Solution to Review Session Problems

(Those who came to review session, see page 3-4)

Quick Problems

1)

We cannot set 3 variables for the case of 2 species and 2 phases.

Gibbs' phase rule: $F = 2 + N - \Pi = 2 + 2 - 2 = 2$. We can only specify two (e.g. T and P)

2)

a) $G^E/RT = \Sigma x_i \ln\gamma_i$ (just plug in expressions, that's it)

b) Three ways to check:

  1) Gibbs-Duhem: $\Sigma x_i d(\ln\gamma_i) = 0$ inconsistent if not 0

  2) If we differentiate G^E/RT to calculate γ_1, we should get the same expression.

  3) Important to check (and easy): At $x_i \rightarrow 1$, $\gamma_i \rightarrow 1$?

  In this problem, all three checks will show that the expression is inconsistent. The third method is easiest. Note that even if an expression passes method 3), it may not pass method 1) and 2).

3)

Ideal gas and ideal solution: Raoult's Law: $y_1P = x_1P_1^{sat}$ $y_2P = x_2P_2^{sat}$

For azeotrope: $y_i = x_i \rightarrow P = P_1^{sat}$ and $P = P_2^{sat}$.

If $P_1^{sat} = P_2^{sat}$ and everything is ideal, then there is no azeotrope because all compositions will be the same. (I guess we can say that all compositions are azeotropes, but that's rather meaningless).

4)

$S = x_1S_1 + x_2S_2 - R\,x_1(Ax_2 + \ln x_1) - Rx_2(Ax_1 + \ln x_2)$ and $H^E = 0$

$S^E = S - S^{id} = S - x_1S_1 - x_2S_2 - x_1\ln x_1 - x_2\ln x_2 = -2ARx_1x_2$

$G^E = H^E - TS^E = 0 + 2\,ARTx_1x_2$.

From this point on, we can calculate $\ln\gamma_1$ as usual from G^E/RT. (See Apr 22 recitation's last problem if you don't know how we get this).

Longer Problems

I'm not going to write the full solution for the ones covered in review session. For those of you who were there, see Problems 2 and 3. If you have problem doing any of these, e-mail me (thio@mit.edu).

1)

a) Method to solve:

i) Figure out the mole fraction of ethanol in solution (from the mass fraction).

ii) Figure out partial molar volume of ethanol and water at that mole fraction from graph.

iii) Calculate the solution molar volume from the partial molar volume.

iv) Calculate number of moles in the solution using the molar volume and total volume (100 cm^3).

v) Get number of moles of water and ethanol using the mole fractions.

vi) Figure out molar volume of pure water and of pure ethanol from graph (at $x_i = 1$).

vii) Finally, $V^t_{water} = n_{water}V_{water}$. Same for ethanol.

b) Method to solve: (one of them anyway)

$$\overline{V}_{eth} = \left[\frac{\partial(nV)}{\partial n_{eth}}\right]_{T,P,n_{water}}$$ = how much total volume (nV) will change when n_{eth} is changed by some amount.

$$\overline{V}_{eth} \approx \frac{\Delta(nV)}{\Delta n_{eth}} \quad \Rightarrow \quad \Delta(nV) = \Delta n_{eth}\overline{V}_{eth}$$

The partial molar volume of water is from the graph at our solution concentration.

Δn_{eth} is the number of moles of ethanol added. What is this? We know we add 0.1 cm^3 of pure ethanol. We can use this and the molar volume of pure ethanol to figure out the number of moles. Then we plug into equation above to get ΔV^t.

2)

Our first instinct may be to find directly the fugacity of water in the vapor phase by:

$\hat{f}_1^V = \hat{\phi}_1 y_1 P$ (for vapor mixture; we're at high pressure [150 atm], can't assume ideal gas).

But we don't know ϕ_i and y_i. But remember that at equilibrium: $\hat{f}_1^V = \hat{f}_1^L$. And for the liquid:

$\hat{f}_1^L = \gamma_1 x_1 \phi_1^{sat} P_1^{sat} \exp\left[\frac{V_1^L (P - P_1^{sat})}{RT}\right]$ Let's analyze it term by term:

$\mathbf{x_1 = 0.5}$; $\ln \gamma_1 = x_2 x_3 (1-2x_1) = x_2 x_3 (1-2(0.5)) = 0$ → $\boldsymbol{\gamma_1 = 1}$ (how convenient!)

$\mathbf{P_1^{sat} = 1}$ **atm** (for water at 100°C; from common knowledge, steam table, or Antoine's equation)

$\boldsymbol{\phi_1^{sat}} = \phi_{water}(100^oC, P_1^{sat}(100^oC)) = \phi_{water}(100^oC, 1 \text{ atm}) \approx \mathbf{1}$ (because 1 atm is reasonably low).

(Note that although the overall P is high, ϕ_1^{sat} is approximately 1 because P_1^{sat} is low).

All that remains is the Poynting correction:

$$\exp\left[\frac{V_1^L (P - P_1^{sat})}{RT}\right] = \exp\left[\frac{18 \text{ cm}^3/\text{mol}(150-1) \text{ atm}}{R(373 \text{ K})}\right] = 1.10$$ (V^L can be calculated from density)

$$\hat{f}_1^V = \hat{f}_1^L = \gamma_1 x_1 \phi_1^{sat} P_1^{sat} \exp\left[\frac{V_1^L (P - P_1^{sat})}{RT}\right] = (1)(0.5)(1)(1 \text{ atm})(1.10) = \mathbf{0.55 \text{ atm}} \quad \textbf{(ans)}$$

MORAL OF THE STORY: Always remember that fugacities (like Gibbs free energy) of species in different phases are equal when they are in equilibrium. We wanted fugacity in vapor but we can get it from fugacity in liquid.

b)

This similar to the one above but now we can make the assumption that the gas is ideal (1 atm). So we get modified Raoult's. γ_1 is same because $x_1$is same as above. Again, P_1^{sat} at 100°C is 1 atm.

$y_1 P = \gamma_1 x_1 P_1^{sat}$ → $y_1 = \gamma_1 x_1 P_1^{sat}/P = (1)(0.5)(1 \text{ atm})/(1 \text{ atm}) = \mathbf{0.5}$ **(ans)**

3)

The following information is given for our two favorite species (1) and (2) at 75°C:
$G^E/RT = x_1x_2(A_{21}x_1 + A_{12}x_2)$ *where* $A_{12} = 0.6$ *and* $A_{21} = 1.5$. $P_1^{sat} = 1.2$ *atm and* $P_2^{sat} = 2.7$ *atm.*
Henry's law constants: $\mathcal{H}_1 = 2.187$ *atm and* $\mathcal{H}_2 = 12.10$ *atm. What is* y_2 *if* $x_1 = 0.99$?

Semi-trick question. We can calculate the vapor composition the usual way using modified Raoult's:

1) Get expression for γ_1 and γ_2 from G^E/RT.
2) Use the 2 modified Raoult's to solve for y_1 and P.

A quicker way since we operate at x_1 close to 1 and x_2 close to 0 is to use Henry's law and Lewis-Randall rule. (Another good reason is also that we have the Henry's law constants. If we don't, we can't use it and we have to use the G^E/RT expression).

$\hat{f}_1^L = x_1P_1^{sat}$ Lewis-Randall rule for species 1 because $x_1 \rightarrow 1$ (basically $\gamma_1 \rightarrow 1$; does this make sense?)

$\hat{f}_2^L = x_2\mathcal{H}_2$ Henry's law for species 2 because $x_2 \rightarrow 1$

$\hat{f}_i^V = \hat{\phi}_i y_i P = y_i P$ we can assume ideal gas because P seems to be low enough.

Thus we have two equilibrium equations (from $\hat{f}_i^V = \hat{f}_i^L$):

$$y_1P = x_1P_1^{sat} \Rightarrow (1 - y_2)P = x_1P_1^{sat}y$$

$$y_2P = x_2\mathcal{H}_2 \Rightarrow y_2P = (1 - x_1)\mathcal{H}_2$$

Dividing the two equations give us:

$$\frac{(1-y_2)}{y_2} = \frac{x_1P_1^{sat}}{(1-x_1)\mathcal{H}_2}$$

we know everything except y_2. Solving for $y_2 \rightarrow$ $y_2 =$ **0.092 (ans)**

If we calculate γ's from G^E/RT and do it the usual way, we will get the same (or, at least, very similar) answer.

4)

a)
An exercise on calculating azeotrope. Since we're at low pressures, we have two modified Raoult's equations as usual, one for species 1, one for species 2. $y_iP = x_i\gamma_iP_i^{sat}$.
We get γ_i from G^E/RT expression. Then we have $\gamma_i = f(x_1, A)$ (because $x_2=1-x_1$)
Since $y_i= x_i$ (azeotrope), we have $P = \gamma_iP_i^{sat} \rightarrow \gamma_2P_2^{sat} = P = \gamma_1P_1^{sat}$
P_i^{sat} can be calculated using the given equation. The only unknown is A (in the γ's).
We can solve for A.
(Once we have A, we have an expression for γ).

b)
In flash calculation like this, main equations:
Material balance: $L + V = F$ (where L = liquid stream, V = vapor, F = feed stream)
$x_1L + y_1V = z_1F$ (x_1 = composition in L, y_1 = in V, z_1 = in F)
Equilibrium equation: $y_1P = x_1\gamma_1P_1^{sat}$
$y_1P = x_1\gamma_1P_1^{sat}$

We are also told L = V. Using this and the first two equations, we can figure out y_1.
Using y_1 and x_1 in the last two equations, we can figure out P and T. (T is embedded in P^{sat}).

This is similar to problem 34c in the pset, except that we are given different knowns and asked to solve for different unknowns.
MAIN POINT: Remember to use material balance AND equilibrium equation in separation problem such as this one.

5)
This is a bubble point and dew point calculation. See problem 33 in pset J.
The main difference here is that we're not given a function for G^E/RT. Instead, we have a graph instead. How do we use this to get γ's?
Remember that the partial molar properties $\overline{M}_i$ **for a binary system** can be acquired from a chart of M vs x_i by drawing tangent line. For example, at x_1=0.5 (see problem), draw a tangent line to the curve and find the intercept at x_1 = 1. That gives you $\frac{\overline{G}_1^E}{RT} = \ln\gamma_1$. The intercept at x_1 = 0 gives us $\ln \gamma_2$. Thus we can use this method to get γ's at any given x_1.

The other parts of the problems are figuring out how to solve for the wanted variables. Please see solution to problem 33 in pset J if you don't know how to do these (bubble and dew point calculation).