

HW 3 KEY

CH 4

P4.4 At 298 K and 1 atm, $\text{CO}_2(\text{g})$. (a) After heating to 320 K at constant P, $\text{CO}_2(\text{g})$. (b) Isothermal compression to 100 atm brings CO_2 into supercritical region. (c) After cooling to 210 K at constant P, $\text{CO}_2(\text{s})$. (d) sublimes, $\text{CO}_2(\text{g})$. (e) Initial conditions, $\text{CO}_2(\text{g})$.

E4.2a $\frac{dP}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V}$; $\Delta_{\text{fus}} S = \frac{dP}{dT} \Delta_{\text{fus}} V \approx \frac{\Delta P}{\Delta T} \Delta_{\text{fus}} V$

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

$$\Delta_{\text{fus}} S = 45.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$\Delta G = \Delta H - T\Delta S$; $\Delta G = 0$ equilibrium

$\Delta_{\text{fus}} H = T\Delta_{\text{fus}} S = (350.75 \text{ K})(45.23 \text{ J K}^{-1} \text{ mol}^{-1})$

$\Delta_{\text{fus}} H = 16 \text{ kJ mol}^{-1}$

E4.5a $\Delta T \approx \frac{\Delta V_{\text{fus}}}{\Delta_{\text{fus}} S} \cdot \Delta P$

$\approx \frac{T_f \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \cdot \Delta P = \frac{T_f \Delta P M}{\Delta_{\text{fus}} H} \times \Delta \left(\frac{1}{\rho} \right)$

$V_m = \frac{M}{\rho}$

$\Delta T \approx \left(\frac{1}{879} - \frac{1}{891} \right) \times \frac{(278.6 \text{ K})(999 \text{ atm})(1.013 \times 10^5 \text{ Pa atm}^{-1})(78.12 \text{ g mol}^{-1})(10^3)}{(10.59 \times 10^3 \text{ J mol}^{-1})}$

$\Delta T \approx 3.18 \text{ K}$

\therefore At 1000 atm, $T_f \approx (278.6 + 3.18) \text{ K} = 281.8 \text{ K}$

E4.8a Integrated Clausius Clapeyron

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

$$\ln\left(\frac{40 \text{ kPa}}{10 \text{ kPa}}\right) = \left(\frac{\Delta_{\text{vap}}H}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \left(\frac{1}{359 \text{ K}} - \frac{1}{392.5 \text{ K}}\right)$$

$$\Delta_{\text{vap}}H = \frac{1.405}{2.86 \times 10^{-5} \text{ J}^{-1} \text{ mol}} = 49 \text{ kJ mol}^{-1}$$

P4.5 (a) $\left(\frac{d\mu(l)}{dP}\right)_T - \left(\frac{d\mu(s)}{dP}\right)_T = V_m(l) - V_m(s) = M \Delta\left(\frac{1}{\rho}\right)$

$$= (18.02 \text{ g mol}^{-1}) \left(\frac{1}{1.000 \text{ g cm}^{-3}} - \frac{1}{0.917 \text{ g cm}^{-3}}\right) = -1.63 \text{ cm}^3 \text{ mol}^{-1}$$

(b) $\left(\frac{d\mu(g)}{dP}\right)_T - \left(\frac{d\mu(l)}{dP}\right)_T = V_m(g) - V_m(l)$

$$= (18.02 \text{ g mol}^{-1}) \left(\frac{1}{0.598 \text{ g dm}^{-3}} - \frac{1}{0.958 \times 10^3 \text{ g dm}^{-3}}\right)$$

$$= 30.1 \text{ dm}^3 \text{ mol}^{-1}$$

At $P = 1 \text{ atm}$ and 100°C , $\mu(l) = \mu(g)$

Thus at $P = 1.2 \text{ atm}$ and 100°C , $\mu(g) - \mu(l) \approx \Delta_{\text{vap}}V \Delta P =$

$$= (30.1 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})(0.2)(1.013 \times 10^5 \text{ Pa}) = 0.6 \text{ kJ mol}^{-1}$$

Since $\mu(g) > \mu(l)$, the gas tends to condense to liquid.

P4.17 In each phase, slopes given by $\left(\frac{d\mu}{dT}\right)_P = -S_m$ (Eq 4.1)

$$\left(\frac{d^2\mu}{dT^2}\right)_P = -\left(\frac{dS_m}{dT}\right)_P = -\frac{1}{T} C_{p,m}$$

Since $C_{p,m}$ must be positive, the curvatures in all states of matter are negative. Since curvature is dependent on $C_{p,m}$ at T , no answer can be given. $C_{p,m}$ is often greatest for liquid state, however.

Ch5

D5.3 All colligative properties are a function of solute concentration, implying the concentration can be determined by measuring these colligative properties.

Knowing the mass of the solute allows for calc of molar mass. $x_B = \frac{m_B/M_B}{m_B/M_B + m_A/M_A}$ → only unknown is M_B

Also see example 5.4 to see how to calc. M from π .

E5.3a Check whether $\frac{P_B}{x_B}$ is equal to a constant (K_B)

x	0.005	0.012	0.019
P/x	6.4×10^3	6.4×10^3	6.4×10^3

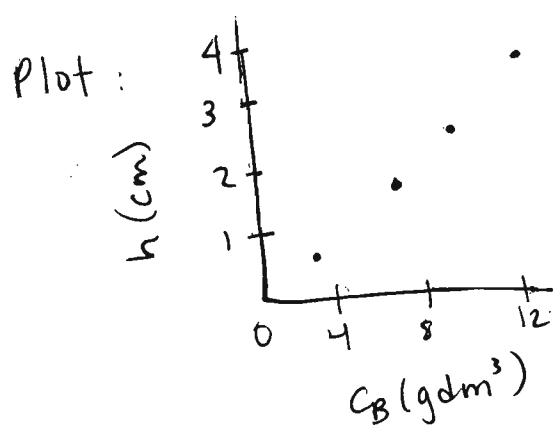
(all in kPa)

∴ $K_B \approx 6.4 \times 10^3$ kPa

E5.14a Best value of molar mass, M , is obtained when data is extrapolated to zero concentration, where $\pi V = n_B RT$ applies.

$$\pi = \frac{n_B RT}{V} = \frac{mRT}{MV} = \frac{cRT}{M} \text{ where } c = \frac{m}{V}$$

$$\pi = \rho g h, \text{ so } h = \left(\frac{RT}{\rho g M} \right) c$$



$$\text{slope} = \frac{RT}{\rho g M} = 0.29 \text{ cm dm}^3 \text{ g}^{-1}$$

$$= 0.29 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1}$$

$$M = \frac{RT}{\rho g (0.29)} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(1.004 \times 10^4 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2})(0.29 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})}$$

$$M = 87 \text{ kg/mol}$$

E5.16a

In an ideal dilute solution, CCl_4 obeys Raoult's law and Br_2 (solute) obeys Henry's law. → solvent

$$P(\text{CCl}_4) = x_{\text{CCl}_4} P_{\text{CCl}_4} = (0.95)(33.85 \text{ torr}) = 32.2 \text{ torr}$$

$$P(\text{Br}_2) = x_{\text{Br}_2} K_{\text{Br}_2} = (0.05)(122.36 \text{ torr}) = 6.1 \text{ torr}$$

$$P_{\text{total}} = (32.2 + 6.1) \text{ torr} = 38.3 \text{ torr}$$

The composition of the vapor in equilibrium w/ the liquid is:

$$y(\text{CCl}_4) = \frac{P_{\text{CCl}_4}}{P_{\text{tot}}} = \frac{32.2}{38.3} = 0.841$$

$$y(\text{Br}_2) = \frac{P_{\text{Br}_2}}{P_{\text{tot}}} = \frac{6.1}{38.3} = 0.159$$

DR. VDB's problems

① $\rho_{H_2O(l)} > \rho_{H_2O(s)}$ $P = \rho gh$ $\Delta_{fus}H = 333.5 \text{ Jg}^{-1}$
 $\text{gcm}^{-3}: 1.000 \quad 0.917$

How thick could a glacier made of pure $H_2O(s)$ get before the bottom of the glacier begins to melt at -5°C ?

$\Delta P = ?$ for $T = -5^\circ\text{C}$

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

$$\Delta V = \frac{1}{\rho_{liq}} - \frac{1}{\rho_{sol}} = \frac{1}{1.000} - \frac{1}{0.917} = \overset{-0.0905}{\cancel{0.083}} \text{ cm}^3 \text{ g}^{-1}$$

change units: $\Delta V = -9.05 \times 10^{-8} \text{ m}^3 \text{ g}^{-1}$

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

$\text{J m}^{-3} = 1 \text{ Pa}$

$$\Delta P = \Delta T \left(\frac{1.35 \times 10^7 \text{ Pa}}{\text{K}} \right) = (-5 \text{ K})(1.35 \times 10^7 \text{ Pa K}^{-1}) = 6.75 \times 10^7 \text{ Pa}$$

$$\Delta P = \rho gh, \text{ so } h = \Delta P / \rho g$$

$$h = \frac{6.75 \times 10^7 \text{ Pa}}{(917 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2})} = \boxed{7.5 \text{ km}} \text{ thickness}$$

② SOLID
 $P_1 = 2.64 \text{ Torr}$ $T_1 = 161.2 \text{ K}$
 $P_2 = 0.263 \text{ Torr}$ $T_2 = 146.7 \text{ K}$

$$\ln\left(\frac{0.263}{2.64}\right) = \frac{-\Delta_{sub}H}{R} \left(\frac{1}{146.7} - \frac{1}{161.2} \right) ; \Delta_{sub}H = +31.27 \text{ kJ mol}^{-1}$$

LIQUID - same way!

$$\Delta_{vap}H = 21.34 \text{ kJ mol}^{-1}$$

② continued

$$\Delta_{\text{fus}} H = \Delta_{\text{sub}} H - \Delta_{\text{vap}} H = 9.93 \text{ kJ mol}^{-1}$$

At triple point $P_{\text{vap}}(l) = P_{\text{vap}}(s)$

$$P_{\text{sol}} = 2.64 \text{ Torr} \quad T_{\text{sol}} = ~~161.2~~ 161.2 \text{ K}$$

$$P_{\text{liq}} = 11.93 \text{ Torr} \quad T_{\text{liq}} = 173.15 \text{ K}$$

It is obvious that triple point lies between

$$\text{Liquid: } \ln\left(\frac{P_{\text{trip}}}{11.93}\right) = \frac{-21.34 \text{ kJ mol}^{-1}}{8.314 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_{\text{trip}}} - \frac{1}{173.15}\right)$$

$$\text{Solid: } \ln\left(\frac{P_{\text{trip}}}{2.64}\right) = \frac{-31.27 \text{ kJ mol}^{-1}}{8.314 \times 10^3 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_{\text{trip}}} - \frac{1}{161.2}\right)$$

2 eqs, 2 unknowns

$$\ln\left(\frac{P_{\text{trip}}}{11.93}\right) - \ln\left(\frac{P_{\text{trip}}}{2.64}\right) = \frac{-21.34}{8.314 \times 10^3} \left(\frac{1}{T_{\text{trip}}} - \frac{1}{173.15}\right) + \frac{31.27}{8.314 \times 10^3} \left(\frac{1}{T_{\text{trip}}} - \frac{1}{161.2}\right)$$

$$\ln\left(\frac{2.64}{11.93}\right) = -2563 \left(\frac{1}{T_{\text{trip}}} - \frac{1}{173.15}\right) + 3761 \left(\frac{1}{T_{\text{trip}}} - \frac{1}{161.2}\right)$$

$$-1.51 = \frac{-2563}{T_{\text{trip}}} + \frac{2563}{173.15} + \frac{3761}{T_{\text{trip}}} - \frac{3761}{161.2} = \frac{1198}{T_{\text{trip}}} - 8.53$$

$$T_{\text{trip}} = 170.6 \text{ K}$$

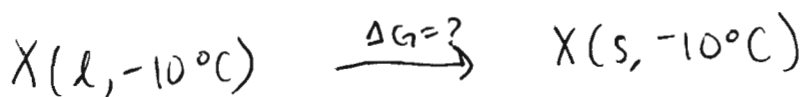
Find P_{triple} using Clausius Clapeyron

$$\ln\left(\frac{P_{\text{trip}}}{11.93}\right) = \frac{-21.34 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{170.6} - \frac{1}{173.15}\right)$$

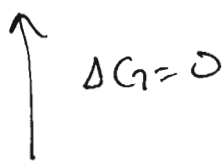
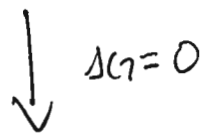
$$P_{\text{trip}} = 9.56 ~~11.93~~ \text{ Torr}$$

③ $T_{\text{fus}} = 0^\circ\text{C}$

supercooled: at -10°C , $P = 2.9 \times 10^3 \text{ bar}$ / solid: -10°C , $P = 2.6 \times 10^3 \text{ bar}$



$\Delta G = 0$ at phase change



$\Delta G = nRT \ln\left(\frac{P_f}{P_i}\right) = (1)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(263 \text{ K}) \ln\left(\frac{2.6}{2.9}\right)$

Let $n = 1 \text{ mol}$

$T = -10^\circ\text{C} = 263 \text{ K}$

$\Delta G = -238 \text{ J mol}^{-1}$

④ T_b, T_f, π of 1L H_2O with 10g NaCl

$\frac{10 \text{ g NaCl}}{1 \text{ L}} \frac{1 \text{ mol}}{58.5 \text{ g}} = 0.171 \text{ M NaCl}$

$\pi = iMRT$, $i = \text{van't Hoff factor} = 2$, $M = \text{molarity}$

(At room temp) $\pi = 2(0.171 \text{ M})(0.08206 \text{ Latm K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = 8.36 \text{ atm}$

Calculate molality = mol solute / kg solvent

$m = \frac{0.171 \text{ mol}}{1 \text{ kg}} = 0.171 \text{ mol kg}^{-1}$

$\Delta T = T_{\text{pure}} - T_{\text{soln}}$

$\Delta T = K_b b = (0.51 \text{ K kg mol}^{-1})(2)(0.171 \text{ mol kg}^{-1}) = 0.174 \text{ K}$

$T_b = 373.15 \text{ K} + 0.174 \text{ K} = 373.32 \text{ K}$

$\Delta T = K_f b = (1.86 \text{ K kg mol}^{-1})(2)(0.171 \text{ mol kg}^{-1})$

$\Delta T = 0.636 \text{ K}$

$T_f = 272.51 \text{ K}$