Solution for final examination for fall semester of 2006/2007

| | (A) | (B) | (C) | (D) |
|---|---|---|---|---|
| ⓿❶ | ● | | | |
| ⓿❷ | | | ● | |
| ⓿❸ | | | | ● |
| ⓿❹ | | ● | | |
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| ⓿❻ | | | | ● |
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**2. (3 marks)** The metal tin undergoes a transition from a gray phase to a white phase at 286 K at ambient pressure. Given that the enthalpy change of this transition is 2090 kJ/mole and that the volume change of this transition is -4.35 cm$^3$/mole, compute the temperature at which this transition occurs at 100 bar.

**Solution**

The Clapeyron equation in finite difference form is given as

$$\Delta T = \Delta P \frac{T\Delta v}{\Delta h}$$

Substitute known values in consistent units

$$\Delta T = (99\times 10^5)\frac{(-4.35\times 10^{-6})286}{2,090,000} = -5.893\times 10^{-3}\ \mathrm{K}$$

$$T_{\text{transition}} = T + \Delta T = 286 - 5.893\times 10^{-3} = 285.99\,\mathrm{K}.$$

This temperature is essentially the same as that at ambient pressure which clearly, demonstrates the weak influence of pressure on solid phase transitions.

**3. (5 marks)** The partial molar enthalpies of species in a simple binary mixture can sometimes be approximated by the following expressions:

$$\bar{h}_1 - h_1 = a_1 + b_1 x_2^2$$
$$\bar{h}_2 - h_2 = a_2 + b_2 x_1^2$$

For these expressions show that $b_1$ must equal $b_2$.

**Solution**

The Gibbs-Duhem equation for a binary mixture is

$$x_1 \left.\frac{\partial \bar{h}_1}{\partial x_1}\right|_{T,P} + x_2 \left.\frac{\partial \bar{h}_2}{\partial x_1}\right|_{T,P} = 0$$

Carrying out the required partial derivatives

$$\left.\frac{\partial \bar{h}_1}{\partial x_1}\right|_{T,P} = 2x_2 b_1 \frac{\partial x_2}{\partial x_1} = -2x_2 b_1$$

$$\left.\frac{\partial \bar{h}_2}{\partial x_1}\right|_{T,P} = 2x_1 b_2$$

Substitute in the Gibbs-Duhem equation to obtain

$$x_1 \left.\frac{\partial \bar{h}_1}{\partial x_1}\right|_{T,P} + x_2 \left.\frac{\partial \bar{h}_2}{\partial x_1}\right|_{T,P} = 0 = 2(b_2 - b_1)x_1 x_2$$

For all mole fractions we have $b_1 = b_2$.

**4. (8 marks)** for an equimolar mixture of ethane and *n*-butane at 373.15 K and 10 bar.

a) Compute the fugacities for ethane and *n*-butane using the virial equation of state.

b) Determine the fugacity in the mixture using the virial EOS.

c) (**Bonus: 4 marks**) Repeat parts a and b using the PR-EOS.

d) Comment on your results.

The following data are available regarding the virial coefficients:

$B_{\text{ET-ET}} = -1.15\times10^{-4}$, $B_{\text{BU-BU}} = -4.22\times10^{-4}$, $B_{\text{ET-BU}} = -2.15\times10^{-4}$ m³/mol.

**Solution**

The mixture second virial coefficient is given by

$$\begin{aligned}B_{\text{mix}} &= \sum\sum y_i y_j B_{ij} = y_{ET}^2 B_{ET-ET} + 2y_{ET}y_{BU}B_{ET-BU} + y_{BU}^2 B_{BU-BU}\\ &= \left[(0.5)^2(-1.15) + 2(0.5)(0.5)(-2.15) + (0.5)^2(-4.22)\right]\times10^{-4} = -2.42\times10^{-4}\ \text{m}^3/\text{mol.}\end{aligned}$$

Calculate mixture's compressibility factor as

$$Z_{\text{mix}} = \frac{1}{2}\left(1+\sqrt{1+\frac{4B_{\text{mix}}P}{RT}}\right) = \frac{1}{2}\left(1+\sqrt{1+\frac{4(-2.42\times10^{-4})(10\times10^5)}{(8.314)(373.15)}}\right) = 0.9148.$$

Calculate the fugacity coefficient from the virial EOS as

$$\ln\frac{f_i^V}{y_iP} = \frac{2P}{Z_{\text{mix}}RT}\sum_j y_jB_{ij} - \ln Z_{\text{mix}}$$

$$\frac{2P}{Z_{\text{mix}}RT} = \frac{2(10\times10^5)}{(0.9184)(8.314)(373.15)} = 704.69$$

$$\ln Z_{\text{mix}} = \ln 0.9184 = -0.089.$$

$$\ln\phi_1 = \ln\frac{f_1^V}{y_1P} = \frac{2P}{Z_{\text{mix}}RT}\left(y_1B_{11} + y_2B_{12}\right) - \ln Z_{\text{mix}} = -0.027247$$

$$\ln\phi_2 = \ln\frac{f_2^V}{y_2P} = \frac{2P}{Z_{\text{mix}}RT}\left(y_1B_{21} + y_2B_{22}\right) - \ln Z_{\text{mix}} = -0.13542$$

$$f_1^V = y_1P\exp(\ln\phi_1) = 4.866\ \text{bar}$$

$$f_2^V = y_2P\exp(\ln\phi_2) = 4.367\ \text{bar.}$$

Fugacity in the mixture is determined as if the mixture were a pure component with a second virial coefficient equal to $B_{\text{mix}}$

$$\ln\phi = \ln\frac{f}{P} = \frac{2PB_{\text{mix}}}{Z_{\text{mix}}RT} - \ln Z_{\text{mix}} = -0.081332$$

$$f = P\exp(\ln\phi) = 9.219\ \text{bar.}$$

The fugacity of each component would be equal if we have used the Lewis-Randall rule. This apparently is not in line with the results obtained using the mixing rules for the cross second virial coefficients. **The values using the PR-EOS are not very far from the predictions of the virial EOS at 4.8333 and 4.3301 bar for ethane and *n*-butane, respectively.**

**5. (10 marks)** A vapor-liquid mixture of water (1) - furfural (2) is maintained at 1.013 bar and 109.5ºC. It is observed that at equilibrium, the water content of the liquid is 10 mol % and that of the vapor is 81 mol %. The temperature of the mixture is changed to 100.6ºC, and some (but not all) of the vapor condenses. Assuming that the vapor phase is ideal and, and the liquid-phase activity coefficients are independent of temperature but dependent on concentration. Compute the equilibrium vapor and liquid compositions at the new temperature.

The following data are available regarding vapor pressure:

$$P_{\mathrm{H_2O}}^{\mathrm{vap}}(T=109.5^{\mathrm{o}}\mathrm{C})=1.4088\ \mathrm{bar}\,,\quad P_{\mathrm{Furf}}^{\mathrm{vap}}(T=109.5^{\mathrm{o}}\mathrm{C})=0.1690\ \mathrm{bar}\,,$$

$$P_{\mathrm{H_2O}}^{\mathrm{vap}}(T=100.6^{\mathrm{o}}\mathrm{C})=1.0352\ \mathrm{bar}\,,\quad P_{\mathrm{Furf}}^{\mathrm{vap}}(T=100.6^{\mathrm{o}}\mathrm{C})=0.1193\ \mathrm{bar}\,.$$

**Solution**

Determine the activity coefficients at the initial equilibrium state assuming modified Raoult's law applies, that is

$$\gamma_i=\frac{y_iP}{x_iP_i^{\mathrm{sat}}}$$

$$\gamma_1=\frac{y_1P}{x_1P_1^{\mathrm{sat}}}=\frac{(0.81)(1.013)}{(0.10)(1.4088)}=5.826$$

$$\gamma_2=\frac{y_2P}{x_2P_2^{\mathrm{sat}}}=\frac{(0.19)(1.013)}{(0.90)(0.1690)}=1.266.$$

Now, that we have two activity coefficients, the van Laar model parameters can be obtained using

$$\alpha=\left(1+\frac{x_2\ln\gamma_2}{x_1\ln\gamma_1}\right)^2\ln\gamma_1=8.5466$$

$$\beta=\left(1+\frac{x_1\ln\gamma_1}{x_2\ln\gamma_2}\right)^2\ln\gamma_2=0.7898$$

The parameters estimated are available for use over the whole composition range provided that they are not temperature dependent. Therefore, they can be used for the second part requesting the equilibrium composition at the new temperature.

$$\ln\gamma_1=\frac{8.5466}{\left(1+10.821\dfrac{x_1}{x_2}\right)^2},\quad \ln\gamma_2=\frac{0.7898}{\left(1+0.092411\dfrac{x_2}{x_1}\right)^2}$$

Again, resort is made to the modified Raoult's law at the new temperature such that

$$y_iP=\gamma_ix_iP_i^{\mathrm{sat}}\Rightarrow\sum y_iP=P=\sum\gamma_ix_iP_i^{\mathrm{sat}}$$

$$P=\gamma_1(\mathbf{x})x_1P_1^{\mathrm{sat}}+\gamma_2(\mathbf{x})x_2P_2^{\mathrm{sat}}$$

This equation necessitates solving a single nonlinear equation with a single unknown, i.e., the mole fraction of any of the two components in the liquid phase.

$$P = \exp\left[\frac{8.5466}{\left(1+10.821\frac{x_1}{(1-x_1)}\right)^2}\right]x_1P_1^{\mathrm{sat}} + \exp\left[\frac{0.7898}{\left(1+0.092411\frac{(1-x_1)}{x_1}\right)^2}\right](1-x_1)P_2^{\mathrm{sat}}$$

I will solve this equation in the following steps:

1. Assume a given value of the mole fraction of the first component $x_1$. Afterwards, calculate the mole fraction of the other component using $x_2 = 1 - x_1$.
2. Calculate the activity coefficients for both components.
3. Substitute in the total pressure equation and check to see if the difference is within a certain convergence criteria: $P - \gamma_1 x_1 P_1^{\mathrm{sat}} + \gamma_2 x_2 P_2^{\mathrm{sat}} < \varepsilon$. This can be checked by the summation of the mole fractions in the vapor phase

A good initial guess would be close to the mole fraction at the higher temperature. One would tend to think that the mole fraction in the liquid phase ought to be higher than the fraction at higher temperature due to reduced vapor pressure. However, this is not the case since the final answer converges to $x_1 = 0.0747$!

| $i$ | $x_1$ | $\gamma_1$ | $\gamma_2$ | $P - \sum \gamma_i x_i P_i^{\mathrm{sat}}$ | $y_1 + y_2$ |
|---|---|---|---|---|---|
| 1 | 0.1 | 5.8243 | 1.2654 | 0.2742 | 0.5952+0.1341 = 0.7293 |
| 2 | 0.08 | 9.6656 | 1.204 | 0.0804 | 0.7902+0.1305 = 0.9207 |
| 3 | 0.07 | 13.408 | 1.1725 | -0.0887 | 0.9591+0.1284 = 1.0875 |
| 4 | 0.075 | 11.300 | 1.1883 | 0.0045 | 0.8661+0.1295 = 0.9956 |
| 5 | **0.0747** | **11.412** | **1.1873** | **-0.00054** | **0.8712+0.1294 = 1.0005** |

Notice how sensitive the activity coefficient of water on the composition compared to that of furfural.

**6. (6 marks)** the equilibrium state in the carbon tetrachloride-water system at 25ºC is two phases: one an aqueous phase containing 0.9708×10$^{-4}$ mol% $CCl_4$, and the other an organic phase containing 0.9403×10$^{-3}$ mol% water.

a) Estimate the activity coefficient of $CCl_4$ in the aqueous phase and water in the organic phase.

b) Provide an estimate of the infinite dilution activity coefficients for $CCl_4$ in the aqueous phase and water in the organic phase.

**Solution**

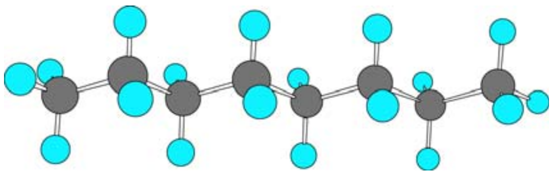
Determine the activity coefficients for essentially immiscible liquids using the assumption that each component in its phase is essentially pure which sets its activity coefficient in that phase to unity. Therefore,

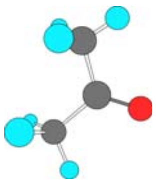
$$\gamma_{\mathrm{CCl_4,aq}} = \frac{x_{\mathrm{CCl_4,org}}\gamma_{\mathrm{CCl_4,org}}}{x_{\mathrm{CCl_4,org}}} = \frac{0.9991(1)}{0.9708\times10^{-4}} = 10,291$$

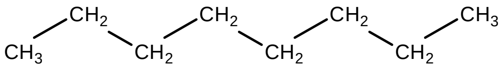
$$\gamma_{\mathrm{H_2O,org}} = \frac{x_{\mathrm{H_2O,aq}}\gamma_{\mathrm{H_2O,aq}}}{x_{\mathrm{H_2O,org}}} = \frac{0.9999(1)}{0.9403\times10^{-3}} = 1,063.4$$

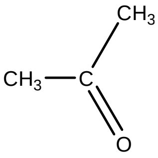
Due to the very low concentrations, the calculated activity coefficients may be considered the infinite dilution activity coefficients!
The activity coefficients calculated are very large indeed compared to VLE activity coefficients. This is to be expected for such a mixture which exhibits differences in shape, size and energy.

**7. (8 marks)** Estimate the activity coefficients for a mixture of 0.5 mole fraction acetone and 0.5 mole fraction n-octane at 298.15 K. Comment on the results regarding the values of the activity coefficients and possible and plausible explanation.









```
ncomps =2
ngroups =3
T =298.15
x = [0.5 0.5]
components ={'acetone' 'n-octane'}
subgroups ={'CH3' 'CH2' 'CH3CO'}
R =[0.9011 0.6744 1.6724]’
Q =[0.848 0.54 1.488]’
k =[1 2 21]
amk =[      0            0        476.4
            0            0        476.4
        26.76        26.76            0]
newk =[1     0     1
     2     6     0]
ri =[2.5735 5.8486]’
qi =[ 2.336 4.936]’
eki =[0.36301       0.3436
            0       0.6564
      0.63699            0]
```

```
taumk =[1            1      0.20233
            1            1      0.20233
      0.91416      0.91416            1]
Betaik =[0.94532      0.94532      0.71043
            1            1      0.20233]
sk =[0.98243      0.98243      0.36555]
Ji =[0.61113 1.3889]’
Li =[0.64246 1.3575]’
lngamcomb =[-0.089215 -0.053905]’
lngamresid =[0.5753 0.46825]’
gamma =[1.6259 1.5134]’
```