow \int_{ln P_1}^{ln P_2} d \ln P = \frac{\Delta_{vap} H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT = \ln \frac{P_2}{P_1} = \frac{\Delta_{vap} H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
$$

a. We know $T_1$ (373 K), $P_1$ (1 atm), and $T_2$ (393 K), so we need to solve for $P_2$:

$$
\ln P_2 = \ln P_1 - \frac{\Delta_{vap} H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
$$

$$
P_2 = P_1 \exp \left[ -\frac{\Delta_{vap} H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]
$$

$$
= (1 \text{ atm}) \exp \left[ -\frac{40.67 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{393 \text{ K}} - \frac{1}{373 \text{ K}} \right) \right]
$$

$$
= 1.95 \text{ atm}
$$

b. We still use the Clausius-Clapeyron equation, but we solve for $T_2$ (since we are given $P_2$):

$$
T_2 = \left[ \frac{1}{T_1} - \frac{\Delta_{vap} H}{R} \ln \frac{P_2}{P_1} \right]^{-1}
$$

$$
= \left[ \frac{1}{373 \text{ K}} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{446 \text{ torr} \ln 760 \text{ torr}} \right]^{-1} = 358.4 \text{ K}
$$
8.5 What is the maximum number of phases that can coexist in a binary system?

**Solution**

The Gibbs phase rule is \( f = c - p + 2 \). For a binary system, \( c = 2 \), so the phase rule becomes \( f = 4 - p \). Since the minimum number of degrees of freedom is 0, the maximum number of phases is 4.

8.6 As this problem illustrates, phase composition can also be described in terms of mass fraction in addition to mole fraction as we have done in class. Water and phenol are partially miscible at 323 K and 1 atm. When these two liquids are mixed at this temperature and pressure, two liquid phases are present. The fraction of water by mass in one of them (call this phase \( \alpha \)) is 0.375 and the other (call this phase \( \beta \)) has a fraction of water by mass of 0.890. If the mixture at this temperature and pressure is comprised of 6.00 g of phenol and 4.00 g of water, what is the mass of water and the mass of phenol in each phase? (A water-phenol phase diagram would be qualitatively similar to Figure 8.20 with a critical temperature around 340 K and where the \( x \)-axis is the total mass fraction of water, \( f_W^{(\text{tot})} \). It might be helpful to make a rough sketch of the phase diagram when working this problem.)

**Solution**

A representative phase diagram is shown to the right. The total mass of the solution is

\[ m_{\text{tot}} = m_W + m_\beta = 10 \text{ g} \]

corresponding to a total water mass fraction of

\[ f_W^{(\text{tot})} = \frac{m_W}{m_{\text{tot}}} = \frac{4 \text{ g}}{10 \text{ g}} = 0.4 \]

Since we're asked to find the amounts of material in each phase, we need to use the lever rule. In terms of masses, the lever rule is

\[ \frac{m_\alpha}{m_\beta} = \frac{L_\alpha}{L_\beta} \]

where

\[ L_\alpha = f_W^{(\text{tot})} - f_W^{(\alpha)} = 0.4 - 0.375 \quad \text{and} \quad L_\beta = f_W^{(\beta)} - f_W^{(\text{tot})} = 0.890 - 0.4 = 0.490 \]

Substituting these back into the lever rule gives

\[ \frac{m_\alpha}{m_\beta} = \frac{0.490}{0.025} = 19.6 \quad \text{(in terms of mass, the most abundant phase is \( \alpha \) which is \sim 20 times greater than phase \( \beta \))} \]

We can find the mass of each phase by writing the mass of one phase in terms of the other and recognizing that the total mass (10 g) is also equal to the sum of the masses of both phases:

\[ m_{\text{tot}} = m_\alpha + m_\beta \]

Now we can solve for \( m_\alpha \) and substitute the result into the lever rule:

\[ m_\alpha = m_{\text{tot}} - m_\beta \quad \Rightarrow \quad \frac{m_\alpha}{m_\beta} = \frac{m_{\text{tot}} - m_\beta}{m_\beta} = 19.6 \]

The only unknown in the resulting expression is \( m_\beta \), so we solve for it:

\[ m_{\text{tot}} - m_\beta = 19.6m_\beta \quad \Rightarrow \quad 19.6m_\beta + m_\beta = m_{\text{tot}} \quad \Rightarrow \quad m_\beta = \frac{m_{\text{tot}}}{19.6 + 1} = \frac{10 \text{ g}}{20.6} = 0.4854 \text{ g} \]

Then, from mass conservation it follows that

\[ m_\alpha = m_{\text{tot}} - m_\beta = 10 \text{ g} - 0.4854 \text{ g} = 9.5146 \text{ g} \]

Now we can calculate the masses of water and phenol in each phase. Start with the mass of water in phase \( \alpha \). This is just the mass of phase \( \alpha \) times the fraction of water in that phase:

\[ m_W^{(\alpha)} = f_W^{(\alpha)} m_\alpha = (0.375)(9.5146 \text{ g}) = 3.568 \text{ g} \]

The mass of phenol in this phase is found using mass conservation:

\[ m_V^{(\alpha)} = m_\alpha - m_W^{(\alpha)} = 9.5146 \text{ g} - 3.568 \text{ g} = 5.947 \text{ g} \]

Do the same thing for phase \( \beta \):

\[ m_W^{(\beta)} = f_W^{(\beta)} m_\beta = (0.890)(0.4854 \text{ g}) = 0.432 \text{ g} \quad \text{and} \quad m_V^{(\beta)} = m_\beta - m_W^{(\beta)} = 0.4854 \text{ g} - 0.432 \text{ g} = 0.053 \text{ g} \]
Consider the following two-component phase diagram. (a) When \( x_B = 0.4 \) and \( T = 390 \text{ K} \), what is the mole fraction of B in each phase (call the A-rich phase \( \alpha \) and the B-rich phase \( \beta \))? (b) If the solution contains a total of 10 mol, estimate the amounts (i.e., number of moles) of phases \( \alpha \) and \( \beta \). (c) Determine the number of moles of A and B in each phase.

**Solution**

a. From a tie line drawn at 390 K (see the figure to the right), we see that the mole fraction of B in phase \( \alpha \) is \( \sim 0.2 \) and the mole fraction of B in phase \( \beta \) is \( \sim 0.8 \).

b. For this part, we use the lever rule:

\[
\frac{N_\alpha}{N_\beta} = \frac{L_\alpha}{L_\beta}
\]

from the figure \( L_\alpha = 0.4 - 0.2 = 0.2 \) and \( L_\beta = 0.8 - 0.4 = 0.4 \)
\[
= \frac{0.4}{0.2} = 2
\]

If there are a total of 10 moles in the solution, then according to mass conservation:
\[
N_\alpha + N_\beta = 10 \text{ mol}
\]

solve for \( N_\alpha \):
\[
N_\alpha = 10 \text{ mol} - N_\beta
\]

Substitute into the lever rule:
\[
\frac{10 \text{ mol} - N_\beta}{N_\beta} = 2
\]

and solve for \( N_\beta \):
\[
10 \text{ mol} - N_\beta = 2 N_\beta \Rightarrow 10 \text{ mol} = 3 N_\beta
\]

\[
N_\beta = \frac{10 \text{ mol}}{3} = 3.33 \text{ mol}
\]

\( N_\alpha \) is then
\[
N_\alpha = 10 \text{ mol} - 3.33 \text{ mol} = 6.67 \text{ mol}
\]

c. Like the previous problem, since we know the mole fractions and the number of moles of each phase, we can calculate the number of moles of each component. For phase \( \alpha \):
\[
N_\alpha^{(\alpha)} = x_B^{(\alpha)} N_\beta = 0.2(6.67 \text{ mol}) = 1.334 \text{ mol} \quad \therefore \quad N_\alpha^{(\alpha)} = N_\alpha - N_\alpha^{(\alpha)} = 5.336 \text{ mol}
\]

For phase \( \beta \):
\[
N_\beta^{(\beta)} = x_B^{(\beta)} N_\beta = 0.8(3.33 \text{ mol}) = 2.664 \text{ mol} \quad \therefore \quad N_\beta^{(\beta)} = N_\beta - N_\beta^{(\beta)} = 0.666 \text{ mol}
\]