Problem Set 9

P2

$$P = \frac{nRT}{V} = \frac{2.38\text{ g} \times \dfrac{1\text{ mol}}{78.11\text{ g mol}^{-1}} \times 0.08314\text{ L bar K}^{-1} \times 298\text{ K}}{5.50\text{ L}} = 0.116\text{ bar}$$

P4

$$P_{total} = x_A P_a^* + y_B P_{total}$$

$$P_a^* = \frac{P_{total} - y_B P_{total}}{x_A} = \frac{0.900\text{ bar}_z (1-0.550)}{0.450} = 0.623\text{ bar}$$

$$x_A = \frac{y_A P_B^*}{P_a^* + (P_B^* - P_A^*) y_A}$$

$$0.650 = \frac{0.450 P_B^*}{P_A^* + 0.450(P_B^* - P_A^*)}$$

$$\frac{P_B^*}{P_A^*} = \frac{0.650 \times (1-0.450)}{0.450 \times (1-0.650)} = 2.27$$

$$P_B^* = 1.414\text{ bar}$$

P7

a) Calculate the total pressure above the solution.

$$y_{chloro} = \frac{P^*_{chloro} P_{total} - P^*_{chloro} P^*_{bromo}}{P_{total}\left(P^*_{chloro} - P^*_{bromo}\right)}$$

$$0.75 = \frac{3790 \text{ Pa} \times \text{P}_{total} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{P_{total} \times (3790 \text{ Pa} - 1394 \text{ Pa})}$$

$$P_{total} = \frac{3790 \text{ Pa} \times 1394 \text{ Pa}}{3790 \text{ Pa} - 0.75 \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 2651 \text{ Pa}$$

b) Calculate the mole fraction of 1-chlorobutane in the solution.

$$P_{total} = x_{chloro} P^*_{chloro} + (1 - x_{chloro}) P^*_{bromo}$$

$$x_{chloro} = \frac{P_{total} - P^*_{bromo}}{P^*_{chloro} - P^*_{bromo}} = \frac{2651 \text{ Pa} - 1394 \text{ Pa}}{3790 \text{ Pa} - 1394 \text{ Pa}} = 0.525$$

c) What value would Z_{chloro} have in order that there are 4.86 moles of liquid and 3.21 moles of gas at a total pressure equal to that in part (a)? (This composition is different than that in part (a).)

$$y_{chloro} = \frac{P^*_{chloro} P_{total} - P^*_{chloro} P^*_{bromo}}{P_{total}\left(P^*_{chloro} - P^*_{bromo}\right)}$$

$$= \frac{3790 \text{ Pa} \times 2651 \text{ Pa} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{2651 \text{ Pa} \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 0.750$$

$$x_{chloro} = \frac{y_{chloro} P^*_{bromo}}{P^*_{chloro} + \left(P^*_{bromo} - P^*_{chloro}\right) y_{chloro}}$$

$$= \frac{0.750 \times 1394 \text{ Pa}}{3790 \text{ Pa} + (1394 \text{ Pa} - 3790 \text{ Pa}) \times 0.750} = 0.525$$

$$n^{tot}_{liq}\left(Z_{chloro} - x_{chloro}\right) = n^{tot}_{vapor}\left(y_{chloro} - Z_{chloro}\right)$$

$$Z_{chloro} = \frac{n^{tot}_{vapor} y_{chloro} + n^{tot}_{liq} x_{chloro}}{n^{tot}_{vapor} + n^{tot}_{liq}} = \frac{3.21 \text{ mol} \times 0.750 + 4.86 \text{ mol} \times 0.525}{3.21 \text{ mol} + 4.86 \text{ mol}} = 0.614$$

P12

Referring to Figure 9.4, it is seen that the maximum pressure results if $Z_A = x_A$.

$$P_{max} = Z_A P_A^* + (1 - Z_A) P_B^*$$

The minimum pressure results if $Z_A = y_A$. Using Equation (9.12),

$$P_{min} = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) Z_A}$$

P14

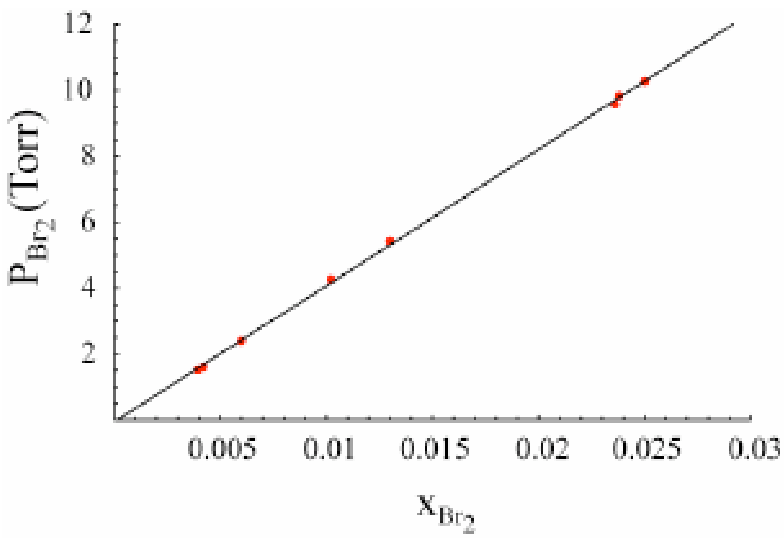
a) for isoproponal $P_1^* = 1008$ Torr

for *n*-decane $P_2^* = 48.3$ Torr

Using the relations $P_i = y_i P_{total}$, $a_i = P_i / P_i^*$, and $\gamma_i = \frac{a_i}{x_i}$, the calculated activities and activity coefficients are shown below.

P(Torr)	x_2	y_2	a_1	a_2	γ_1	γ_2
942.6	0.1312	0.0243	0.912	0.474	1.05	3.61
909.6	0.2040	0.0300	0.875	0.565	1.10	2.77
883.3	0.2714	0.0342	0.846	0.625	1.16	2.30
868.4	0.3360	0.0362	0.831	0.651	1.25	1.94
830.2	0.4425	0.0411	0.790	0.706	1.42	1.60
786.8	0.5578	0.0451	0.745	0.735	1.69	1.32
758.7	0.6036	0.0489	0.716	0.768	1.81	1.27+

P16



The best fit line in the plot is $P_{Br_2}\,(\text{Torr}) = 413\,x_{Br_2} - 0.063$. Therefore, the Henry's law constant in terms of mole fraction is 413 Torr.

P18

$$V = n_{H_2O}\overline{V}_{H_2O} + n_{Et}\overline{V}_{Et}$$

$$\overline{V}_{H_2O} = 17.0 \text{ cm}^3 \text{ mol}^{-1} \text{ and } \overline{V}_{Et} = 57.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$n_{H_2O} = 2.00 \text{ and } x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Et}} = 0.600$$

$$\frac{2 \text{ mol}}{2 \text{ mol} + n_{Et}} = 0.600; \quad n_{Et} = 1.333$$

The total mixed volume is given by

$$\begin{aligned}
V_{mixed} &= n_{H_2O}\overline{V}_{H_2O} + n_{Et}\overline{V}_{Et} \\
&= 2.00 \text{ mol} \times 17.0 \text{ cm}^3 \text{ mol}^{-1} + 1.333 \text{ mol} \times 57.0 \text{ cm}^3 \text{ mol}^{-1} \\
&= 109.98 \text{ cm}^3
\end{aligned}$$

$$\begin{aligned}
V_{unmixed} &= n_{H_2O}\frac{M_{H_2O}}{\rho_{H_2O}} + n_{Et}\frac{M_{Et}}{\rho_{Et}} \\
&= 2.00 \text{ mol} \times 18.02 \text{ g mol} \times \frac{1 \text{cm}^{-3}}{0.997 \text{ g}} \\
&+ 1.333 \text{ mol} \times 46.07 \text{ g mol}^{-1} \times \frac{1 \text{cm}^{-3}}{0.7873 \text{ g}} \\
&= 36.15 \text{ cm}^3 + 78.00 \text{ cm}^3 \\
&= 114.15 \text{ cm}^3
\end{aligned}$$

$$\Delta V = V_{mixed} - V_{unmixed} = 109.98 \text{ cm}^3 - 114.15 \text{ cm}^3 = -4.2 \text{ cm}^3$$

P22

$$\pi V_m^* + RT\ln x_{solvent} = \pi V_m^* + RT\ln\frac{n_{sucrose}}{n_{solvent}+n_{sucrose}} = 0$$

$$\rho g h V_m^* + RT\ln\frac{\dfrac{\rho A h}{M}}{\dfrac{\rho A h}{M}+n_{sucrose}} = \rho g h V_m^* + RT\ln\frac{1}{1+\dfrac{n_{sucrose}M}{\rho A h}} = 0$$

Expanding the argument of the logarithmic term in a Taylor series, $\ln\frac{1}{1+x}\approx -x$

$$\rho g h V_m^* - RT\,\frac{n_{sucrose}M}{\rho A h} = 0$$

$$h = \sqrt{\frac{RTn_{sucrose}M}{\rho^2 A g V_m^*}} = \sqrt{\frac{RTn_{sucrose}}{\rho A g}}$$

$$= \sqrt{\frac{8.314\ \mathrm{J\,mol^{-1}K^{-1}}\times 298\ \mathrm{K}\times\dfrac{1.25\times10^{-3}\mathrm{kg}}{0.18016\ \mathrm{kg\,mol^{-1}}}}{997\,\mathrm{kg\,m^{-3}}\times 3.14\mathrm{x}10^{-4}\mathrm{m^2}\times 9.81\ \mathrm{m\,s^{-2}}}} = 2.37\ \mathrm{m}$$

$$\pi = \rho g h = 997\,\mathrm{kg\,m^{-3}}\times 9.81\ \mathrm{m\,s^{-2}}\times 2.37\ \mathrm{m} = 2.32\times10^4\mathrm{Pa}$$

P27

$$V = n_{H_2O}\overline{V}_{H_2O} + n_{ethanol}\overline{V}_{ethanol}$$

$$\frac{V}{n_{total}} = x_{H_2O}\overline{V}_{H_2O} + x_{ethanol}\overline{V}_{ethanol} = 0.80\times17.8\times10^{-3}\,\mathrm{L\,mol^{-1}} + 0.20\times55.2\times10^{-3}\,\mathrm{L\,mol^{-1}}$$

$$\frac{V}{n_{total}} = 0.0253\ \mathrm{L\,mol^{-1}}$$

$$n_{total} = \frac{1.00\ \mathrm{L}}{0.0253\ \mathrm{L\,mol^{-1}}} = 39.6\ \mathrm{mol} = n_{H_2O} + n_{ethanol}$$

$$\frac{x_{ethanol}}{x_{H_2O}} = \frac{n_{ethanol}}{n_{H_2O}} = \frac{1}{4};\quad n_{H_2O} = 31.7\ \mathrm{mol}\quad n_{ethanol} = 7.90\ \mathrm{mol}$$

$$V_{ideal} = n_{ethanol}\frac{M_{ethanol}}{\rho_{ethanol}} + n_{H_2O}\frac{M_{H_2O}}{\rho_{H_2O}}$$

$$= 7.90\ \mathrm{mol}\times\frac{46.07\times10^{-3}\,\mathrm{kg\,mol^{-1}}}{789\ \mathrm{kg\,m^{-3}}} + 31.7\ \mathrm{mol}\times\frac{18.02\times10^{-3}\,\mathrm{kg\,mol^{-1}}}{998\ \mathrm{kg\,m^{-3}}} = 1.034\ \mathrm{L}$$

$$\Delta V = V - V_{ideal} = -0.034\ \mathrm{L}$$

P30

By Dalton's law, $P_{O_2} = 0.2099P$. At sea level,

$$n = n_{H_2O} x_{O_2} = n_{H_2O} \frac{P_{O_2}}{k_H^{O_2}} = \frac{\rho_{H_2O} V P_{O_2} f_{sat}}{k_H^{O_2} M_{H_2O}}$$

$$n = \frac{998 \text{ kg m}^{-3} \times 10^{-3} \text{m}^3 \times 0.2099 \text{ bar} \times 0.95}{4.95 \times 10^4 \text{bar} \times 18.02 \times 10^{-3} \text{kg mol}^{-1}} = 2.31 \times 10^{-4} \text{mol}$$

$$\text{mass} = nM = 2.31 \times 10^{-4} \text{mol} \times 32.0 \text{ g mol}^{-1} = 7.14 \times 10^{-3} \text{g}$$

At 18,000 feet,

$$n = n_{H_2O} x_{O_2} = n_{H_2O} \frac{P_{O_2}}{k_H^{O_2}} = \frac{\rho_{H_2O} V P_{O_2} f_{sat}}{k_H^{O_2} M_{H_2O}}$$

$$n = \frac{998 \text{ kg m}^{-3} \times 10^{-3} \text{m}^3 \times 0.2099 \times 0.500 \text{ bar} \times 0.71}{4.95 \text{ bar} \times 18.02 \times 10^{-3} \text{kg mol}^{-1}} = 8.34 \times 10^{-5} \text{mol}$$

$$\text{mass} = nM = 8.34 \times 10^{-5} \text{mol} \times 32.0 \text{ g mol}^{-1} = 2.67 \times 10^{-3} \text{g}$$