

Problems: Q9.2, P9.6, P9.7

HW10

Due Wednesday (03/12/08)

Q9.2) For a pure substance, the liquid and gaseous phases can only coexist for a single value of the pressure at a given temperature. Is this also the case for an ideal solution of two volatile liquids?

Use the Gibbs Phase Rule to bolster your conclusion.

P9.6) The vapor pressures of 1-bromobutane and 1-chlorobutane can be expressed in the form $\ln \frac{P_{bromo}}{\text{Pa}} = 17.076 - \frac{1584.8}{\frac{T}{\text{K}} - 111.88}$ and $\ln \frac{P_{chloro}}{\text{Pa}} = 20.612 - \frac{2688.1}{\frac{T}{\text{K}} - 55.725}$. Assuming

ideal solution behavior, calculate x_{bromo} and y_{bromo} at 300.0 K and a total pressure of 8741 Pa.

Use the derivate rule $\Delta H = \frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial \left(\frac{1}{T} \right)}$, applied to the above equation for Chlorobutane to

determine the enthalpy of vaporization (as a function of temperature).

P9.7) Assume that 1-bromobutane and 1-chlorobutane form an ideal solution. At 273 K, $P_{chloro}^* = 3790$ Pa and $P_{bromo}^* = 1394$ Pa. When only a trace of liquid is present at 273 K, $y_{chloro} = 0.75$.

a) Calculate the total pressure above the solution.

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

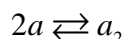
c) What value would Z_{chloro} have in order for there to be 4.86 mol of liquid and 3.21 mol of gas at a total pressure equal to that in part (a)? [Note: This composition is different from that of part (a).]

Before you begin the problem determine where on the phase diagram of Figure 9.4 (and the associated lever rule) you are located.

Additional questions to study for the final:

Suppose you have a gas that is an ideal gas except that it can form dimers. Both the monomer and the dimer individually obey the ideal gas equation but because the dimer formation occurs it appears that the gas taken as a whole does not obey the ideal gas relation.

The first thing to do is determine how much gas is dimerized and how that depends on the pressure. So there is a K_p for dimerization for the reaction:



Assume that n_o represents the number of moles of monomers before any dimerization can take place. Writing the problem this way (sort of) implies that dimer constant is small and that there is only a small amount of dimer forming. A different form of this problem is done as example 6.9 of your text. See if you can do it on your own, as practice. You want to solve for the extent of advancement or the number of moles of monomer and dimer. If X is the number of moles of dimer formed, then $y = \frac{X}{n_o}$, is a very convenient quantity to solve for, in terms of $P \cdot K_p$. Solve this problem.

You will have to go through a quadratic equation. Determine which sign of the square root is meaningful by choosing the correct limiting value of y as K_p goes to zero. Explain how you decided this.

Using Dalton's law of partial pressures, write the equation of state for the system in terms of the extent of advancement or $y = \frac{X}{n_o}$ and the other variables needed. You should notice some similarities between this EoS and the vdW gas EoS even at this point.

What is the physical range of $y = \frac{X}{n_o}$, and does it follow this range as $P \cdot K_p$ goes from zero to infinity?

Now to make the connection with fugacity and vdW equation of state, using the above expressions:

Show that the compressibility Z can be written in terms of y .

If we now simplify $y = \frac{X}{n_o}$ to be

$$y = \frac{K_p \cdot P}{1 + 4K_p \cdot P}$$

compute the fugacity coefficient, γ from the $\ln(\gamma)$, from this EoS using equation 7.21,

and the simplified version of $y = \frac{X}{n_o}$ (the dimer formation advancement parameter). The

integral should be analytic and well behaved. The result should show that the coefficient is fractional and positive: $0 \leq \gamma \leq 1$. How does the coefficient change with increasing K_p ? What does this imply about how the fugacity changes as K_p increases? What does this imply about how the pressure changes as K_p increases?

Now let's estimate the fugacity coefficient from a different source. Let's assume that there is a gas that obeys the vdW EoS but that $b = 0$ so that:

$$P = \frac{RT}{V_m} - \frac{a}{V_m^2} \quad \Rightarrow \quad Z = 1 - \frac{a/RT}{V_m}$$

From this EoS we want to compute the fugacity coefficient. This leads to a somewhat tricky integral that we can simplify by assuming that

$$P \cdot V_m \approx RT$$

in the integrand. This will enable you to get an analytic answer for the activity coefficient. Again show that this result implies that $0 \leq \gamma \leq 1$, which is the same range as the above problem.

We have often suggested in class that the additional term of the vdW EoS is an attractive term. If that is the case then there should be some connection between the a of the vdW equation and the K_p for dimer formation as shown above. Use the two expressions you have for the activity coefficient -- one from the dimer formation and the other from the attractive part of the vdW gas -- and equate them to find a in terms of the dimer formation constant.

Explain whether a increases or decreases with an increasing dimer formation constant, K_p . What would you expect on physical grounds?

Some hints if you are stuck:

$$y = \frac{1}{2} \left[1 - \sqrt{1 - \frac{4KP}{1 + 4KP}} \right]$$

$$\ln \gamma = \frac{-1}{4} \ln(1 + 4KP)$$

$$\ln \gamma = -\frac{aP}{(RT)^2}$$