10.213 Chemical Engineering Thermodynamics
Spring 2002

Test 3 Solution

Problem 1 (20 points)

Indicate whether each of the following statements is true or false (1 point each) and provide suitable explanations and justifications for each of your answers (4 points each).

a) $\sum\left(x_i d\hat{\phi}_i\right) = 0$ *by the Gibbs-Duhem relationship.*

False. The Giibs-Duhem relationship applies to partial molar properties. $\hat{\phi}_i$ is not a partial molar property, so the statement is false. The following is true: $\sum\left(x_i d\ln\hat{\phi}_i\right) = 0$ as $\ln\hat{\phi}_i$ is a partial molar property.

b) S^E *for an ideal solution =* $-R\sum\left(x_i \ln x_i\right)$ *in order to accommodate the effects of mixing (i.e., that S for a solution* $\neq \sum x_i S_i$ *).*

False. Any excess property (M^E) for an ideal solution is, by definition, 0. The $-R\sum\left(x_i \ln x_i\right)$ term is not an excess property because it is part of the ideal mixing process. It is part of the expression for S of an ideal solution.

c) *Modified Raoult's expression assumes that the interactions between molecules in the gas phase and between molecules in the liquid phase are both zero.*

False. Modified Raoult's does assume that molecular interactions in the *gas* phase are zero (ideal gas). However, it makes no assumption about the interactions in the liquid phase. For ideal liquid solutions (not the case for Modified Raoult's), the interactions in the liquid are assumed to be non-zero but the same between different molecules. For non-ideal solutions, these different interactions are contained in the activity coefficient term, γ_i.

d) *At equilibrium, a flavoring ingredient dissolved in salad dressing (a phase of oil on a phase of water) would have the same molar concentration.*

False. At equilibrium, the fugacity of the species in the oil phase and in the water phase would be the same ($\hat{f}_1^{oil} = \hat{f}_1^{water}$). The molar concentrations, however, need not be equal.

Problem 2 (35 points)

At atmospheric pressure, acetone (1) and chloroform (2) form an azeotrope that boils at 64.6 ºC and has a mole fraction of acetone in the liquid of 0.335. The saturation vapor pressures of acetone and chloroform at 64.6 ºC are 1.31 and 0.98 atm, respectively.

a) *Calculate the activity coefficients of acetone and chloroform at the azeotrope.*

Low P's → okay to assume ideal gas → modified Raoult's. Also, azeotrope: $x_1=y_1$ and $x_2=y_2$.

$y_1P = \gamma_1 x_1 P_1^{sat} \rightarrow P = \gamma_1 P_1^{sat} \rightarrow \gamma_1 = P/P_1^{sat} = 1 \text{ atm}/1.31 \text{ atm} = \mathbf{0.76}$

$y_2P = \gamma_2 x_2 P_2^{sat} \rightarrow P = \gamma_2 P_2^{sat} \rightarrow \gamma_2 = P/P_2^{sat} = 1 \text{ atm}/0.98 \text{ atm} = \mathbf{1.02}$ **(ans)**

b) *Determine a value for G^E in kcal/mol for the azeotrope.*

$G^E/RT = \Sigma x_i \ln \gamma_i \rightarrow G^E = RT\, \Sigma x_i \ln \gamma_i \rightarrow G^E = RT\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$

$G^E = (1.99 \text{ cal/mol K})\,(273.1 + 64.6) \text{ K } [0.335 \ln(0.76) + 0.665 \ln(1.02)] = -\ \mathbf{0.0529 \text{ kcal/mol}}$ **(ans)**

If enthalpic factors were to dominate in influencing G^E for this system, would the adiabatic mixing of pure acetone with pure chloroform (each at 64.6 ºC) to generate a solution at the composition of the azeotrope produce a solution that was warmer or cooler than 64.6 ºC?

$G^E = H^E - TS^E < 0$. "Enthalpic factor dominates" means contribution from TS^E is small.

So very likely, $H^E < 0$. For adiabatic mixing from pure components, $\Delta H = H^E$.

Therefore, $\Delta H < 0$ → exothermic process → T will be **higher / warmer**. Reasoning: $\Delta H < 0$ → if we want T = constant, we have to decrease H (take out heat). But process is adiabatic → T will go up.

c) *Using your values in part a), calculate the composition of the vapor over a liquid solution at 64.6 ºC that contains 12 mol percent acetone. Consider the van Laar equations (p.433 of SVNA) to describe the behavior of this system and note that:*

$$\frac{\ln\gamma_2}{\ln\gamma_1} = \frac{A'_{12}}{A'_{21}}\left[\frac{x_1}{x_2}\right]^2 \quad (1)$$

van Laar: $\ln\gamma_1 = A'_{12}\left[1+\frac{A'_{12}}{A'_{21}}\frac{x_1}{x_2}\right]^{-2}$ (2) and $\ln\gamma_2 = A'_{21}\left[1+\frac{A'_{21}}{A'_{12}}\frac{x_2}{x_1}\right]^{-2}$ (3)

Strategy: 1) figure out A'$_{12}$ and A'$_{21}$ using azeotrope, 2) use A'$_{12}$ and A'$_{21}$ to get γ's to solve VLE

At the azeotrope, $x_1 = 0.335 \rightarrow \gamma_1 = 0.76$ and $\gamma_2 = 1.02$ (part a)

Re-arranging equation (1): $\frac{A'_{12}}{A'_{21}} = \frac{\ln\gamma_2}{\ln\gamma_1}\left[\frac{x_2}{x_1}\right]^2 = \frac{\ln 1.02}{\ln 0.76}\left[\frac{0.665}{0.335}\right]^2 = -0.284$

Re-arranging equation (2) to solve for A'$_{12}$:

$$A'_{12} = \ln\gamma_1\left[1+\frac{A'_{12}}{A'_{21}}\frac{x_1}{x_2}\right]^2 = \ln 0.76\left[1+(-0.284)\frac{0.335}{0.665}\right]^2 = -0.201\ ; \quad A'_{21} = \frac{A'_{12}}{A'_{12}/A'_{21}} = \frac{-0.196}{-0.295} = 0.708$$

We calculated parameters for van Laar using our knowledge of the azeotrope. Now to use them:

Using equation (2) and (3): at $x_1 = 0.12$, $\ln\gamma_1 = -0.21$; $\ln\gamma_2 = 0.0012 \rightarrow \gamma_1 = 0.81$; $\gamma_2 = 1.00$

Modified Raoult's:

$y_1P = \gamma_1 x_1 P_1^{sat} \rightarrow \quad y_1P = (0.81)(0.12)(1.31 \text{ atm}) \rightarrow \quad y_1P = 0.13 \text{ atm}$

$y_2P = \gamma_2 x_2 P_2^{sat} \rightarrow (1-y_1)P = (1.00)(0.88)(0.98 \text{ atm}) \rightarrow (1-y_1)P = 0.86 \text{ atm}$

Solving the two equations give us: $\mathbf{y_1 = 0.13}$ **(ans part c)** **P = 0.99 atm (ans part d)**

d) *Calculate the total pressure over the solution at the condition of part c).* See part c) **above**.

Problem 3 (30 points)

In generating expressions from G^E/RT from VLE data, a convenient approach is to plot values of G^E/RTx_1x_2 vs x_1 and fitting the results with an appropriate function. Consider if such data were fit by the expression: $G^E/RTx_1x_2 = A + Bx_1^2$.

a) *From the assumed expression for G^E/RT, provide expressions for $\ln\gamma_1$ and $\ln\gamma_2$ that are functions of A, B, x_1, and x_2.*

For a binary mixture: $\overline{M}_1 = M + x_2\dfrac{dM}{dx_1}$ and $\overline{M}_2 = M - x_1\dfrac{dM}{dx_1}$

thus, $\ln\gamma_1 = \overline{G}_1^E/RT = G^E/RT + x_2\dfrac{dG^E/RT}{dx_1}$ and $\ln\gamma_2 = \overline{G}_2^E/RT = G^E/RT - x_1\dfrac{dG^E/RT}{dx_1}$

$$\frac{dG^E/RT}{dx_1} = \frac{d}{dx_1}\left[(x_1 - x_1^2)(A + Bx_1^2)\right] = (1-2x_1)(A+Bx_1^2) + (x_1 - x_1^2)(2Bx_1)$$

$$\ln\gamma_1 = (x_1 - x_1^2)(A + Bx_1^2) + (1 - x_1)[(1-2x_1)(A+Bx_1^2) + (x_1 - x_1^2)(2Bx_1)]$$

$$\ln\gamma_2 = (x_1 - x_1^2)(A + Bx_1^2) - x_1[(1-2x_1)(A+Bx_1^2) + (x_1 - x_1^2)(2Bx_1)]$$

(ans)

We can simplify this further but these expressions are sufficient.

Also valid: $\ln\gamma_i = \dfrac{\overline{G}_i^E}{RT} = \left(\dfrac{\partial(nG^E/RT)}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ We should get the same answer (though may seem different).

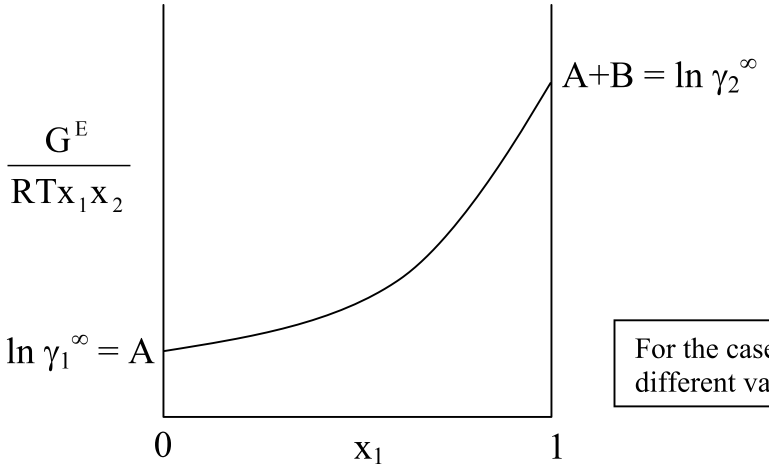
b) *For your expressions in a), relate A and B to the parameters $\ln\gamma_1^\infty$ and $\ln\gamma_2^\infty$ noting your approach. If you were unable to solve part a), you should still be able to provide an answer to how you would solve this problem.*

$x_1 \rightarrow 0$, $\ln\gamma_1 \rightarrow \ln\gamma_1^\infty$; $\ln\gamma_1^\infty = (0)(A+B(0)) + (1-0)\,[(1-0)(A+B(0))+(0)2B(0)] = A$

$x_2 \rightarrow 0$, $\ln\gamma_2 \rightarrow \ln\gamma_2^\infty$; $\ln\gamma_2^\infty = (1-1)(A+B(1)) - 1\,[(1-2(1))(A+B(1))+(1-1)(2B)] = (-1)(-1)(A+B) = A+B$

$\ln\gamma_1^\infty = A$ $\quad$ $\ln\gamma_2^\infty = A+B$ $\quad$ (ans)

c) *Provide a sketch of $A + Bx_1^2$ on a graph of G^E/RTx_1x_2 vs x_1, noting the limiting locations of $\ln\gamma_1^\infty$ and $\ln\gamma_2^\infty$ on this graph. Provide relationships for A and for B to $\ln\gamma_1^\infty$ and $\ln\gamma_2^\infty$ and any other parameters needed using the plot.*



For the case of positive and different values of A and B.

Problem 4 (15 points)

A cylinder of propane (1) at 60 bar and 30 ºC contains some liquid water (2). The propane is sparingly soluble in the water under these conditions. Assume that ln γ_1 *can be described by the expression ln* $\gamma_1 = Ax_2^2$*. Note whether propane behaves as an ideal gas under these conditions and where conditions of an ideal solution in the gas phase apply. The saturation pressure of propane at this temperature is 10.8 bar.*

a) What is the fugacity of propane in either phase?

In *either* phase, because $\hat{f}_1^L = \hat{f}_1^V$. So if we know one, we know both. We can try:

$\hat{f}_1^L = x_1\gamma_1 P_1^{sat}$ but we don't know the composition x_1. So we try the vapor phase. Now the vapor is mostly propane. Note that the question states "contains some *liquid* water". Also we can check the steam tables that P_2^{sat} at 30 °C is 0.04 atm (or ~0.04 bar), much lower than P_1^{sat}, so propane is much more volatile than water.
Thus the vapor phase fugacity is approximately that of pure propane:
$\hat{f}_1^V = \hat{\phi}_1 y_1 P \approx \phi_1 P$ We know P = 60 bar. ϕ_1 we can get from generalized correlation.
Propane's $P_c = 42.48$ bar, $T_c = 369.8$ K, $\omega = 0.152$.

$$\left.\begin{array}{l} P_r = 60\text{ bar} / 42.48\text{ bar} = 1.41 \\ T_r = 303\text{ K} / 369.8\text{ K} = 0.82 \end{array}\right\} \quad \text{From table E.15-6:} \quad \begin{array}{l} \phi^0 \approx 0.21 \qquad \phi^1 \approx 0.36 \\ \phi = (\phi^0)(\phi^1)^{\omega} = (0.21)(0.36)^{0.152} = 0.18 \end{array}$$

$\hat{f}_1^V = \phi_1 P = (0.18)(60\text{ bar}) \approx$ **10.8 bar** **(ans)**

b) Provide a value for the Henry's law constant for propane in water at this pressure that is a function only of A.

Henry's law: $x_1 \to 0$, $\hat{f}_1^L = x_1 \mathcal{H}_1$
From modified Raoult's: $\hat{f}_1^L = x_1\gamma_1 P_1^{sat}$ when $x_1 \to 0$, $\hat{f}_1^L = x_1\gamma_1^{\infty} P_1^{sat}$
where $\gamma_1^{\infty} = \gamma_1(x_1 \to 0) = \exp(A(1)) = e^A$

Comparing the two expressions:
$\mathcal{H}_1 = \gamma_1^{\infty} P_1^{sat} = e^A$ (10.8 bar) = **10.8e^A bar** **(ans)**

Note:
A more rigorous solution requires us to calculate the most general expression for $\hat{f}_1^L = x_1\gamma_1 P_1^{sat}\phi_1^{sat}\exp\left[V_1^L(P - P_1^{sat})/RT\right]$, making $\mathcal{H}_1 = \gamma_1^{\infty} P_1^{sat}\phi_1^{sat}\exp\left[V_1^L(P - P_1^{sat})/RT\right]$.
In the case above, we assumed the last two terms ≈ 1. But let us evaluate them:

a) The Poynting correction ≈ 1, since 60 bar is still not high enough for the factor to vary much from 1.
b) ϕ_1^{sat} is ϕ_1 at T=30°C and P_1^{sat}(30°C)=10.8 bar. P_r=10.8 bar / 42.48 = 0.25, not low enough to assume $\phi_1^{sat} \approx 1$. The method is the same as what we did in part a) for ϕ_1 (evaluated at T=30°C and P=60 bar). Doing this, we'll find that $\phi_1^{sat} \approx 0.8$. Thus, in fact:
$$\mathcal{H}_1 = \gamma_1^{\infty} P_1^{sat}\phi_1^{sat} = e^A\ (10.8\text{ bar})(0.8) = 8.6\, e^A\text{ bar}$$