

Problem Set 8

P1

a) By what amount does the chemical potential of water exceed that of ice at -5.00°C ?

$$\Delta\mu = \Delta G_m = -\Delta S_m \Delta T \text{ at constant } P$$

$$\Delta\mu = \Delta G_m = -(S_{H_2O,l}^\circ - S_{H_2O,s}^\circ)(\Delta T) = (70.0 \text{ J K}^{-1}\text{mol}^{-1} - 48.0 \text{ J K}^{-1}\text{mol}^{-1})(-5.00^\circ\text{C}) \\ = 110 \text{ J mol}^{-1}$$

b) By what amount does the chemical potential of water exceed that of steam at 105.00°C ?

$$\Delta\mu = \Delta G_m = -(S_{H_2O,l}^\circ - S_{H_2O,g}^\circ)(\Delta T) = -(70.0 \text{ J K}^{-1}\text{mol}^{-1} - 188.8 \text{ J K}^{-1}\text{mol}^{-1}) \times (5.00^\circ\text{C}) \\ = 594 \text{ J mol}^{-1}$$

P6

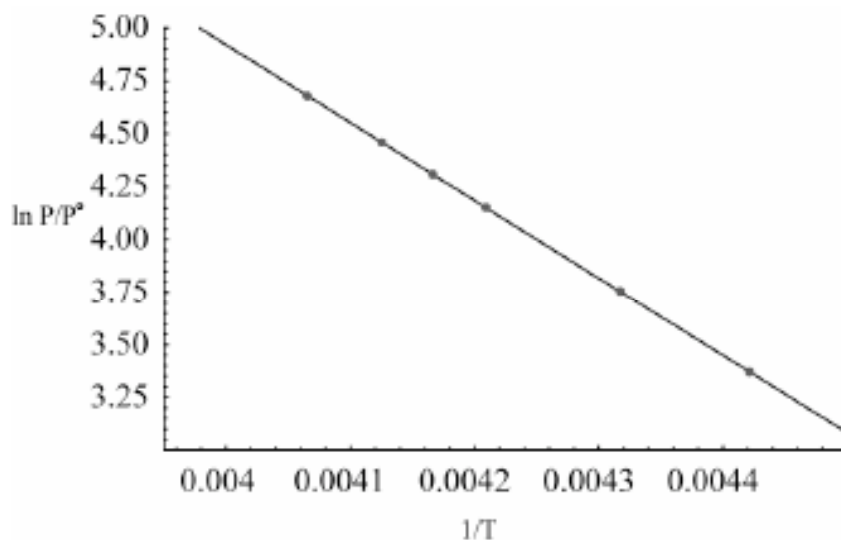
$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_m^{\text{vaporization}}}{R \left(\frac{\Delta H_m^{\text{vaporization}}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 760 \text{ Pa}$.

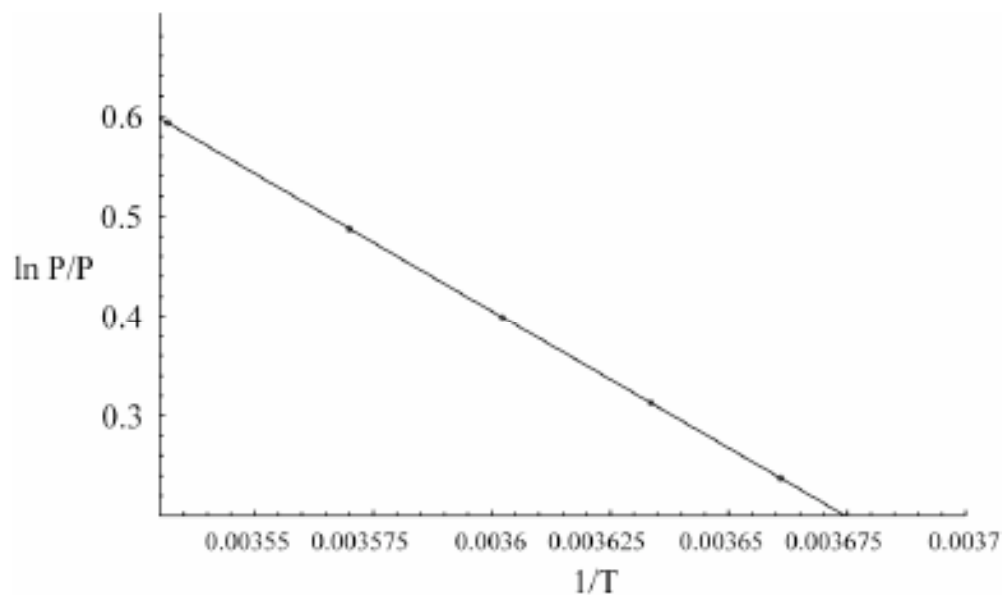
$$T_{b,\text{normal}} = \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \left(\frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 373.15 \text{ K}} - \ln \frac{380 \text{ Torr}}{760 \text{ Torr}} \right)} = 354.4 \text{ K}$$

P8



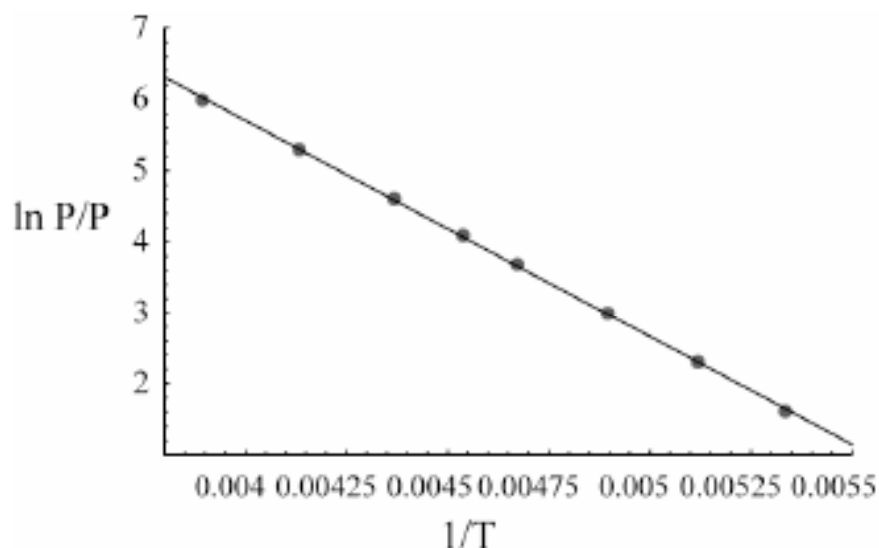
A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 30.58 \text{ kJ mol}^{-1}$.

P9



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 22.88 \text{ kJ mol}^{-1}$.

P11



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 25.28 \text{ kJ mol}^{-1}$.

P16

a) If the enthalpy of vaporization is current

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vaporization}}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln P_2 = \ln(0.4741) - \frac{27.66 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{373.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) = 1.4964$$

$$P_2 = 4.66 \text{ barr}$$

b) If the enthalpy of vaporization is given by

$$\Delta H_{\text{vaporization}}^{\circ}(T) = \Delta H_{\text{vaporization}}^{\circ}(T_0) + \Delta C_p(T - T_0)$$

$$\int \frac{dP}{P} = \int_{T_0}^T \frac{\Delta H_{\text{vaporization}}^{\circ}}{RT^2} dT = \int_{T_0}^T \frac{\Delta H_{\text{vaporization}}^{\circ}(T_0) + \Delta C_p (T - T_0)}{RT^2} dT$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vaporization}}^{\circ}(T_0)}{8.314} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_p T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_p}{R} \ln \frac{T}{T_0}$$

$$\ln P_2 = \ln(0.4741) - \frac{27.66 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{373.15} - \frac{1}{298.15} \right)$$

$$+ \frac{(45.4 - 75.7) \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{373.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(45.4 - 75.7) \text{ J mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \ln \frac{373.15 \text{ K}}{298.15 \text{ K}}$$

$$\ln P_2 = 1.411$$

$$P_2 = 4.10 \text{ bar}$$

P18

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{\text{sublimation}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_f}{P_i} = -\frac{6.008 \times 10^3 \text{ J mol}^{-1} + 40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{262.65 \text{ K}} - \frac{1}{273.16 \text{ K}} \right) = 0.822205$$

$$\frac{P_f}{P_i} = 0.439; \quad P_f = 0.439 \times 611 \text{ Pa} = 269 \text{ Pa}$$

P20

For a liquid-gas equilibrium involving a single species, $K_p = \frac{P}{P^{\circ}}$

$$\Delta H = -R \frac{d \ln K_p}{d \left(\frac{1}{T} \right)} = RT^2 \frac{d \ln K_p}{dT} = RT^2 \frac{d \left(A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} \right)}{dT}$$

$$\Delta H = \frac{RT^2 A(2)}{\left[\frac{T}{\text{K}} + A(3) \right]^2}$$

P25

$$\ln \frac{P(298 \text{ K})}{\text{Pa}} = 20.801 - \frac{2.6524 \times 10^3}{298 - 33.402}$$

$$\frac{P(298 \text{ K})}{\text{Pa}} = 4.79 \times 10^4$$

$$\ln \left(\frac{P}{P_0} \right) = \frac{V_m^{\text{liquid}} (P - P_0)}{RT} = \frac{M}{\rho_{\text{liquid}} RT} (P - P_0)$$

$$\ln \left(\frac{P}{P_0} \right) = \frac{76.14 \times 10^{-3} \text{ kg mol}^{-1}}{1255 \text{ kg m}^{-3}} \times (200 \times 10^5 \text{ Pa} - 4.789 \times 10^4 \text{ Pa})$$

$$= \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{0.488576}$$

$$P = 1.6299 P_0 = 1.6299 \times 4.789 \times 10^4 \text{ Pa} = 7.806 \times 10^4 \text{ Pa}$$

P29

$$\left(\frac{dP}{dT} \right)_{\text{fusion}} = \frac{\Delta S_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} = \frac{\Delta H_m^{\text{fusion}}}{T_{\text{fusion}} M \left(\frac{1}{\rho_{\text{liquid}}} - \frac{1}{\rho_{\text{solid}}} \right)}$$

$$= \frac{6008 \text{ J mol}^{-1}}{273.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{998 \text{ kg m}^{-3}} - \frac{1}{917 \text{ kg m}^{-3}} \right)} = -1.38 \times 10^7 \text{ Pa K}^{-1}$$

$$\left(\frac{dP}{dT} \right)_{\text{fusion}} = -138 \text{ bar K}^{-1}$$

$$\Delta T = -\frac{\Delta P}{138 \text{ bar K}^{-1}} = -0.72 \text{ K at 100 bar and } -3.62 \text{ K at 500 bar}$$