

Chapter 5 Homework Solutions

5.1 S(rhombic) → S(monoclinic)

$$\Delta S_m = S_m^\circ(\text{monoclinic}) - S_m^\circ(\text{rhombic}) = 32.60 \text{ J/mol-K} - 31.80 \text{ J/mol-K} = 0.80 \text{ J/mol-K}$$

$$\Delta H_m = 568 \text{ J/mol}$$

(a) $\Delta G_m = 568 \text{ J/mol} - T(0.80 \text{ J/mol-K})$ [= +330 J/mol at 298 K]

Yes, because ΔG_m will decrease as T rises, and eventually become negative.

(b) At equilibrium, $\Delta G_m = 0$. We'll solve for the temperature.

$$\Delta G_m = 568 \text{ J/mol} - T(0.80 \text{ J/mol-K}) = 0$$

$$\text{Therefore, } T = \frac{568 \text{ J/mol}}{0.80 \text{ J/mol} \cdot \text{K}} = 710 \text{ K} = 437^\circ \text{C}$$

5.2 (a) $P_1 = 17.7 \text{ kPa}$ $T_1 = 303 \text{ K}$ $P_2 = 37.7 \text{ kPa}$ $T_2 = 323 \text{ K}$

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

$$\text{Therefore } \Delta_{\text{vap}}H^\circ = -\frac{(8.314 \text{ J/mol} \cdot \text{K}) \cdot \ln\left(\frac{37.7 \text{ kPa}}{17.7 \text{ kPa}}\right)}{\frac{1}{323 \text{ K}} - \frac{1}{303 \text{ K}}} = +30,760 \text{ J/mol} = 30.76 \text{ kJ/mol}$$

(b) $P_1 = 17.7 \text{ kPa}$ $T_1 = 303 \text{ K}$ $P_2 = ??$ $T_2 = 283 \text{ K}$ $\Delta_{\text{vap}}H^\circ = 30.76 \text{ kJ/mol}$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] = -\frac{30.76 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left[\frac{1}{283 \text{ K}} - \frac{1}{303 \text{ K}} \right] = -0.863$$

$$P_2 = P_1 e^{-0.863} = 17.7 \text{ kPa} \cdot 0.422 = 7.5 \text{ kPa}$$

(c) $P_1 = 17.7 \text{ kPa}$ $T_1 = 303 \text{ K}$ $P_2 = 100 \text{ kPa}$ $T_2 = T_b^\circ = ??$ $\Delta_{\text{vap}}H^\circ = 30.76 \text{ kJ/mol}$

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

$$\frac{1}{T_2} = \frac{1}{303 \text{ K}} - \frac{8.314 \text{ J/mol} \cdot \text{K}}{30.75 \times 10^3 \text{ J/mol}} \ln\left(\frac{100 \text{ kPa}}{17.7 \text{ kPa}}\right) = 2.832 \times 10^{-3} \text{ K}^{-1}$$

$$T_2 = \frac{1}{2.832 \times 10^{-3} \text{ K}^{-1}} = 353 \text{ K} = 80^\circ \text{C}$$

5.3 Multi-Step process:

$$n = 120 \text{ g} / 78 \text{ g/mol} = 1.54 \text{ mol}$$

[1] Gas(393 K) → Gas(353 K)

[2] Gas(353 K) → Liquid(353 K)

[3] Liquid(353 K) → Liquid(279 K)

[4] Liquid(279 K) → Solid(279 K)

[5] Solid(279 K) → Solid(253 K)

$$\Delta H_1 = nC_{P,m}(\text{gas})\Delta T = 1.54 \text{ mol}(81.7 \text{ J/mol-K})(353 \text{ K} - 393 \text{ K}) = -5030 \text{ J} = -5.0 \text{ kJ}$$

$$\Delta H_2 = n\Delta_{\text{cond}}H^\circ = 1.54 \text{ mol}(-30.8 \text{ kJ/mol}) = -47.4 \text{ kJ}$$

$$\Delta H_3 = nC_{P,m}(\text{liq})\Delta T = 1.54 \text{ mol}(136.1 \text{ J/mol-K})(279 \text{ K} - 353 \text{ K}) = -15,500 \text{ J} = -15.5 \text{ kJ}$$

$$\Delta H_4 = n\Delta_{\text{crys}}H^\circ = 1.54 \text{ mol}(-9.9 \text{ kJ/mol}) = -15.2 \text{ kJ}$$

$$\Delta H_5 = nC_{P,m}(\text{sol})\Delta T = 1.54 \text{ mol}(61.2 \text{ J/mol-K})(253 \text{ K} - 279 \text{ K}) = -2450 \text{ J} = -2.5 \text{ kJ}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = -85.6 \text{ kJ}$$

5.4 $A \rightarrow B$ $\Delta V_m = V_m(B) - V_m(A) = 17.2 \text{ mL/mol} - 23.8 \text{ mL/mol} = -6.6 \text{ mL/mol} = -6.6 \times 10^{-3} \text{ L/mol}$

$$\Delta G^\circ = 6.0 \text{ kJ/mol} = 6.0 \times 10^3 \text{ J/mol} = 6.0 \times 10^3 \text{ kPa-L/mol}$$

$$\Delta G_m = \Delta G_m^\circ + \Delta V_m(P - P^\circ) = 0 \text{ at equilibrium.}$$

$$\begin{aligned} P &= P^\circ - \frac{\Delta G_m^\circ}{\Delta V_m} = 100 \text{ kPa} - \frac{6.0 \times 10^3 \text{ kPa} \cdot \text{L/mol}}{-6.6 \times 10^{-3} \text{ L/mol}} \\ &= 100 \text{ kPa} + 9.1 \times 10^5 \text{ kPa} \approx 9.1 \times 10^5 \text{ kPa} \cdot \frac{1 \text{ bar}}{100 \text{ kPa}} = 9100 \text{ bar} \end{aligned}$$

- 5.5**
- (a) A
 - (b) D
 - (c) A
 - (d) D
 - (e) B
 - (f) A