

## Solutions to Homework Problem Set 14

Stowe 14.43

(a) The molar volume of iron in the solid phase is  $v_{sol} = \frac{55.8\text{g/mol}}{7.80\text{g/cm}^3} = 7.15\text{cm}^3/\text{mol} = 7.15 \times 10^{-6}\text{m}^3/\text{mol}$ . The molar volume of iron in the liquid phase is  $v_{liq} = \frac{55.8\text{g/mol}}{7.06\text{g/cm}^3} = 7.90\text{cm}^3/\text{mol} = 7.90 \times 10^{-6}\text{m}^3/\text{mol}$ .

(b) The change in the molar volume when the solid iron melts is therefore  $\Delta v = v_{liq} - v_{sol} = 0.75 \times 10^{-6}\text{m}^3/\text{mol}$ .

(c) The differential relation between the phase equilibrium pressure and temperature is given by  $\frac{dP}{dT} = \frac{L}{T\Delta v}$ . Here,  $\Delta v$  refers to the volume change when a solid melts, or when a liquid evaporates, and  $L$  ( $> 0$ ) is the latent heat absorbed by the substance to melt or to evaporate by overcoming the cohesive intermolecular force. The phase equilibrium temperature  $T$  is always positive. Therefore, if  $\Delta v$  is positive,  $dP/dT$  is also positive, indicating that when the solid melts at higher temperature, the phase equilibrium pressure also increases. Equivalently, we may say that the melting point (equilibrium temperature) increases with pressure.

(d) Integrating the relation in (c), we may arrive at  $P = P_0 + \frac{L}{\Delta v} \ln \frac{T}{T_0}$ , assuming that  $L$  and  $\Delta v$  are both constant.  $T_0$  is the melting point at the atmospheric pressure  $P_0 = 1\text{atm}$ . So  $P = P_0 + \frac{1.49 \times 10^4 \text{J/mol}}{0.75 \times 10^{-6} \text{m}^3/\text{mol}} \ln \frac{1600+273\text{K}}{1530+273\text{K}} = 7.57 \times 10^8 \text{Pa} = 7.49 \times 10^3 \text{atm}$ .

Stowe 14.44

(a) The procedures are the same as in the previous problem. For water, the molar volume in the solid phase (ice) is  $v_{sol} = \frac{18\text{g/mol}}{0.917\text{g/cm}^3} = 1.96 \times 10^{-5}\text{m}^3/\text{mol}$ . The molar volume in the liquid phase is  $v_{liq} = \frac{18\text{g/mol}}{0.9999\text{g/cm}^3} = 1.80 \times 10^{-5}\text{m}^3/\text{mol}$ .

(b) The change in the molar volume when the solid iron melts is therefore  $\Delta v = v_{liq} - v_{sol} = -0.16 \times 10^{-5}\text{m}^3/\text{mol}$ .

(c) In this case, because  $\Delta v$  is negative when ice water melts into liquid water,  $dP/dT < 0$ . So at a lower temperature, the phase equilibrium pressure increases. Equivalently, the melting point of water decreases with higher pressure. This situation is different from the case of iron. It explains why ice melts when you step on ice.

(d) Using the relation from the previous problem,  $P = P_0 + \frac{L}{\Delta v} \ln \frac{T}{T_0} = P_0 + \frac{6.01 \times 10^3 \text{J/mol}}{-0.16 \times 10^{-5} \text{m}^3/\text{mol}} \ln \frac{-30+273\text{K}}{273\text{K}} = 4.37 \times 10^8 \text{Pa} = 4.33 \times 10^3 \text{atm}$ . So when the pressure raises to more than 4,000 atmospheric pressure, ice water would melt at -30 Celsius degree.

Stowe 14.47

We start from the differential relation  $\frac{dP}{dT} = \frac{L}{T\Delta v}$ . For an ideal gas,  $\Delta v \approx v_{gas} = \frac{RT}{P}$ , and with  $L = A + BT$ , we get

$$\frac{dP}{dT} = \frac{(A + BT)P}{RT^2}$$

or

$$\frac{dP}{P} = \frac{(A + BT)dT}{RT^2}$$

Integrating the relation, we get

$$\ln P = \frac{B}{R} \ln T - \frac{A}{RT} + \text{const.} = \ln \left[ T^{\frac{B}{R}} e^{-\frac{A}{RT}} \right] + \text{const.}$$

or

$$P = CT^{\frac{B}{R}} e^{-\frac{A}{RT}}$$

where  $C$  is a constant.