



I. (20%)

a) (10%) Show that the osmotic pressure  $\Pi = MRT$ , where M is molarity. State all your assumptions.

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi) = \mu_A^*(p + \Pi) + RT \ln x_A$$

$$\mu_A^*(p + \Pi) = \mu_A^*(p) + \int_p^{p + \Pi} V_m dp \quad (V_m = \text{molar volume of pure solvent})$$

$$\therefore \cancel{\mu_A^*(p)} = \cancel{\mu_A^*(p)} + \int_p^{p + \Pi} V_m dp + RT \ln x_A$$

$$\Rightarrow -RT \ln x_A = \int_p^{p + \Pi} V_m dp$$

$$\text{Assume liquid is incompressible} \Rightarrow -RT \ln x_A = V_m \int_p^{p + \Pi} dp$$

$$\ln x_A \approx \ln(1 - x_B) \approx -x_B \quad (\text{if } x_B \text{ is small})$$

$$\therefore RT x_B = \Pi V_m \Rightarrow \Pi = RT \frac{x_B}{V_m}$$

$$\text{Assume solution is dilute} \Rightarrow x_B \approx \frac{n_B}{n_A}$$

$$\therefore \Pi = RT \frac{n_B}{n_A V_m} = RT \frac{n_B}{V} \quad \text{where } V = n_A V_m \equiv \text{total volume of solvent}$$

$$\Rightarrow \Pi = RT [B] \quad \text{where } [B] = \text{molarity of dilute soln}$$

b. (10%) Derive Gibbs phase rule ( $f = r + 2 - n$ )

For a phase composed of  $r$  non-reacting components, there are  $(r+1)$  intensive variables:

$$\underbrace{T_\alpha, P_\alpha}_2, \underbrace{X_1^{(\alpha)}, X_2^{(\alpha)}, \dots, X_{r-1}^{(\alpha)}}_{r-1}$$

If we have  $n$  phases  $\Rightarrow n(r+1)$  intensive variables.

The conditions for thermal, mechanical, & chemical equilibria are:

$$\begin{array}{l} 2 \left\{ \begin{array}{l} P_1 = P_2 = \dots = P_n \\ T_1 = T_2 = \dots = T_n \end{array} \right. \\ r \left\{ \begin{array}{l} \mu_1^{(1)} = \mu_1^{(2)} = \dots = \mu_1^{(n)} \\ \vdots \\ \mu_r^{(1)} = \mu_r^{(2)} = \dots = \mu_r^{(n)} \end{array} \right. \\ \underbrace{\hspace{10em}}_{n-1} \end{array}$$

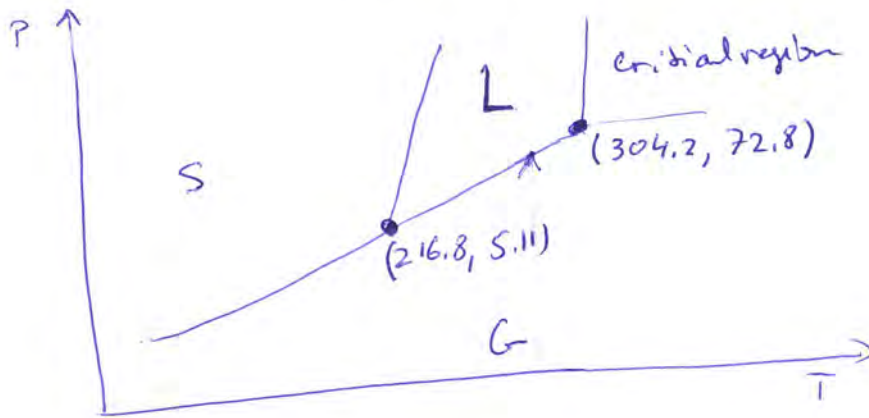
$\therefore$  there are  $(r+2)(n-1)$  constraints.

$\Rightarrow$  Total number of degrees of freedom are:

$$f = n(r+1) - (r+2)(n-1) = r + 2 - n.$$

II. (30 %) Carbon dioxide has a critical point at  $T_c = 304.2 \text{ K}$ ,  $p_c = 72.8 \text{ bar}$  and a triple point at  $T_3 = 216.8 \text{ K}$ ,  $p_3 = 5.11 \text{ bar}$ .  $\Delta_{\text{fus}}H = 8.34 \text{ kJ mol}^{-1}$ . Assume all the enthalpy changes are independent of temperature. (Hint: you may want to draw the phase diagram for guidance)

a) (10 %) Use the data above to estimate the enthalpy of vaporization and sublimation.



Using Clausius - Clapeyron:

$$\ln \frac{p_c}{p_3} = \frac{\overline{\Delta H_{\text{vap}}}}{R} \left( \frac{1}{T_c} - \frac{1}{T_3} \right) = \frac{\overline{\Delta H_{\text{vap}}}}{R} \left( \frac{T_c - T_3}{T_3 T_c} \right)$$

$$\overline{\Delta H_{\text{vap}}} = \left( \frac{T_3 T_c}{T_c - T_3} \right) \times R \times \ln \left( \frac{p_c}{p_3} \right) = \left( \frac{216.8 \times 304.2}{304.2 - 216.8} \right) \times 8.315 \times \ln \left( \frac{72.8}{5.11} \right)$$

$$\Rightarrow \overline{\Delta H_{\text{vap}}} = 16.67 \text{ kJ/mol}$$

$$\overline{\Delta H_{\text{vap}}} = \overline{\Delta H_{\text{sub}}} - \overline{\Delta H_{\text{fus}}} \Rightarrow \overline{\Delta H_{\text{sub}}} = 16.67 + 8.34 = 25.01 \text{ kJ/mol}$$



b) (10 %) What minimum pressure is required to liquefy carbon dioxide at 298 K?

$$\ln\left(\frac{P_{\min}}{P_3}\right) = \frac{\overline{\Delta H_{\text{vap}}}}{R} \left( \frac{T_{\min} - T_3}{T_{\min} \times T_3} \right) \Rightarrow$$

$$\ln \frac{P_{\min}}{5.11} = \frac{16.67 \times 10^3}{8.315} \left( \frac{298 - 216.8}{298 \times 216.8} \right) = 2.52$$

$$\Rightarrow \ln P_{\min} = \ln 5.11 + 2.52 = 4.45 \Rightarrow P_{\min} = 63.43 \text{ bar}$$

c) (10%) What is the sublimation temperature of carbon dioxide at 1 bar?

$$\ln\left(\frac{P}{P_3}\right) = \frac{\overline{\Delta H_{\text{sub}}}}{R} \left( \frac{T - T_3}{T \times T_3} \right) \Rightarrow$$

$$\ln\left(\frac{1}{5.11}\right) = \frac{25.01 \times 10^3}{8.315} \left( \frac{T - 216.8}{216.8 \times T} \right) \rightarrow$$

$$-0.00054 = \frac{T - 216.8}{216.8 \times T} \Rightarrow -0.118T = T - 216.8$$

$$\Rightarrow T = 194.0 \text{ K}$$

III. (20%) At 25°C, the density of a 50% by mass solution of ethanol/water is 0.914 g/mL. The partial molar volume of water under these conditions is 17.4 mL/mol.

a) (10%) What is the partial molar volume of ethanol?

$$\text{Let } M_{\text{solution}} = 100 \text{ g} \Rightarrow V_{\text{soln}} = \frac{100 \text{ g}}{0.914 \frac{\text{g}}{\text{mL}}} = 109.41 \text{ mL}$$

$$V_{\text{soln}} = n_w \bar{V}_w + n_{\text{et}} \bar{V}_{\text{et}} \Rightarrow \bar{V}_{\text{et}} = \frac{V_{\text{soln}} - n_w \bar{V}_w}{n_{\text{et}}} \Rightarrow$$

$$\bar{V}_{\text{et}} = \frac{109.41 - \frac{50}{48} \times 17.4}{\frac{50}{46}} = 56.11 \text{ mL}$$

b) (10%) If the density of pure water at 25 °C is 0.993 g/mL and that of ethanol is 0.779 g/mL, by what fraction did the volume of the solution change from the ideal case?

$$V_{\text{id}} = V_w + V_{\text{et}} = \frac{50}{0.993} + \frac{50}{0.779} = 114.54 \text{ mL}$$

$$\Delta V = V_{\text{id}} - V_{\text{real}} = 114.54 - 109.41 = 5.13$$

$\therefore$  shrinkage by 5.13 mL.

IV. (30%) Assume the systems considered below exhibit properties expected of ideal solutions.

a) (10%) At 300 K, pure substances A and B exist in liquid form, with vapour pressures of 43.3 kPa and 11.3 kPa respectively. Calculate the total vapour pressure and the composition of the vapour phase above a mixture of these two liquids, at 300 K with a mole fraction  $x_A = 0.3$ .

$$P_A^{\circ} = 43.3 \text{ kPa}; P_B^{\circ} = 11.3 \text{ kPa}.$$

$$P_{\text{tot}} = x_A P_A^{\circ} + x_B P_B^{\circ} \quad (\text{Raoult's Law})$$

$$P_{\text{tot}} = 0.3 \times 43.3 + 0.7 \times 11.3 = 20.81 \text{ kPa}$$

Composition in vapour:

$$y_A = \frac{P_A}{P_{\text{tot}}} = \frac{x_A P_A^{\circ}}{P_{\text{tot}}} = \frac{0.3 \times 43.3}{20.81} = 0.62$$

$$y_B = 1 - y_A = 0.38$$

b) (10%) Calculate the Gibbs energy of mixing and the entropy of mixing when 71 g of decane ( $C_{10}H_{22}$  (l)) is added to 129 g of hexane ( $C_6H_{14}$  (l)) at a temperature of 300 K. What is the enthalpy of mixing for this process?

Assume ideal mixing:

$$n_{\text{dec}} = \frac{71}{144} = 0.493; \quad n_{\text{hex}} = \frac{129}{86} = 1.50; \quad n_{\text{tot}} = 1.993$$

$$x_{\text{dec}} = \frac{0.493}{0.493+1.5} = 0.247; \quad x_{\text{hex}} = 0.753$$

$$\Delta S_{\text{mix}} = -n_{\text{tot}} R (x_A \ln x_A + x_B \ln x_B) = -1.993 \times 8.31 \left( \underbrace{0.247 \ln 0.247}_{-0.35} + \underbrace{0.753 \ln 0.753}_{-0.21} \right) = +9.27 \text{ J/K}$$

$$\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}} = -(300 \text{ K}) \times (9.27 \text{ J/K}) = -2782.4 \text{ J} = -2.78 \text{ kJ}$$

$$\Delta H_{\text{mix}} = 0 \quad \left( \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} \right)$$

c) (10%) A substance C has a freezing point of 343 K and an enthalpy of fusion of  $3.9 \text{ kJ mol}^{-1}$ . A saturated solution of C has a mole fraction  $x_C = 0.73$ . What is the temperature?

$$\ln x_B = -\frac{\Delta_{\text{fus}} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \Rightarrow -\frac{R}{\Delta_{\text{fus}} H} \ln x_B + \frac{1}{T^*} = \frac{1}{T}$$

$$\Rightarrow \frac{1}{T} = \frac{1}{343} - \frac{8.31 \times \ln(0.73)}{3.9 \times 10^3}$$

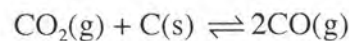
$$\Rightarrow T = 278.86 \text{ K}$$



V. (30%) Standard molar heat capacities at constant pressure,  $C_p^\circ$ , are provided in the table below for the substances indicated, at 298 K. The heat capacities given can be assumed to be constant over the temperature range 298-600 K.

Substance	$C_p^\circ / \text{Jmol}^{-1} \text{K}^{-1}$
C (s)	8.5
CO <sub>2</sub> (g)	37.1
CO (g)	29.1

For the reaction



$\Delta G^\circ$  is 120.02 kJ mol<sup>-1</sup> and  $\Delta H^\circ$  is 172.45 kJ mol<sup>-1</sup> both measured at a temperature of 298 K. For this reaction, calculate:

a) (10%)  $\Delta S^\circ$  and the equilibrium constant  $K_p$  both at 298 K.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \Rightarrow \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{(172.45 - 120.02) \times 10^3}{298} = 176.93 \frac{\text{J}}{\text{K}}$$

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{120.02 \times 10^3}{8.31 \times 298}\right) = \exp(-48.46) \approx 0$$

b) (10%)  $\Delta H^\circ$  at 600 K

$$\frac{\partial \Delta H_{\text{rxn}}}{\partial T} = \Delta C_p \Rightarrow \Delta H^\circ(600\text{K}) = \Delta H^\circ(298) + \Delta C_p^\circ (600 - 298)$$

$$\Delta C_p^\circ = 2 C_p^\circ(\text{CO}, \text{g}) - C_p^\circ(\text{C}, \text{s}) - C_p^\circ(\text{CO}_2, \text{g}) = 2 \times 29.1 - 8.5 - 37.1 = 12.6 \frac{\text{J}}{\text{molK}}$$

$$\Delta H^\circ(600) = 172.45 \times 10^3 + 12.6 \times (600 - 298) = 176.25 \text{ kJ}$$

c) (10%) the equilibrium constant  $K_p$  at 600 K.

$$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R} \Rightarrow \ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H(T) + \Delta C_p(T-T_1)}{RT^2} dT$$

$$\ln K_2 = \ln K_1 + \frac{\Delta H(298)}{R} \left(\frac{T_2 - T_1}{T_1 \times T_2}\right) + \frac{\Delta C_p^\circ}{R} \ln\left(\frac{T_2}{T_1}\right) - \frac{\Delta C_p^\circ T_1}{R} \left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$$

$$= -48.46 + 35.1 + 1.1 - 0.76 = -13.02 \Rightarrow K_2 = 2.2 \times 10^{-6}$$