

Chem 531: Problem Set #7

Due in class: Tues, November 7th

- (1) Species A and B form an ideal solution. At a total pressure of 0.900 bar, $y_A = 0.450$ and $x_A = 0.650$. Using this information, calculate the vapor pressures of pure A and pure B.

from y_A ,

$$P_A = y_A P_{\text{total}} = (0.450)(0.900) = 0.405 \text{ bar}$$

$$P_B = (1 - y_A) P_{\text{total}} = (0.550)(0.900) = 0.495 \text{ bar}$$

$$(\text{or } P_B = P_{\text{total}} - P_A)$$

Raoult's law, $P_A = x_A P_A^*$

$$P_A^* = \frac{P_A}{x_A} = \frac{0.405}{0.650} = 0.623 \text{ bar}$$

$$P_B^* = \frac{P_B}{1 - x_A} = \frac{0.495}{0.350} = 1.414 \text{ bar}$$

(2) At -47°C the vapor pressure of pure ethyl bromide is 10.0 Torr and that of pure ethyl chloride is 40.0 Torr. Assume that the solution is ideal and that only a trace of liquid is present. The mole fraction of ethyl chloride in the vapor is 0.80.

(a) What is the total pressure and the mole fraction of ethyl chloride in the liquid?

(b) If there are 5.00 mol of liquid and 3.00 mol of vapor present at the same pressure as in part (a), what is the overall composition of the system in terms of Z_i ?

(a) for the total pressure with this info, use the dew point eqn.

$$P_{\text{total}} = \frac{P_{ec}^* P_{eb}^*}{P_{ec}^* + (P_{eb}^* - P_{ec}^*) y_{ec}}$$
$$= \frac{(40.0)(10.0)}{40.0 + (10.0 - 40.0)(0.80)} = 25.0 \text{ Torr}$$

$$P_{ec} = (0.80)(25.0 \text{ Torr}) = 20.0$$

since ideal, $X_{ec} = \frac{P_{ec}}{P_{ec}^*} = \frac{20.0}{40.0} = 0.50$

(b) $n_l = 5.00 \text{ mol}$
 $n_v = 3.00 \text{ mol}$

$$n_l^{ec} = X_{ec} n_l = (0.50)(5.00) = 2.50 \text{ mol}$$
$$n_v^{ec} = y_{ec} n_v = (0.80)(3.00) = 2.40 \text{ mol}$$

$$Z_{ec} = \frac{n_l^{ec} + n_v^{ec}}{n_{\text{total}}} = \frac{2.5 + 2.4}{8.0} = 0.613$$

$$Z_{eb} = 1 - Z_{ec} = 0.387$$

(3) At -31.2°C pure propane and *n*-butane have vapor pressures of 1200 and 200 Torr, respectively.

(a) Calculate the mole fraction of propane in the (ideal) liquid mixture that boils at -31.2°C at a pressure of 760 Torr.

(b) Calculate the mole fraction of propane in the vapor that is in equilibrium with the liquid of part (a).

$$\textcircled{a} \quad P_{\text{total}} = 760 \text{ Torr} = x_p P_p^* + (1-x_p) P_b^*$$

$$\text{so} \quad x_p = \frac{760 - P_b^*}{P_p^* - P_b^*} = \frac{760 - 200}{1200 - 200}$$

$$= 0.560$$

$$\textcircled{b} \quad \text{since ideal,} \quad P_p = x_p P_p^* = (0.560)(1200) \\ = 672 \text{ Torr}$$

$$y_p = \frac{P_p}{P_{\text{total}}} = \frac{672}{760} = 0.884$$

(4) At 39.9°C a solution of ethanol ($x_1 = 0.9006$, $P_1^* = 130.4$ Torr) and isooctane ($P_2^* = 43.9$ Torr) forms a vapor phase with $y_1 = 0.6667$ at a total pressure of 185.9 Torr.

(a) Calculate the activity coefficient and activity (Raoult's law std. state) of each component.

(b) Calculate the total pressure that the solution would have if it was ideal.

$$\textcircled{a} \quad a_i = \frac{P_i}{P_i^*} \quad \gamma_i = \frac{P_i}{x_i P_i^*}$$

ethanol: $P_1 = y_1 P_{\text{total}} = (0.6667)(185.9) = 123.9$ Torr

$$a_1 = \frac{P_1}{P_1^*} = \frac{123.9}{130.4} = 0.950$$

$$\gamma_1 = \frac{P_1}{x_1 P_1^*} = \frac{a_1}{x_1} = \frac{0.950}{0.9006} = 1.055$$

isooctane: $P_2 = P_{\text{total}} - P_1 = 185.9 - 123.9 = 62.0$ Torr

$$a_2 = \frac{62.0}{43.9} = 1.412$$

$$\gamma_2 = \frac{a_2}{x_2} = \frac{a_2}{1-x_1} = \frac{1.412}{1-0.9006} = 14.20$$

$$\textcircled{b} \quad P_{\text{total}} = x_1 P_1^* + (1-x_1) P_2^*$$

$$= (0.9006)(130.4) + (1-0.9006)(43.9) = 121.8 \text{ Torr}$$

(5) At 39.9°C the vapor pressure of water is 55.03 Torr (component A) and that of methanol (component B) is 255.6 Torr. Using the data below, calculate the activity coefficients for both components using a Raoult's law standard state.

x_A	y_A	P (Torr)
0.0490	0.0175	257.9
0.3120	0.1090	211.3
0.4750	0.1710	184.4
0.6535	0.2550	156.0
0.7905	0.3565	125.7

$$\gamma_i = \frac{P_i}{x_i P_i^*} \quad \text{where} \quad P_i = y_i P_{\text{total}}$$

$$x_B = 1 - x_A$$

$$y_B = 1 - y_A$$

see following page from Excel.

		<u>Given data</u>		<u>Calculated quantities</u>			
		yA	P(Torr)	P(A)	P(B)	$\gamma(A)$	$\gamma(B)$
PB*	0.0000	0.0000	255.6	0.00	255.60		1.000
	0.0490	0.0175	257.9	4.51	253.39	1.674	1.042
	0.3120	0.1090	211.3	23.03	188.27	1.341	1.071
	0.4750	0.1710	184.4	31.53	152.87	1.206	1.139
	0.6535	0.2550	156.0	39.78	116.22	1.106	1.312
	0.7905	0.3565	125.7	44.81	80.89	1.030	1.511
PA*	1.0000	1.0000	55.0	55.03	0.00	1.000	

(6) Use the data from the following table to determine the Henry's law constant for Br_2 in CCl_4 at 25°C in terms of molality. Use a graphical method.

m_{Br_2}	P (Torr)	m_{Br_2}	P (Torr)
0.026	1.52	0.086	5.43
0.028	1.60	0.157	9.57
0.039	2.39	0.158	9.83
0.067	4.27	0.167	10.27

$$\text{Henry's law: } P_x = X_x k_x^H$$

$$\text{in molality: } P_x = m_x k_x^{H'}$$

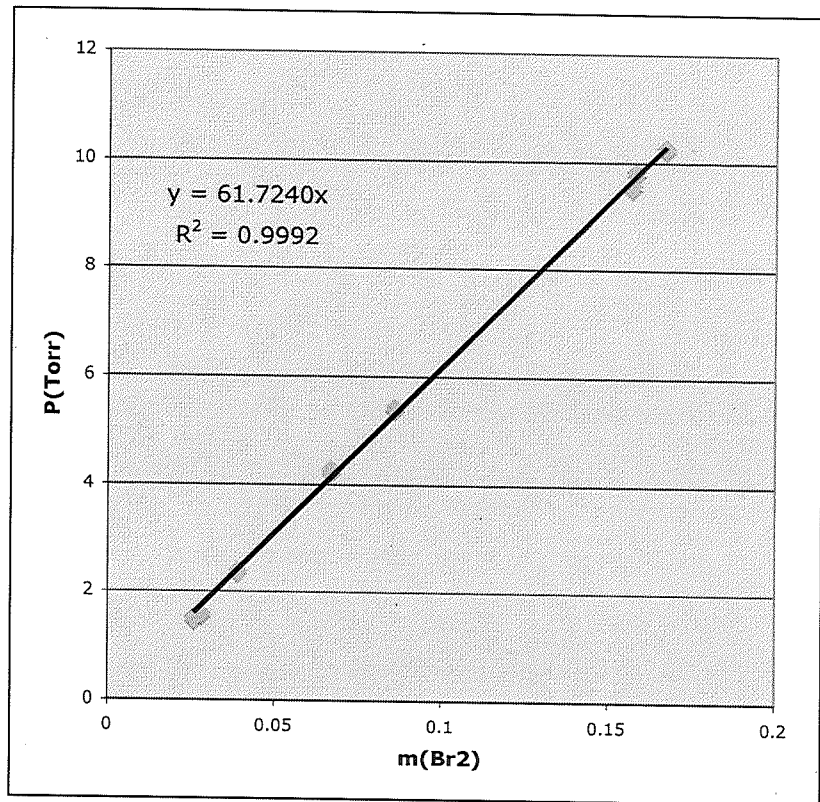
\therefore plot P_{Br_2} vs. m_{Br_2} forcing the y-intercept = 0

$$\Rightarrow \text{slope} = k_{\text{Br}_2}^{H'}$$

see accompanying plot

$$k_{\text{Br}_2}^{H'} = 61.7 \text{ Torr}$$

m(Br2)	P(Torr)
0.026	1.52
0.028	1.6
0.039	2.39
0.067	4.27
0.086	5.43
0.157	9.57
0.158	9.83
0.167	10.27



(7) Calculate the activity coefficient and activity for CS₂ in a CS₂-Acetone solution with $x_{\text{CS}_2} = 0.7220$ for both a Raoult's law and a Henry's law standard state.

Some relevant data: $P_{\text{CS}_2} = 446.9$ Torr, $P_{\text{acetone}} = 207.7$ Torr, $P_{\text{CS}_2}^* = 512.3$ Torr,

$k_{\text{CS}_2}^H = 2010$ Torr

Raoult's law

$$a_{\text{CS}_2}^R = \frac{P_{\text{CS}_2}}{P_{\text{CS}_2}^*} = \frac{446.9}{512.3} = 0.872$$

$$\gamma_{\text{CS}_2}^R = \frac{P_{\text{CS}_2}}{x_{\text{CS}_2} P_{\text{CS}_2}^*} = \frac{a_{\text{CS}_2}}{x_{\text{CS}_2}} = \frac{0.872}{0.7220} = 1.208$$

Henry's law

$$a_{\text{CS}_2}^H = \frac{P_{\text{CS}_2}}{k_{\text{CS}_2}^H} = \frac{446.9}{2010} = 0.222$$

$$\gamma_{\text{CS}_2}^H = \frac{P_{\text{CS}_2}}{x_{\text{CS}_2} k_{\text{CS}_2}^H} = \frac{a_{\text{CS}_2}^H}{x_{\text{CS}_2}} = \frac{0.222}{0.7220} = 0.307$$

- (8) The partial molar volumes of water and ethanol in a solution with $x_{\text{H}_2\text{O}} = 0.60$ at 25°C are 17 and $57 \text{ cm}^3 \text{ mol}^{-1}$, respectively. Calculate the volume change upon mixing sufficient ethanol with 2 mol of water to give this concentration. The densities of water and ethanol are 0.997 and 0.7873 g cm^{-3} , respectively, at this temperature.

$$\bar{V}_{\text{H}_2\text{O}} = 17 \frac{\text{cm}^3}{\text{mol}}$$

$$\bar{V}_{\text{eth}} = 57 \frac{\text{cm}^3}{\text{mol}}$$

$$x_{\text{H}_2\text{O}} = 0.60$$

for $n_{\text{H}_2\text{O}} = 2 \text{ mol}$

$$x_{\text{H}_2\text{O}} = 0.60 = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{eth}}}$$

$$= \frac{2}{2 + n_{\text{eth}}}$$

$$n_{\text{eth}} = 1.333 \text{ mol}$$

total mixed vol: $V = n_{\text{H}_2\text{O}} \bar{V}_{\text{H}_2\text{O}} + n_{\text{eth}} \bar{V}_{\text{eth}}$

$$= (2)(17) + (1.333)(57)$$

$$= 109.98 \text{ cm}^3$$

unmixed: $\bar{V} = n_{\text{H}_2\text{O}} \bar{V}_{\text{H}_2\text{O}}^* + n_{\text{eth}} \bar{V}_{\text{eth}}$

$$= 2 \times \frac{18.01 \text{ g/mol}}{0.997 \text{ g/cm}^3} + 1.33 \times \frac{46.07 \text{ g/mol}}{0.7873 \text{ g/cm}^3}$$

$$= 114.13 \text{ cm}^3$$

$$\Delta V_{\text{mix}} = -4.15 \text{ cm}^3$$