

CHM 3400 – Problem Set 6
Due date: Wednesday, March 11th.

Do all of the following problems. Show your work.

“A mathematician may say anything he pleases, but a physicist must at least be partially sane.”

- J. Willard Gibbs

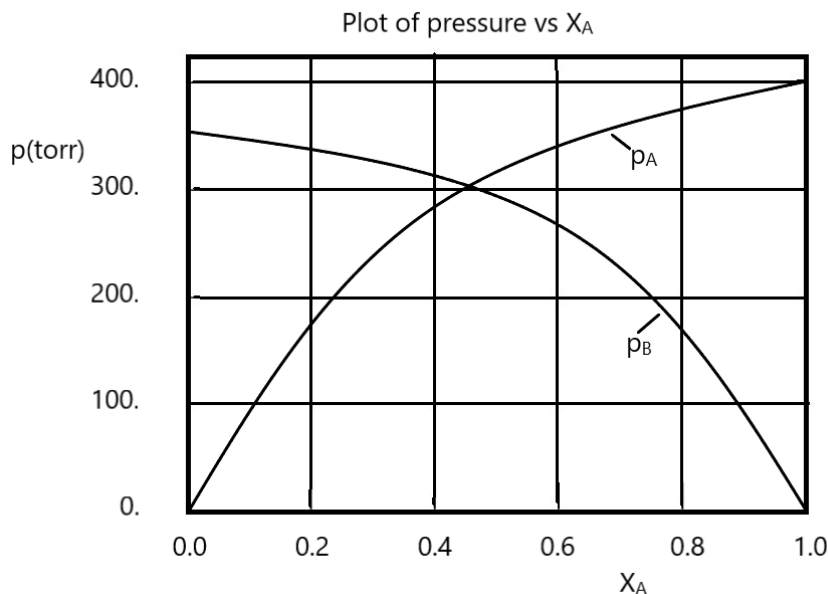
1) There are various ways in which Henry's Law can be written. One common expression for Henry's Law is

$$[B] = K_H p_B \quad (1.1)$$

where $[B]$ is the concentration of dissolved gas in a liquid at equilibrium when the partial pressure of gas above the liquid is p_B .

The Henry's law constant for oxygen (O_2 , $M = 32.0$ g/mol) in water, at $T = 25.0$ °C, is $K_H = 1.26$ mol/bar·m³. What is the concentration of dissolved oxygen in water at equilibrium with air (in units of mg/L) at $T = 25.0$ °C? Assume an atmospheric pressure of 1.00 bar, and $X(O_2) = 0.21$ in air. Note that while the concentration is low, it is sufficient to support animal life in water.

2) Consider a two component liquid solution at a constant temperature $T = 35.0$ °C. A diagram indicating the partial pressure of A and B at equilibrium is given below and can be used to answer the following questions.



- Do A and B form an ideal solution (yes/no)? Justify your answer.
- What are p_A^* and p_B^* , the vapor pressures of pure A and pure B, at $T = 35.0$ °C?
- What are the values for a_A and a_B (the activities of A and B) when $X_A = 0.80$?
- We may define Y_A and Y_B as the mole fraction of A and B in the vapor phase. What is the value for Y_A when $X_A = 0.20$? (Note: You may assume that A and B in the vapor phase both obey the ideal gas law.)

3) A liquid solution is prepared by dissolving 347.3 mg of an unknown nonvolatile solute in 39.67 g of carbon tetrachloride (CCl_4 , $MW = 153.82$ g/mol). The vapor pressure of pure carbon tetrachloride, measured at $T = 25.0$ °C, is $p^* = 115$ torr. The vapor pressure of the solution, measured at the same temperature, is 1.38 torr lower than that of the pure liquid. Based on this information, find the molecular weight of the solute.

4) As discussed in class, the derivation of the equations for boiling point elevation and freezing point depression lead to the following expressions for the boiling point elevation constant (K_b) and freezing point depression constant (K_f).

$$K_b = \frac{R(T_b^*)^2 M_A}{\Delta H_{\text{vap}}^\circ} \qquad K_f = \frac{R(T_f^*)^2 M_A}{\Delta H_{\text{fus}}^\circ} \qquad (4.1)$$

where T_b^* and T_f^* are the boiling point and freezing point temperatures for the pure liquid, and M_A is the molecular weight of the liquid (expressed in units of kg/mol).

Using the data below, find K_b and K_f for benzene (C_6H_6).

$$MW(C_6H_6) = 78.12 \text{ g/mol}$$

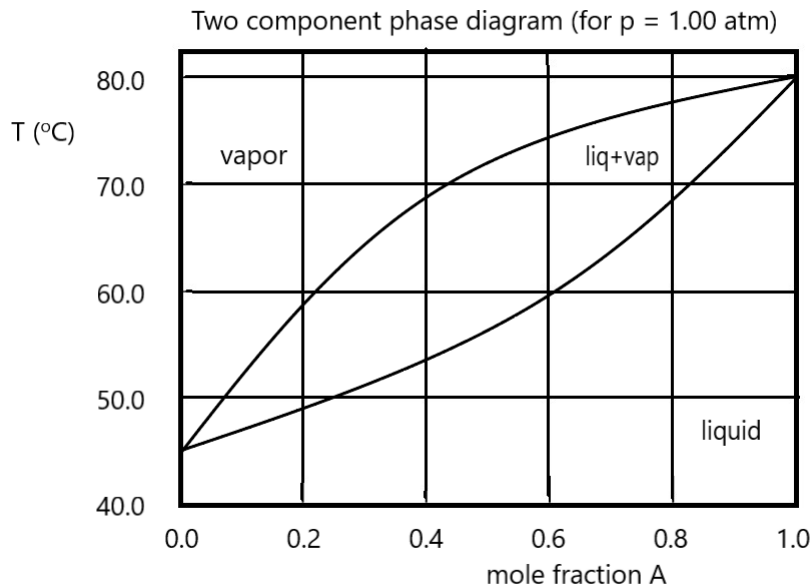
$$T_f^* = 5.46 \text{ }^\circ\text{C}$$

$$\Delta H_{\text{fus}}^\circ = 10.59 \text{ kJ/mol}$$

$$T_b^* = 80.0 \text{ }^\circ\text{C}$$

$$\Delta H_{\text{vap}}^\circ = 30.8 \text{ kJ/mol}$$

5) A phase diagram for a mixture of A and B, at a constant pressure $p = 1.00 \text{ atm}$, is given below, and may be used to answer the following questions.



a) What are $T_{A,\text{vap}}^\circ$ and $T_{B,\text{vap}}^\circ$, the normal boiling point for pure A and pure B?

b) Consider a liquid solution containing 0.400 moles of A and 1.600 moles of B, initially at a temperature $T = 40.0 \text{ }^\circ\text{C}$. Describe what happens as the temperature of the system slowly increases to a final value $T = 80.0 \text{ }^\circ\text{C}$. Indicate what phase or phases are present in the system for each range of temperatures, where boiling of the liquid solution begins, and where boiling of the liquid solution ends. You may assume a closed system at constant pressure $p = 1.00 \text{ atm}$.

c) Now consider a system containing 0.600 moles of A and 1.400 moles of B, at a temperature $T = 60.0 \text{ }^\circ\text{C}$. At this temperature X_A (mole fraction of A in the liquid phase) is $X_A = 0.605$ and Y_A (mole fraction of A in the vapor phase) is $Y_A = 0.216$. Based on this information, find n_ℓ , the total number of moles in the liquid phase.

Solutions.

1) $[B] = K_H p_B$ But for O_2 , $p_B = X(O_2) p = 0.21 (1.00 \text{ bar}) = 0.21 \text{ bar}$

So $[B] = (1.26 \text{ mol/bar}\cdot\text{m}^3) (0.21 \text{ bar})$

$$= 0.2646 \frac{\text{mol}}{\text{m}^3} \cdot \frac{1 \text{ m}^3}{1000 \text{ L}} \cdot \frac{32.0 \text{ g}}{\text{mol}} \cdot \frac{1000 \text{ mg}}{\text{g}} = 8.5 \text{ mg/L}$$

2) a) NO. If A and B formed an ideal solution, the plots of partial pressure vs mole fraction A would be straight lines, as A and B would obey Raoult's law. Since that does not happen, A and B must not form an ideal solution.

b) We read these values off of the figure $p_A^* = 400. \text{ torr}$ (value for p_A when $X_A = 1.0$)
 $p_B^* = 355. \text{ torr}$ (value for p_B when $X_B = 1.0$, and so $X_A = 0.0$)

c) To find the values for activity, we need the values for pressure when $X_A = 0.80$. These can be read off of the figure.

$$p_A = 380. \text{ torr} \quad a_A = p_A/p_A^* = (380. \text{ torr})/(400. \text{ torr}) = 0.96$$
$$p_B = 175. \text{ torr} \quad a_B = p_B/p_B^* = (175. \text{ torr})/(355. \text{ torr}) = 0.49$$

d) For an ideal gas $p_A V = n_A RT$ $n_A = (V/RT) p_A = (\text{const.}) p_A$

and so $Y_A = \frac{n_A(g)}{n_A(g) + n_B(g)} = \frac{p_A}{p_A + p_B}$

When $X_A = 0.20$, then from the figure $p_A = 180. \text{ torr}$ $p_B = 330. \text{ torr}$

and so $Y_A = \frac{(180. \text{ torr})}{(180. \text{ torr} + 330. \text{ torr})} = 0.35$

3) The molecular weight of the unknown solute will be $MW = m_B/n_B$. We know $m_B = 347.3 \times 10^{-3} \text{ g}$.

For vapor pressure lowering $\Delta p_A = X_B p_A^*$

so $X_B = \frac{\Delta p_A}{p_A^*} = \frac{1.38 \text{ torr}}{115. \text{ Torr}} = 0.0120$

Since $X_B = \frac{n_B}{n_A + n_B}$

then $X_B (n_A + n_B) = n_B$

or, solving for n_B $n_B = \frac{n_A X_B}{(1 - X_B)}$ $n_A = n_{CCl_4} = 39.67 \text{ g} \cdot \frac{1 \text{ mol}}{153.82 \text{ g}} = 0.2579 \text{ mol CCl}_4$

Substituting, we get $n_B = \frac{(0.2579 \text{ mol})(0.012)}{(1. - 0.012)} = 3.132 \times 10^{-3} \text{ mol B}$

And so the molecular weight is $MW = \frac{347.3 \times 10^{-3} \text{ g}}{3.132 \times 10^{-3} \text{ mol}} = 111. \text{ g/mol}$

4) If we substitute into the formulas for K_b and K_f , we get (note $MW(C_6H_6) = 78.12 \text{ g/mol} = 78.12 \times 10^{-3} \text{ kg/mol}$)

$$K_B = \frac{(8.3145 \text{ J/mol}\cdot\text{K}) (353.15 \text{ K})^2 (78.12 \times 10^{-3} \text{ kg/mol})}{30800. \text{ J/mol}} = 2.63 \frac{\text{kg}\cdot\text{K}}{\text{mol}}$$

$$K_f = \frac{(8.3145 \text{ J/mol}\cdot\text{K}) (278.61 \text{ K})^2 (78.12 \times 10^{-3} \text{ kg/mol})}{10590. \text{ J/mol}} = 4.76 \frac{\text{kg}\cdot\text{K}}{\text{mol}}$$

5) a) We read these values off of the figure $T_{A,\text{vap}}^\circ = 80.0 \text{ }^\circ\text{C}$ (value when $X_A = 1.0$)
 $T_{B,\text{vap}}^\circ = 46.0 \text{ }^\circ\text{C}$ (value when $X_B = 1.0$, and so $X_A = 0.0$)

b) At $T = 40.0 \text{ }^\circ\text{C}$ there is a single liquid phase present, with $Z_A = 0.400/(0.400 + 1.600) = 0.20$. At $T = 49.0 \text{ }^\circ\text{C}$, the liquid begins to boil. As liquid is converted into vapor, temperature increases. Boiling continues until $T = 58.5 \text{ }^\circ\text{C}$, at which point only vapor is present in the system. At temperatures above $58.5 \text{ }^\circ\text{C}$, only a single vapor phase is present.

$$\text{c) } Z_A = (0.600)/(0.600 + 1.400) = 0.30 \qquad n = 0.600 \text{ mol} + 1.400 \text{ mol} = 2.000 \text{ mol}$$

$$\text{By the lever rule} \quad \frac{n_g}{n_\ell} = \frac{X_A - Z_A}{Z_A - Y_A} = \frac{0.605 - 0.300}{0.300 - 0.216} = 3.63 \qquad n_g = 3.63 n_\ell$$

$$\text{But} \quad n = n_\ell + n_g = n_\ell + 3.63 n_\ell = 4.63 n_\ell$$

$$n_\ell = \frac{n}{4.63} = \frac{2.000 \text{ mol}}{4.63} = 0.432 \text{ moles}$$