Some people asked via e-mail and in my office about vapor pressure and vapor pressure lowering for a solution. In particular they've had general questions and specific questions about 13.67 and 13.68. Both deal with vapor pressure above a solution, in particular when both solute and solvent are volatile. We're dealing with the vapor (gas) above the solution due to any volatile substance vaporizing from liquid to gas.

In a solution the vapor pressure of any volatile substance is given by Raoult's Law:

$$P_A = X_A P_A^o$$

P_A = vapor pressure of A above solution
X_A = mole fraction of A in **liquid phase**
P_A^o = V.P. of pure A

The total vapor pressure above a solution is given by Dalton's Law of Partial Pressures and is due to both the solvent and solute.

$P_{soln} = P_{solvent} + P_{solute}$ Dalton's Law P_{soln} = total vapor pressure above the solution

If the solute is NONvolatile it won't vaporize (or its vapor pressure is so low it can be ignored). Thus,

$$P_{solute} = 0$$

and the total pressure is due just to the solvent,

$$P_{soln} = P_{solvent} = X_{solvent} P_{solvent}^o \qquad \text{(eqn13.10 in book)}$$

The VP lowering, the change in VP going from pure solvent to solution upon the addition of a nonvolatile solute is given by two equations,

$$\Delta P = P_{solvent}^o - P_{above\ soln\ due\ to\ solvent}$$

I showed in class that VP lowering can also be given by the following eqn.,

$$\Delta P = X_{solute} P_{solvent}^o \qquad \text{(eqn 13.11 in book)}$$

***** continued on next page *****

How does one determine the total vapor pressure of a solution of two volatile substances? Also, one often wants to know the mole fractions of both substances in the gas phase.

Both volatile substance will contribute to the vapor pressure above the solution. Assume that both follow Raoult's Law and the gas mixture follows Dalton's of Partial Pressures.

$$P_A = X_A P_A^o \qquad P_B = X_B P_B^o \qquad \text{Raoult's Law}$$

P_A = vapor pressure of A above solution $\quad$ P_B = vapor pressure of B above solution

X_A = mole fraction of A in **liquid phase** $\quad$ X_B = mole fraction of B in **liquid phase**

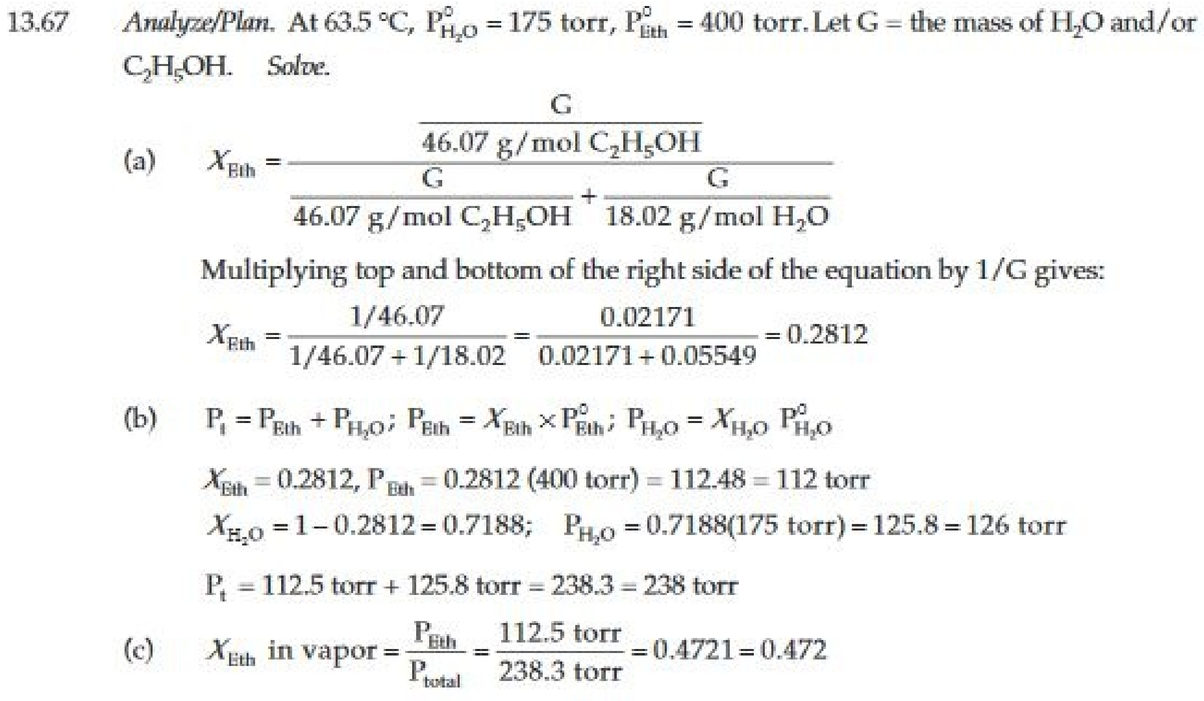
P_A^o = V.P. of pure A $\quad$ P_B^o = V.P. of pure B

$$P_T = P_A + P_B \qquad \text{Dalton's Law} \qquad P_T = \text{total vapor pressure above the solution}$$

$$P_T = X_A P_A^o + X_B P_B^o \qquad \text{for two volatile substances}$$

How does one know both substances are volatile in a problem? You would be given a VP for each pure substance at the temp of interest in the problem.

13.67. This deals with the VP above a soln of water, H_2O, and ethanol, C_2H_6O at 63.5C with VP for each pure substance of 175 torr and 400 torr (3 s.f.) in which equal masses are used to make the soln.



13.67 *Analyze/Plan.* At 63.5 °C, $P^o_{H_2O}$ = 175 torr, P^o_{Eth} = 400 torr. Let G = the mass of H_2O and/or C_2H_5OH. *Solve.*

(a) $$X_{Eth} = \frac{\dfrac{G}{46.07\text{ g/mol }C_2H_5OH}}{\dfrac{G}{46.07\text{ g/mol }C_2H_5OH} + \dfrac{G}{18.02\text{ g/mol }H_2O}}$$

Multiplying top and bottom of the right side of the equation by 1/G gives:

$$X_{Eth} = \frac{1/46.07}{1/46.07 + 1/18.02} = \frac{0.02171}{0.02171 + 0.05549} = 0.2812$$

(b) $P_t = P_{Eth} + P_{H_2O}$; $P_{Eth} = X_{Eth} \times P^o_{Eth}$; $P_{H_2O} = X_{H_2O}\, P^o_{H_2O}$

$X_{Eth} = 0.2812$, $P_{Eth} = 0.2812\ (400\text{ torr}) = 112.48 = 112\text{ torr}$

$X_{H_2O} = 1 - 0.2812 = 0.7188$; $\quad P_{H_2O} = 0.7188(175\text{ torr}) = 125.8 = 126\text{ torr}$

$P_t = 112.5\text{ torr} + 125.8\text{ torr} = 238.3 = 238\text{ torr}$

(c) $$X_{Eth}\text{ in vapor} = \frac{P_{Eth}}{P_{total}} = \frac{112.5\text{ torr}}{238.3\text{ torr}} = 0.4721 = 0.472$$

13.67 (cont.)

Part (a): It asks for the mole fractions of each component for equal masses. You need to remember a couple of things, mole fraction and molar mass.

$$X_A = \frac{\text{mol A}}{\text{mol A} + \text{mol B}} \qquad MM_A = \frac{m}{n} \qquad m = \text{mass},\ n = \text{moles}$$

Now lets solve for moles, n, from MM and mass for each substance and substitute into mole fraction.

$$X_A = \frac{m_A/MM_A}{m_A/MM_A + m_B/MM_B} \qquad MM_A = \frac{m}{n} \qquad m = \text{mass},\ n = \text{moles}$$

You might ask how does this help, no masses were given. Ah, you don't need the actual masses if you have some way to relate the two masses. This problem states the solution is made by using equal masses.

$m_A = m_B$ so substitute m_B for m_A above (the solns manual used G for the masses)

$$X_A = \frac{m_A/MM_A}{m_A/MM_A + m_A/MM_B} = \frac{1/MM_A}{1/MM_A + 1/MM_B}$$

The masses cancel. So, you could have done this by simply picking a mass and using that to calculate the moles for each substance.

What if the masses aren't equal, lets say the mass of B is twice the mass of A,

$$m_B = 2\, m_A$$

$$X_A = \frac{m_A/MM_A}{m_A/MM_A + 2m_A/MM_B} = \frac{1/MM_A}{1/MM_A + 2/MM_B}$$

Again, just pick a mass for A or B and do the appropriate calculations and things will work out.

Part (b): Just use what is shown above from the solutions manual.

$$P_{soln} = X_{H2O}\, P^{o}_{H2O} + X_{C2H6O}\, P^{o}_{C2H6O}$$

$$= (0.7188)(175 \text{ torr}) + (0.2812)(40\underline{\mathbf{0}} \text{ torr})$$

$$= 12\underline{\mathbf{5}}.79 \text{ torr} + 11\underline{\mathbf{2}}.48 \text{ torr}$$

$$= 23\underline{\mathbf{8}}.27 \text{ torr} \qquad \text{(total pressure of gases above the soln)}$$

13.67 (cont.)

Part (c): this part deals with finding the composition, mole fractions, in the vapor phase (i.e. the gas phase above the solution).

Remember, if there's a gas mixture the partial pressure of a gas A can be found by using the following:

$$P_{A,\,g} = X_{A,g} * P_{total} \qquad \text{(from chapter 10)}$$

$P_{total} = P_{soln}$ (Pressure above the soln)

$P_{A,\,g}$ (the pressure of volatile substance A in the gas phase, also determined using Raoult's Law as shown on previous page)

$X_{A,g}$ (mole fraction of A in vapor phase, i.e. the gaseous state of A)

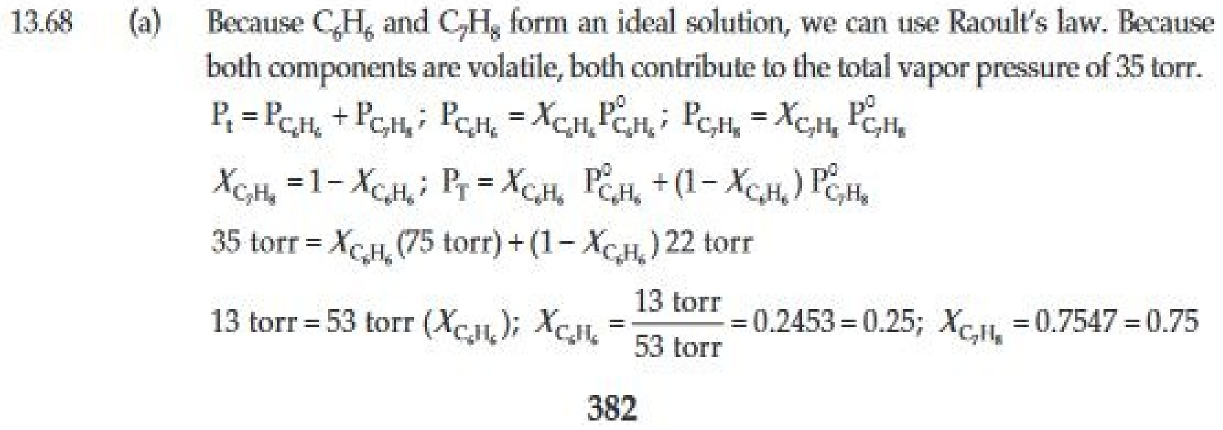
$$X_{A,g} = \frac{P_{A,\,g}}{P_{total}}$$

For this problem we can calculate the mole fraction of the ethanol in the vapor phase from this:

$$X_{Eh,g} = \frac{P_{Et,\,g}}{P_{total}} = \frac{11\underline{\mathbf{2}}.48 \text{ torr}}{23\underline{\mathbf{8}}.27 \text{ torr}} = 0.472$$

NOTE: The vapor phase is richer in the more volatile substance than it was in the liquid solution phase (0.472 compared to 0.2812).

13.68. This problem is similar to above so you need to be using the same eqns.



13.68 (a) Because C_6H_6 and C_7H_8 form an ideal solution, we can use Raoult's law. Because both components are volatile, both contribute to the total vapor pressure of 35 torr.

$$P_t = P_{C_6H_6} + P_{C_7H_8};\ P_{C_6H_6} = X_{C_6H_6}P^o_{C_6H_6};\ P_{C_7H_8} = X_{C_7H_8}\ P^o_{C_7H_8}$$

$$X_{C_7H_8} = 1 - X_{C_6H_6};\ P_T = X_{C_6H_6}\ P^o_{C_6H_6} + (1 - X_{C_6H_6})\ P^o_{C_7H_8}$$

$$35 \text{ torr} = X_{C_6H_6}(75 \text{ torr}) + (1 - X_{C_6H_6})\ 22 \text{ torr}$$

$$13 \text{ torr} = 53 \text{ torr}\ (X_{C_6H_6});\ X_{C_6H_6} = \frac{13 \text{ torr}}{53 \text{ torr}} = 0.2453 = 0.25;\ X_{C_7H_8} = 0.7547 = 0.75$$

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Part (a): Want the mole fractions of the solute and solvent in the vapor phase given the VP of the two volatile components and the total VP above the soln. Think about the eqn for total VP above a soln of two volatile components.

$$P_T = X_A P^o_A + X_B P^o_B$$

total pressure above a soln for two volatile substances

This eqn has 5 variables. Given four of them we can solve for the remaining one. We want mole fractions give the pressures of the pure substance and the total VP above the soln.

Remember, mole fractions add up to 1.

$$X_B = (1 - X_A)$$

Substitute this in the eqn for the total pressure,

$$P_T = X_A P^o_A + (1-X_A) P^o_B$$

This can be solved for X_A and then get X_B from $1-X_A$.

Part (b): Similar to 13.67(c) so I won't go through it again here.