

Homework 3

4.4) a) CO_2 @ 1.0 atm & 298K raised to 320K is still a gas.

b) The sample is now a super-critical liquid.

c) @ 210K, the sample is a solid.

d) The sample will ~~sublime~~ sublime at 1.0 atm & 210K.

e) The CO_2 is now a gas, as it was in a).

$$E 4.2a) \frac{dP}{dT} = \frac{\Delta T_{fus} S}{\Delta T_{fus} V}$$

$$\Delta S_{fus} = \Delta_{fus} V \times \left(\frac{dP}{dT} \right) \approx \Delta_{fus} V \times \frac{\Delta P}{\Delta T}$$

$$\Delta_{fus} S = [163.3 - 161.0] \times 10^{-6} \text{ m}^3/\text{mol} \cdot \left(\frac{(100-1) \times (1.013 \times 10^5 \text{ Pa})}{(351.26 - 350.75) \text{ K}} \right)$$

$$= \boxed{45.23 \text{ J/K}\cdot\text{mol}}$$

$$\Delta_{fus} H = T_f \Delta S = (350.75 \text{ K}) \times (45.23 \text{ J/K}\cdot\text{mol}) = \boxed{16 \text{ kJ/mol}}$$

$$4.5a) \Delta T \approx \frac{\Delta_{fus} V}{\Delta_{fus} S} \times \Delta P \approx \frac{T_f \Delta_{fus} V \times \Delta P}{\Delta_{fus} H} = \frac{T_f \Delta_{fus} V}{\Delta_{fus} H} \times \Delta \left(\frac{1}{P} \right)$$

$$\cancel{P} \quad V_m = \frac{M}{\rho}$$

$$\approx \left(\frac{278.6 \text{ K} \times (999) \times (1.013 \times 10^5 \text{ Pa}) \times (78.12 \times 10^{-3} \text{ kg/mol})}{10.59 \times 10^3 \text{ J/mol}} \right) \cdot \left(\frac{1}{999} - \frac{1}{991} \right) \frac{1}{\text{kg/m}^3}$$

$$\approx \boxed{3.18 \text{ K}}$$

$$@ \cancel{1000 \text{ K}} \quad 1000 \text{ atm}, T_f \approx (278.6 + 3.18) \text{ K} = \boxed{281.8 \text{ K}}$$

E 4.8a) $\ln(P_2/P_1) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ Clausius - Clapeyron

a) ~~$\ln\left(\frac{40 \text{ kPa}}{10 \text{ kPa}}\right) = \frac{\Delta_{\text{vap}}H}{R}$~~

a) $\ln\left(\frac{5.3 \text{ kPa}}{1.3 \text{ kPa}}\right) = \frac{\Delta_{\text{vap}}H}{(8.314 \text{ J/K}\cdot\text{mol})} \times \left(\frac{1}{359 \text{ K}} - \frac{1}{392.5 \text{ K}}\right) = \boxed{49.1 \text{ kJ/mol}}$

b) Normal boiling point corresponds to 760 Torr

$\ln\left(\frac{101.3 \text{ kPa}}{5.3 \text{ kPa}}\right) = \left(\frac{49.1 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K}\cdot\text{mol}}\right) \times \left(\frac{1}{392.5 \text{ K}} - \frac{1}{T_b}\right)$

$2.95 = \frac{15.04 \text{ k}}{T_b} - 15.04 - \frac{5905 \text{ k}}{T_b}$; $\boxed{T_b = 488 \text{ K} = 215^\circ\text{C}}$

c) $\Delta_{\text{vap}}S(T_b) = \frac{\Delta_{\text{vap}}H(T_b)}{T_b} \approx \frac{49.1 \times 10^3 \text{ J/mol}}{488 \text{ K}} = \boxed{101 \text{ J/K}\cdot\text{mol}}$

P 4.5) a) ~~$\frac{\partial V}{\partial P}$~~ $\left(\frac{\partial V}{\partial P}\right)_T = V_m$

$\left(\frac{\partial V(l)}{\partial P}\right)_T - \left(\frac{\partial V(s)}{\partial P}\right)_T = V_{m,l} - V_{m,s}$

$= \frac{1.00 \text{ g}}{1 \text{ cm}^3} - 0.917 \text{ g/cm}^3$; $V_{m,l} = (1.00 \text{ cm}^3/\text{g}) \cdot 18 \text{ g/mol} = 18 \text{ cm}^3/\text{mol}$
 $V_{m,s} = (1.09 \text{ cm}^3/\text{g}) \cdot 18 \text{ g/mol} = 19.63 \text{ cm}^3/\text{mol}$

$\Delta\left(\frac{\partial V}{\partial P}\right)_T, l \rightarrow s = -1.63 \text{ cm}^3/\text{mol}$

$$b) \left(\frac{\partial u(l)}{\partial p} \right)_T - \left(\frac{\partial u(g)}{\partial p} \right)_T = V_{m,g} - V_{m,l}$$

$$V_{m,g} = 1.67 \text{ dm}^3/\text{g} \cdot 18 \text{ g/mol} = 30.1 \text{ dm}^3/\text{mol} = 0.0301 \text{ m}^3/\text{mol}$$

$$V_{m,l} = 1.04 \text{ cm}^3/\text{g} \cdot 18 \text{ g/mol} = \frac{1.04}{18.72} \text{ cm}^3/\text{mol} = \frac{0.00104}{0.01872} \text{ dm}^3/\text{mol}$$

$$\Delta \left(\frac{\partial u}{\partial p} \right)_{T, g \rightarrow l} = \boxed{30.1 \text{ dm}^3/\text{g}}$$

$$c) \Delta u_{\text{gas}} = \frac{V_m}{p} \Delta u_l = \frac{(M \Delta p)}{p} = \frac{(1.802 \times 10^{-2} \text{ kg/mol})(0.2 \text{ atm} \cdot 101325 \text{ Pa})}{\cancel{0.379 \text{ kg/m}^3} 961 \text{ kg/m}^3}$$

$$p = \frac{1}{1.04 \text{ cm}^3/\text{g}} = \frac{\cancel{0.379 \text{ kg/m}^3}}{961 \text{ kg/m}^3}$$

$$\Delta u_l = 0.3798 \text{ J/mol}; p = \frac{1}{1.67 \text{ dm}^3/\text{g}} = 0.598 \text{ kg/m}^3$$

$$\Delta u_g = \frac{(1.802 \times 10^{-2} \text{ kg/mol})(0.2 \text{ atm} \cdot 101325 \text{ Pa/atm})}{0.598 \text{ kg/m}^3} = 609.55 \text{ J/mol}$$

$$609.55 \text{ J/mol} - 0.3798 \text{ J/mol} = 609 \text{ J/mol} \text{ or } \boxed{0.6 \text{ kJ/mol}}$$

$$4.17) \left(\frac{\partial u}{\partial T} \right)_p = -S_m; \frac{\partial}{\partial T} \left(\frac{\partial u}{\partial T} \right)_p = \left(\frac{-\partial S_m}{\partial T} \right)_p = -\frac{1}{T} \times C_{p,m}$$

Heat capacity is always positive \therefore the curvature is always negative.
State w/ the greatest curvature will determine depends on the substance.

E 5.3) If solution obeys Henry's law, then $\frac{P_B}{x_B} = \text{constant}$

$$\frac{P_B}{x_B} = \frac{32.0}{0.005} = 6.4 \times 10^3 \text{ kPa}; \quad \frac{76.7}{0.012} = 6.4 \times 10^3 \text{ kPa}, \quad \frac{121.8}{0.019} = 6.4 \times 10^3 \text{ kPa}$$

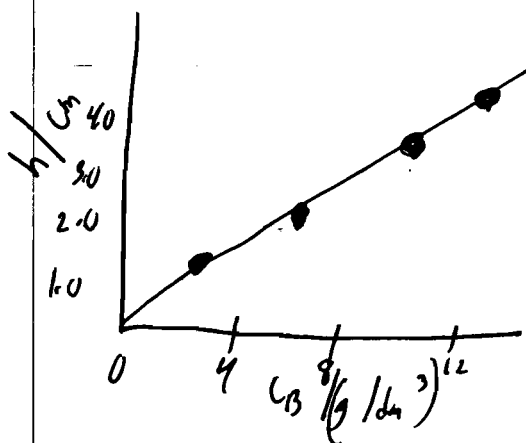
$$\therefore \boxed{K_B = 6.4 \times 10^3 \text{ kPa}}$$

D E 5.3) Colligative properties are function of concentration.
If you know the mass of a solute, then one can calculate the molar mass (g/mol).

Review eqns. 5.33, 5.34, 5.36, 5.37 & 5.40.

$$5.19a) \pi V = n_B RT, \quad \pi = \frac{n_B RT}{MV} = \frac{C RT}{M}; \quad C = \frac{m}{V}$$

where $\pi = \rho g h$ (hydrostatic pressure) $h = \left(\frac{RT}{\rho g M} \right) c$



$$\text{Slope} = \frac{RT}{\rho g M} = \frac{0.29 \text{ cm}}{9 \text{ dm}^{-3}} = 0.29 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1}$$

$$M = \frac{RT}{(\rho g) (0.29 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})}$$

$$= \frac{(8.314 \text{ J/Kmol}) (298.15 \text{ K})}{(1004 \times 10^3 \text{ kg/m}^3) (9.81 \text{ m/s}^2) (0.29 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})} = \boxed{87 \text{ kg/mol}}$$

E 5, 16a) ideal + dilute: obey Raoult's law. (CCl_4)
 Br_2 obeys Henry's law

$$p(\text{CCl}_4) p^*(\text{CCl}_4) = (0.950)(33.85) \text{ Torr} = 32.2 \text{ Torr}$$

$$p(\text{Br}_2) = x(\text{Br}_2) K(\text{Br}_2) = (0.050)(122.36 \text{ Torr}) = 6.1 \text{ Torr}$$

$$p(\text{Total}) = (32.2 + 6.1) \text{ Torr} = \boxed{38.3 \text{ Torr}}$$

Composition of the Vapor

$$y(\text{CCl}_4) = \frac{p(\text{CCl}_4)}{P(\text{Total})} = \frac{32.2 \text{ Torr}}{38.3 \text{ Torr}} = \boxed{0.841}$$

$$y(\text{Br}_2) = \frac{p(\text{Br}_2)}{P(\text{Total})} = \frac{6.1 \text{ Torr}}{38.3 \text{ Torr}} = \boxed{0.16}$$

1.

$$\Delta P = ? \quad \text{for} \quad \Delta T = -5 \text{ K}$$

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{T \Delta V}$$

$$\Delta V = \frac{1}{\text{density liq}} - \frac{1}{\text{density sol}} = \frac{1}{1} - \frac{1}{.917} = -.0905 \text{ cm}^3$$

$$\Delta V = -9.05 \cdot 10^{-2} \text{ cm}^3 \text{ g}^{-1} = -9.05 \cdot 10^{-8} \text{ m}^3 \text{ g}^{-1}$$

$$\frac{\Delta P}{\Delta T} = \frac{333.5 \text{ J g}^{-1}}{(273.15 \text{ K})(-9.05 \cdot 10^{-8} \text{ m}^3 \text{ g}^{-1})} = -1.35 \cdot 10^7 \frac{\text{Pa}}{\text{K}}$$

$$\Delta P = (-1.35 \cdot 10^7 \frac{\text{Pa}}{\text{K}})(-5 \text{ K}) = 6.75 \cdot 10^7 \text{ Pa}$$

$$\Delta P = \rho g h \quad \rho \text{ in } \text{kg m}^{-3} \quad \begin{matrix} 0.917 \text{ g cm}^{-3} \\ 9.17 \cdot 10^2 \text{ kg m}^{-3} \end{matrix}$$

$$h = \frac{\Delta P}{\rho g} = \frac{6.75 \cdot 10^7 \text{ Pa}}{(917 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2})} = \underline{7.5 \text{ km!}}$$

2)

VP @ various T for l & s

X find $\Delta_{\text{sub}} H$, $\Delta_{\text{vap}} H$, $\Delta_{\text{fus}} H$ and the triple pt

VP X(s) 2.64 TORR @ -112°C
0.263 TORR @ -126.5°C

VP X(l) 11.93 TORR @ -100°C
55.36 TORR @ -80°C

$$\int_{\ln p^*}^{\ln p} d \ln p = - \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

$$\ln \left(\frac{p}{p^*} \right) = - \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

for liq X

$$\ln \left(\frac{11.93}{55.36} \right) = - \frac{\Delta_{\text{vap}} H}{R} \left(\frac{1}{173\text{K}} - \frac{1}{193\text{K}} \right)$$

$$\Delta_{\text{vap}} H = 21.3 \text{ kJ/mole}$$

for solid X

$$\ln \left(\frac{2.64}{0.263} \right) = - \frac{\Delta_{\text{sub}} H}{R} \left(\frac{1}{161} - \frac{1}{146.5} \right)$$

$$\text{use } R = 8.314 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{sub}} H = 31.2 \text{ kJ/mole}$$

$$\Delta_{\text{fus}} H = \Delta_{\text{sub}} H - \Delta_{\text{vap}} H = 31.2 \text{ kJ/mole} - 21.3 \text{ kJ/mole}$$

$$= \cancel{52.5 \text{ kJ/mole}} = 9.9 \text{ kJ/mol}$$

$$\Delta_{\text{sub}} H = H_{\text{gas}} - H_{\text{sol}}$$

$$- (H_{\text{gas}} - H_{\text{liq}}) = H_{\text{liq}} - H_{\text{sol}}$$

find the Triple point

P_{15} & T_{15} known for solid P_{Trip} & T_{Trip} unknown

$$\ln\left(\frac{P_{\text{Trip}}}{P_{15}}\right) = \frac{-\Delta H_{\text{sub}}}{R} \left[\frac{1}{T_{\text{Trip}}} - \frac{1}{T_{15}} \right]$$

$$P_{15} = 2.64 \text{ TORR}$$
$$T_{15} = 161 \text{ K}$$

P_{12} & T_{12} known P_{Trip} & T_{Trip} unknown

$$\ln\left(\frac{P_{\text{Trip}}}{P_{12}}\right) = \frac{-\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_{\text{Trip}}} - \frac{1}{T_{12}} \right]$$

$$P_{12} = 11.93 \text{ TORR}$$
$$T_{12} = 163 \text{ K}$$

$$\ln P_{\text{Trip}} = \frac{-\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_{\text{Trip}}} - \frac{1}{T_{12}} \right] + \ln P_{12}$$

$$\ln P_{\text{Trip}} = \frac{-\Delta H_{\text{sub}}}{R} \left[\frac{1}{T_{\text{Trip}}} - \frac{1}{T_{15}} \right] + \ln P_{15}$$

set equal

$$\frac{-\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_{\text{Trip}}} - \frac{1}{T_{12}} \right] + \ln P_{12} = \frac{-\Delta H_{\text{sub}}}{R} \left[\frac{1}{T_{\text{Trip}}} - \frac{1}{T_{15}} \right] + \ln P_{15}$$

$$\frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_{\text{Trip}}} \right) + \frac{\Delta H_{\text{sub}}}{R} \left(\frac{1}{T_{\text{Trip}}} \right) = \frac{-\Delta H_{\text{sub}}}{R T_{12}} - \ln P_{12} + \frac{\Delta H_{\text{sub}}}{R T_{15}} + \ln P_{15}$$

$$\frac{1}{T_{\text{Trip}}} = \frac{\left(\frac{-\Delta H_{\text{vap}}}{R T_{12}} + \frac{\Delta H_{\text{sub}}}{R T_{15}} + \ln\left(\frac{P_{15}}{P_{12}}\right) \right)}{\left(\frac{-\Delta H_{\text{vap}}}{R} + \frac{\Delta H_{\text{sub}}}{R} \right)}$$

$$\frac{1}{T_{TRIP}} = \left(\frac{-21.3 \text{ kJ/mole} \cdot \text{K}}{\text{mole} \cdot 8.314 \cdot 10^{-3} \text{ kJ} \cdot 163 \text{ K}} + \frac{31.2 \text{ kJ/mole} \cdot \text{K}}{\text{mole} \cdot 8.314 \cdot 10^{-3} \text{ kJ} \cdot 161 \text{ K}} + \ln \left(\frac{2.64 \text{ TORR}}{11.95 \text{ TORR}} \right) \right)$$

$$\frac{8.314 \text{ J}}{\text{mole} \cdot \text{K}} \left(\frac{\text{kJ}}{1000 \text{ J}} \right) = \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mole} \cdot \text{K}}$$

$$\left(\frac{-21.3 \text{ kJ/mole} \cdot \text{K}}{\text{mole} \cdot 8.314 \cdot 10^{-3} \text{ kJ}} + \frac{31.2 \text{ kJ/mole} \cdot \text{K}}{\text{mole} \cdot 8.314 \cdot 10^{-3} \text{ kJ}} \right)$$

$$\frac{1}{T_{TRIP}} = 0.0051 \text{ K}^{-1}$$

$$T_{TRIP} = 195.75 \text{ K}$$

sub into eq. to find P_{TRIP}

$$\ln \left(\frac{P_{TRIP}}{P_{15}} \right) = \frac{-\Delta H_{\text{sub}}}{R} \left(\frac{1}{T_{TRIP}} - \frac{1}{T_{15}} \right)$$

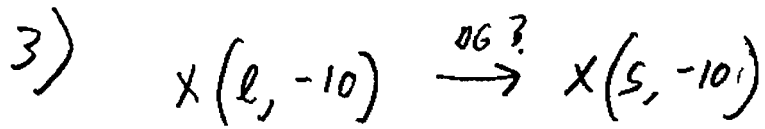
$$\ln \frac{P_{TRIP}}{P_{15}} = \frac{-\Delta H_{\text{sub}}}{R} \left(\frac{1}{T_{TRIP}} - \frac{1}{T_{15}} \right)$$

$$= \frac{-31.2 \text{ kJ/mole} \cdot \text{K}}{\text{mole} \cdot 8.314 \cdot 10^{-3} \text{ kJ}} \left(\frac{1}{195.75 \text{ K}} - \frac{1}{161 \text{ K}} \right)$$

$$e^{\left(\ln \frac{P_{TRIP}}{P_{15}} = 4.14 \right)} \rightarrow 2.64 \text{ TORR}$$

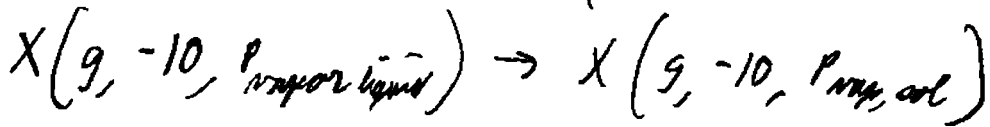
$$P_{TRIP} = \left(e^{4.14} \right) P_{15}$$

$$P_{TRIP} = 165.8 \text{ TORR}$$



$$\downarrow \Delta G = 0$$

$$\uparrow \Delta G = 0$$



$$\Delta G = nRT \ln \left(\frac{P_f}{P_i} \right) = \cancel{1 \text{ mole}} \frac{8.314 \text{ J} \cdot 263 \text{ K}}{\cancel{\text{K} \cdot \text{mole}}} \ln \left(\frac{2.6 \times 10^{-3} \text{ bar}}{2.9 \times 10^{-3} \text{ bar}} \right)$$

$$\text{say } n = 1$$

$$T = 263 \text{ K}$$

$$\Delta G = -238.77 \text{ J}$$

5) a) bp, fp and osmotic pressure
 1L H₂O w/ 10g NaCl 23+35.5g/mole = 58.5g/mole

$v = -0.6$

$\Delta T = K_b b$

$K_b_{H_2O} = 0.51 \text{ K}\cdot\text{kg/mole}$

$\frac{10\text{g/mole}}{(58.5\text{g})} = 0.17 \text{ moles NaCl}$

density of H₂O $\frac{1\text{g}}{\text{mL}} \left(\frac{1000\text{mL}}{\text{L}} \right) = \frac{1000\text{g}}{\text{L}}$

$1000\text{g} \left(\frac{\text{mole}}{18\text{g}} \right) = 55.6 \text{ moles H}_2\text{O}$

$\frac{\text{mole of solute}}{\text{kg of solvent}}$

due to dissociation of the NaCl ← calc molality, b
 $b = \frac{2(0.17) \text{ moles solute}}{1\text{kg}}$
 $b = 0.34 \text{ moles/kg}$

$\Delta T = \frac{0.51 \text{ K}\cdot\text{kg}}{\text{mole}} \cdot \frac{0.34 \text{ mole}}{\text{kg}}$

$\Delta T = 0.1734$
 $T_{b,H_2O} = 373.15 + 0.1734$
 $T_{b,H_2O} = 373.323 \text{ K}$

Bp

$\Delta T = K_f b = \frac{1.86 \text{ K}\cdot\text{kg}}{\text{mole}} \cdot \frac{0.34 \text{ mole}}{\text{kg}} = 0.6324$

$\Delta T = 0.6324$
 $T_f = 273.15 - 0.6324$
 $T_f = 272.518 \text{ K}$

fp

$\Pi = [b]RT$
 $b = \frac{2 \cdot 0.17 \text{ moles}}{1\text{L H}_2\text{O}}$
 $b = 0.34 \text{ M}$

$\Pi = \frac{0.34 \text{ moles}}{\text{mole}\cdot\text{L}} \left(8.314 \times 10^{-2} \text{ K}\cdot\text{bar} \right) 298 \text{ K}$

$T = 298 \text{ K}$

$\Pi = 8.42 \text{ bar}$ Osmotic Pressure