<u>Homework Set #6 solutions</u>   October 17, 2001

From Atkins: 6.8, 6.12, 6.14, 6.16, 6.17, 6.19, 6.22

6.8) The partial molar volumes of propanone and trichloromethane in a mixture in which the mole fraction of $CHCl_3$ is 0.4693 are 74.166 and 80.235 $cm^3 \, mol^{-1}$, respectively. What is the volume of a solution of total mass 1.000 kg?

Like many problems in Physical Chemistry, there are a couple of ways to tackle this one. I admit to doing it the hard way the first time around. Here's the more straightforward method:

   First we find the molecular weight of the <u>solution</u>, convert the 1000g to moles to obtain the total number of moles of solution, and then use the mole fractions and partial molar volumes to obtain the total volume.

For 1 mol of solution, there are 0.4693 moles of $CHCl_3$ and (1–0.4693)=0.5307 moles of propanone. The molecular weights of $CHCl_3$ and propanone are 119.37 and 58.08 g/mol, respectively, so that the molecular weight of the solution is:

$$0.4693 \; mol \times \frac{119.37 \; g}{1 \; mol} + 0.5307 \; mol \times \frac{58.08 \; g}{1 \; mol} = 86.843 \; g/mol$$

1000 g of solution corresponds to $1000 \; g \times \dfrac{1 \; mol}{86.843 \; g} = 11.515$ mol of solution

Then, (note, c = $CHCl_3$, p = propanone)

$$\begin{aligned}
V &= n_c V_c + n_p V_p \\
&= x_c n_{total} V_c + x_p n_{total} V_p \\
&= (0.4693)(11.515)(80.235) + (0.5307)(11.515)(74.166) \\
&= 887 \; cm^3
\end{aligned}$$

6.12) Calculate (a) the (molar) Gibbs energy of mixing, (b) the (molar) entropy of mixing when the two major components of air (nitrogen and oxygen) are mixed to form air at 298 K. The mole fractions of N_2 and O_2 are 0.78 and 0.22, respectively. Is the mixing spontaneous?

a) For one mole,

$$\Delta G_{mix} = RT(x_A \ln x_A + x_B \ln x_B)$$
$$= (8.31451)(298)(0.78 \ln 0.78 + 0.22 \ln 0.22)$$
$$= -1305.5 \text{ J}$$
$$= -1.3 \text{ kJ/mol} \quad ; \quad \text{spontaneous}$$

b) For one mole,

$$\Delta S_{mix} = -R(x_A \ln x_A + x_B \ln x_B)$$
$$= -\frac{\Delta G_{mix}}{T}$$
$$= -\frac{-1305}{298} = +4.4 \text{ J/mol} \quad ; \quad \text{spontaneous}$$

6.14) A solution is prepared by dissolving 1.23 g of C_{60} (buckminsterfullerene) in 100.0 g of toluene (methylbenzene). Given that the vapor pressure of pure toluene is 5.00 kPa at 30ºC, what is the vapor pressure of toluene over the solution?

$$1.23 \text{ g } C_{60} \times \frac{1 \text{ mol}}{720.66 \text{ g}} = 0.0017068 \text{ mol}$$

$$100.0 \text{ g toluene } \times \frac{1 \text{ mol}}{92.14 \text{ g}} = 1.0853 \text{ mol}$$

$n_{total} = 1.087012$ mol, so that $x(C60) = 1.5702 \times 10^{-3}$, $x(\text{toluene}) = 0.99843$

Using Raoult's law, $p_{toluene} = x(\text{toluene}) \ p*_{toluene}$

$$p_{toluene} = (0.99843)(5.00) = 4.99 \text{ kPa}$$

6.16) At 300 K, the vapor pressure of dilute solutions of HCl in liquid GeCl4 as as
follows:

x(HCl)	0.005	0.012	0.019
p/kPa	32.0	76.9	121.8

Show that the solution obeys Henry's law in this range of mole fractions and
calculate the Henry's law constant at 300 K.

Henry's law is $p_B = x_B K_B$, where B = HCl in this case. If this solution obeys
Henry's law in this mole fraction range, a plot of mole fraction versus vapor
pressure should yield a straight line with a slope given by the Henry's law constant.
A more accurate method is to fit the data to a quadratic polynomial in x and
evaluate the first derivative at $x=0$ (this yields the tangent to the curve). Both
methods are shown in the plot below and yield essentially the same result. From the
linear fit, one obtains K=6411 kPa or 6.4 MPa, while the 1st derivative of the
quadratic yields 6402 kPa or also 6.4 MPa. Certainly Henry's law is obeyed for
these concentration ranges.

—y = -0.025485 + 6411.2x R= 1

$Y = M0 + M1*x + ... M8*x^8 + M9*x^9$	
M0	-0.0067728
M1	6402.2
M2	471.08
R	1
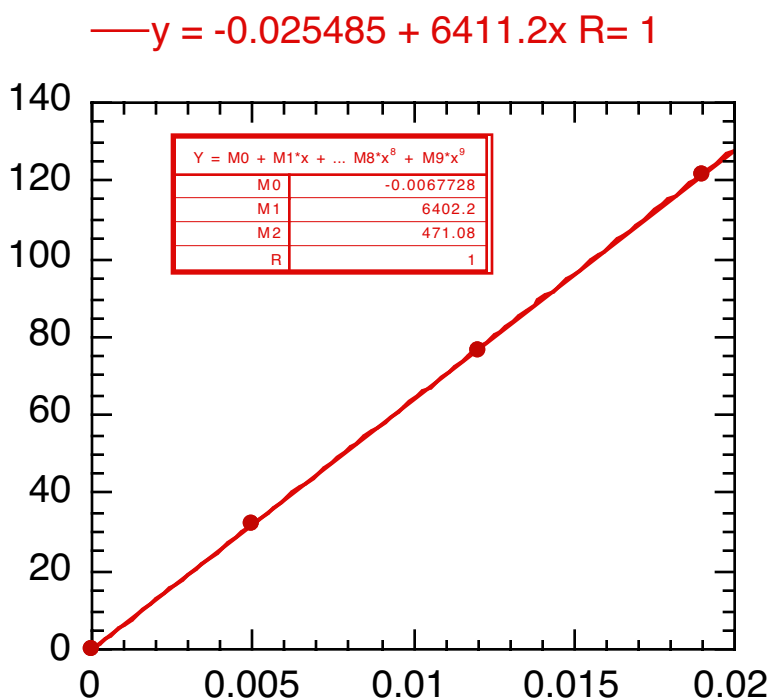
An even simpler test in this case would be to calculate the ratios of p_B/x_B for each set of data points and determine if the resulting K_B are consistent with each other. In this case all three K_B's calculated in this way yield 6.4 MPa. Note that this is the least accurate way to find a Henry's law constant.

6.17) Calculate the concentration of carbon dioxide in fat given that the Henry's law constant is 8.6 x 10^4 Torr and the partial pressure of carbon dioxide is 55 kPa.

$$p = 55 \text{ kPa } \times \frac{1 \text{ Torr}}{0.13332 \text{ kPa}} = 412.54 \text{ Torr}$$

From Henry's law, $x = \dfrac{p}{K} = \dfrac{412.54}{8.6 \times 10^4} = 0.0048$

6.19) The mole fractions of N_2 and O_2 in air at sea level are approximately 0.78 and 0.21. Calculate the molalities of the solution formed in an open flask of water at 25ºC.

For a total pressure of 760 Torr,

$$p_{N_2} = (0.78)(760) = 592.8 \text{ Torr}$$

$$p_{O_2} = (0.21)(760) = 159.6 \text{ Torr}$$

From Henry's law (H.L. constants from the text):

$$x_{N_2} = \frac{p_{N_2}}{K_{N_2}} = \frac{592.8}{6.51 \times 10^7} = 9.106 \times 10^{-6}$$

$$x_{O_2} = \frac{p_{O_2}}{K_{O_2}} = \frac{159.6}{3.30 \times 10^7} = 4.836 \times 10^{-6}$$

The definition of molality: $\quad m_A = \dfrac{n_A}{kg \text{ H}_2\text{O}}$

For 1kg of water, $\quad x_A = \dfrac{n_A}{n_A + \dfrac{1000 \text{ g}}{18.02 \text{ g/mol}}} \approx \dfrac{n_A}{\dfrac{1000 \text{ g}}{18.02 \text{ g/mol}}}$

For this case, n_A is the number of moles of solute in 1 kg of solvent, which is the

definition of molality: $$m_A = x_A \frac{1000 \text{ g}}{18.02 \text{ g/mol}}$$

$$m_{N_2} = (9.106 \times 10^{-6})(1000/18.02) = 5.05 \times 10^{-4} \text{ moles/kg}$$

$$m_{O_2} = (4.836 \times 10^{-6})(1000/18.02) = 2.68 \times 10^{-4} \text{ moles/kg}$$

Note that the approximation we made above is valid since the number of moles

of N_2 and O_2 are both much smaller than the number of moles of water.

6.22) The vapor pressure of a sample of benzene is 400 Torr at 60.6ºC, but it fell to

386 Torr when 0.125 g of an organic compound was dissolved in 5.00 g of the

solvent. Calculate the molar mass of the compound.

For A = benzene and using Raoult's law,

$$x_A = \frac{p_A}{P_A^*} = \frac{386}{400} = 0.965$$

From the definition of the mole fraction,

$$x_A = \frac{n_A}{n_A + n_x} = \frac{5.00/78.12}{\frac{5.00}{78.12} + \frac{0.125}{MW_x}}$$

$$0.965 = \frac{0.06400}{0.06400 + \frac{0.125}{MW_x}}$$

Solving for the MW of the unknown, $MW_x = 53.85$ g/mol