

From Atkins: 5.2, 5.9, 5.12, 5.13, 5.15, 5.17, 5.21

5.2) The density of rhombic sulfur is  $2.070 \text{ g cm}^{-3}$  and that of monoclinic sulfur is  $1.957 \text{ g cm}^{-3}$ . Can the application of pressure be expected to make monoclinic sulfur more stable than rhombic sulfur? (See Exercise 5.1.)

From 5.1,  $\Delta G_f(\text{S}_{\text{rho}}) = 0.0 \text{ kJ/mol}$ ;  $\Delta G_f(\text{S}_{\text{mono}}) = 0.33 \text{ kJ/mol}$

At constant T, G depends on  $p$  via:  $dG_m = V_m dp$ , hence as  $p$  increases, so does G in proportion to  $V_m$ . The molar volume is related to the density by:

$$V_m = \frac{MW}{\rho}, \text{ therefore, } V_m \propto \frac{1}{\rho}$$

$\rho(\text{rho}) > \rho(\text{mono})$ , hence  $V_m(\text{rho}) < V_m(\text{mono})$  so increasing the pressure will make the monoclinic form less stable relative to the rhombic form rather than more stable. (i.e., G of the monoclinic form will increase faster than G of the rhombic form)

5.9) The standard molar entropy of rhombic sulfur is  $31.80 \text{ J K}^{-1} \text{ mol}^{-1}$  and that of monoclinic sulfur is  $32.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . (a) Can an increase in temperature be expected to make monoclinic sulfur more stable than rhombic sulfur? (b) If so, at what temperature will the transition occur at 1 bar? (See Exercise 5.1)

a)  $G_m$  depends on temperature via:  $dG_m = -S_m dT$ . Hence as T increases,  $G_m$  decreases in proportion to  $S_m$ . Since  $S_m(\text{mono}) > S_m(\text{rho})$ ,  $G_m(\text{mono})$  will decrease faster than that of the rhombic form, so eventually a suitable increase in temperature will make monoclinic sulfur more stable than the rhombic form.

b) Assuming the molar entropies are independent of temperature for the range of interest,  $\Delta G_m = -S_m \Delta T$

At the transition,  $G_m(\text{rhom}) = G_m(\text{mono})$

For  $G_m$  relative to the  $\Delta G_f$  of the rhombic form (i.e., the monoclinic form lies 0.33 kJ/mol above the rhombic form):

$$0.0 + \Delta G_m(\text{rhom}) = 0.33 + \Delta G_m(\text{mono}) \quad (\Delta G_m \text{ is the change in } G_m \text{ due to } T)$$

$$0.0 - S_m(\text{rhom})(T_f - 298) = 0.33 - S_m(\text{mono})(T_f - 298)$$

Solving for the final temperature:  $T_f = 710 \text{ K}$

5.12) An open vessel containing (a) water, (b) benzene, (c) mercury stands in a laboratory measuring 6.0 m x 5.3 m x 3.2 m at 25°C. What mass of each substance will be found in the air if there is no ventilation? (The vapor pressures are (a) 24 Torr, (b) 98 Torr, (c) 1.7 mTorr.)

total volume of the room:  $(6.0 \text{ m})(5.3 \text{ m})(3.2 \text{ m}) = 101.76 \text{ m}^3$

$$\text{a) } p = 24 \text{ Torr} \times \frac{1 \text{ atm}}{760 \text{ Torr}} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 3.1997 \text{ kPa}$$

$$n = \frac{(3.1997 \times 10^3 \text{ Pa})(101.76 \text{ m}^3)}{(8.31451)(298 \text{ K})} = 131.41 \text{ moles of water}$$

$$131.41 \text{ mol} \times \frac{18.02 \text{ g}}{\text{mol}} = 2368 \text{ g} = 2.4 \text{ kg of water in the room's air}$$

b)  $p = 98 \text{ Torr}$  which equals 13.066 kPa

$$n = \frac{(13.066 \times 10^3 \text{ Pa})(101.76 \text{ m}^3)}{(8.31451)(298 \text{ K})} = 536.60 \text{ moles of benzene}$$

$$536.60 \text{ mol} \times \frac{78.12 \text{ g}}{\text{mol}} = 41.92 \times 10^3 \text{ g} = 42. \text{ kg}$$

c)  $p = 1.7 \text{ mTorr}$  which equals  $0.2266 \text{ Pa}$

$$n = \frac{(0.2266 \text{ Pa})(101.76 \text{ m}^3)}{(8.31451)(298 \text{ K})} = 0.009308 \text{ moles of mercury}$$

$$0.009308 \text{ mol} \times \frac{200.59 \text{ g}}{\text{mol}} = 1.87 \text{ g} = 1.9 \text{ g}$$

5.13) (a) Use the Clapeyron equation to estimate the slope of the solid-liquid phase boundary of water given that the enthalpy of fusion is  $6.008 \text{ kJ mol}^{-1}$  and the densities of ice and water at  $0^\circ\text{C}$  are  $0.91671$  and  $0.99984 \text{ g cm}^{-3}$ , respectively.

(b) Estimate the pressure required to lower the melting point of ice by  $1^\circ\text{C}$ .

a) For the solid-liquid phase boundary:

$$\frac{dp}{dT} = \frac{\Delta S_{trans}}{\Delta V_{trans}} = \frac{\Delta H_{fus}/T_f}{\Delta V_{fus}}$$

To determine  $\Delta V_{fus}$ :

$$V_m(s) = \frac{18.016 \text{ g/mol}}{0.91671 \text{ g/cm}^3} = 19.6529 \text{ cm}^3/\text{mol} = 19.6529 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$V_m(l) = \frac{18.016 \text{ g/mol}}{0.99984 \text{ g/cm}^3} = 18.01888 \text{ cm}^3/\text{mol} = 18.0189 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\text{So, } \Delta V_m = (18.0189 - 19.6529) \times 10^{-6} = -1.6340 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\begin{aligned} \frac{dp}{dT} &= \frac{6.008 \times 10^3}{(273.15)(-1.6340 \times 10^{-6})} = -1.346 \times 10^7 \text{ Pa/K} \\ &= -134.6 \text{ bar/K} \end{aligned}$$

b) to change the equilibrium by  $1 \text{ K}$  ( $1^\circ\text{C}$ ),  $p \sim 134.6 \text{ bar}$  (definition of the slope)

5.15) The vapor pressure of mercury at 20°C is 160 mPa; what is its vapor pressure at 50°C given that its enthalpy of vaporization is 59.30 kJ mol<sup>-1</sup>?

Using the integrated Clausius-Clapeyron eqn.:

$$\begin{aligned}\ln p' &= \ln p + \frac{\Delta H_{vap}}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) \\ &= \ln(160 \times 10^{-3}) + \frac{59.30 \times 10^3}{8.31451} \left( \frac{1}{293.15} - \frac{1}{323.15} \right) \\ &= 0.42605 \\ p' &= 1.53 \text{ Pa}\end{aligned}$$

5.17) Estimate the boiling point of benzene given that its vapor pressure is 20 kPa at 35°C and 50.0 kPa at 58.8°C.

1st find  $\Delta H_{vap}$  from the data using the integrated C-C equation:

$$\Delta H_{vap} = \frac{R \ln \frac{p'}{p}}{\left( \frac{1}{T} - \frac{1}{T'} \right)} = \frac{(8.31451) \ln \frac{50}{20}}{\left( \frac{1}{308.15} - \frac{1}{331.95} \right)} = 32744 \text{ J/mol}$$

The boiling point is defined as the temperature when the vapor pressure is equal to 1 atm or 101.325 kPa :

Solving for T' and using one of the data points given:

$$\begin{aligned}T' &= \left[ \frac{1}{T} - \frac{R \ln \frac{p'}{p}}{\Delta H_{vap}} \right]^{-1} \\ &= \left[ \frac{1}{331.95} - \frac{(8.31451) \ln 101.325 / 50.0}{32744} \right]^{-1} \\ &= 353 \text{ K}\end{aligned}$$

5.21) Use the phase diagram in Fig. 5.17 to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K, is subjected to the following cycle: (a) constant-pressure heating to 320 K, (b) isothermal compression to 100 atm, (c) constant-pressure cooling to 210 K, (d) isothermal decompression to 1.0 atm, (e) constant-pressure heating to 298 K.

- a) CO<sub>2</sub> is a gas at the initial conditions and as the gas heats at constant pressure, its molar volume increases
- b) it stays a gas during the isothermal compression, but its molar volume greatly decreases and it becomes very dense. Note that this final temperature and pressure are above the critical point, hence the gas is now supercritical.
- c) As the gas is cooled from 320 K it condenses to a liquid at the critical temperature, but without a discernable phase transition. No pause in the temperature drop would be observed if we were withdrawing heat at a constant rate. During this process the molar volume decreases. At about 220 K, we would observe a sharp liquid-solid phase transition with its accompanying pause in the temperature drop. The molar volume also will decrease as all of the liquid is converted into solid. At the final temperature, CO<sub>2</sub> is a solid.
- d) The molar volume slightly increases as we go from 100 atm to 1.0 atm at constant temperature. At a pressure of about 2 atm, a sharp phase transition would be observed as the solid sublimates directly to the gas phase. A large increase in the molar volume is observed.
- e) The gas expands slightly back to its original molar volume.