

Key

Don't get bogged down, and show your work! If you're stuck, try another problem. Remember to put units on everything!

True or False Section [2 points each; +2 for correct, 0 for no response, -1 for incorrect!]

i) The fugacity of a pure liquid increases if the pressure is increased isothermally:

True

ii) Negative deviations from Raoult's Law can be observed when a non-ideal vapor is in equilibrium with an ideal solution. True

iii) Henry's law applies to a component in a solution when the mole fraction of that component approaches 1.0

False

iv) The upper critical solution temperature (UCST) describes the minimum temperature that liquid-liquid equilibrium could exist in for a binary system. False

v) This criterion is sufficient for determining if a binary liquid system will phase split: the Gibbs free energy of the mixture of the two components is lower than the total Gibbs free energy of the components unmixed.

False

1. **Problem 1 [30 points]:** This problem considers two separate vapor liquid mixtures at 300K and 0.3 bar.

(i) benzene ($p^*[300K]=0.14$ bar) and C^{13} -benzene. The mole fraction of benzene in the vapor and liquid phase are 0.51 and 0.49, respectively.

(ii) benzene and n-octane ($p^*[300K]=0.02$ bar). The mole fraction of benzene in the vapor and liquid phase are 0.65 and 0.53, respectively.

(a) Find the activity coefficients of each component in (i) and (ii)

→ Two sol'n's:

$$\gamma_B = \gamma_{C^{13}B} = 1.0 \text{ (perfect ideal sol'n)}$$

If you crunched #'s:

$$\gamma_B = \frac{(0.51)(0.3 \text{ bar})}{(0.49)(0.14 \text{ bar})} = 2.25$$

$$\gamma_{C^{13}B} = 2.06$$

$$(ii) \quad \gamma_B = \frac{(0.65)(0.3 \text{ bar})}{(0.53)(0.14 \text{ bar})} = 2.62$$

$$\gamma_{oct} = \frac{(0.35)(0.3 \text{ bar})}{(0.47)(0.02 \text{ bar})} = 11.17$$

(b) Find the bubble point pressure and the composition of the vapor in equilibrium with a liquid mixture of n-octane and benzene at 70 mol% n-octane at 300K.

$$\gamma_B = 2.62 = \exp \left[x_0^2 (A_{12} + 2x_B (A_{21} - A_{12})) \right]$$

$$\gamma_0 = 11.17 = \exp \left[x_B^2 (A_{11} + 2x_0 (A_{12} - A_{11})) \right]$$

$$\text{Analyze @ } x_B = 0.53 \text{ \& } x_0 = 0.47$$

$$\begin{array}{l} \text{Two Eqs} \\ \text{Two Unknowns} \end{array} \quad \begin{array}{l} A_{12} = 8.84 \\ A_{11} = 4.63 \end{array}$$

$$\gamma_B^{NEW} = \exp \left[0.7^2 (8.84 + 2(0.3)(4.63 - 8.84)) \right] = 22.1$$

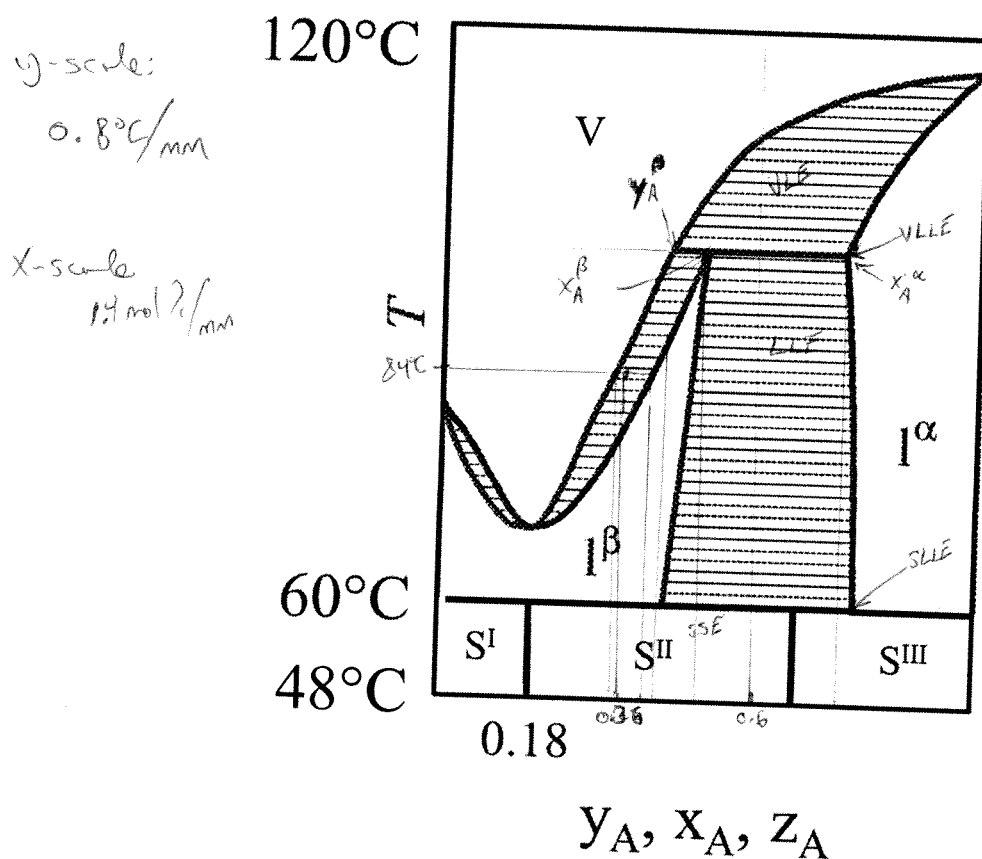
$$\gamma_0^{NEW} = 2.58$$

$$P_{BP} = x_B \gamma_B^{NEW} p_B^{Sat} + x_0 \gamma_0^{NEW} p_0^{Sat}$$

$$P_{BP} = 0.96 \text{ bar}$$

$$y_B = 0.97$$

Problem 2 [30 points]: The figure below shows the complex phase behavior of a binary mixture of A & B at 1 atm as a function of temperature and composition. A peculiarity of this system is that in addition to the pure solids, it can form mixed solids with three distinct stoichiometries, S^I , S^{II} , S^{III} (each are made up of A & B).



A binary vapor mixture at 60 mol% of A is slowly cooled down isobarically from 120°C to 40°C .

(a) What is the progression of phases that will be encountered during this process? Mark these on the plot.

$V \rightarrow VLE \rightarrow VLL \rightarrow LLE \rightarrow SLE \rightarrow SSE$

(b) What is the approximate temperature and composition at the VLLE condition? A ruler is helpful here.

$T: 61 \text{ mm} \rightarrow$
 $T_{VLLE} = 96.8^\circ\text{C}$
 $y_A^{VLLE} = 0.406$ (29 mm)
 $x_A^{B, VLLE} = 0.49$ (35 mm)
 $x_A^{\alpha, VLLE} = 0.756$ (54 mm)

(c) Describe what is happening at the odd "U" shape between 60°C and 120°C. Give details associated with this phenomenon.

This is an a V-L azeotrope, where $x_A = y_A$ & the relative volatility is 1.0.

(d) One mole of a 36 mol% A vapor mixture is cooled to 84°C. What are molar amounts in each phase at this condition?

$$y_A = 0.336 \quad x_A = 0.392$$

$$n = 1.0 \text{ mol} = n_L + n_V$$

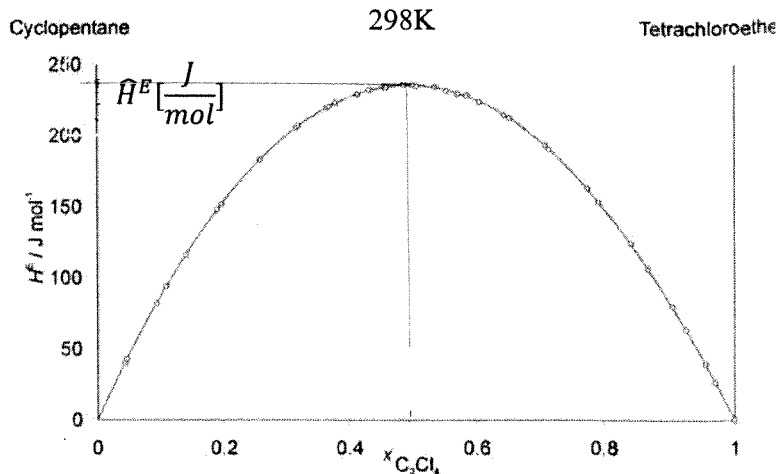
$$n_A = 0.36 \text{ mol} = n_L(0.392) + n_V(0.336)$$

$n_L = 0.43 \text{ mol}$
$n_V = 0.57 \text{ mol}$

Problem 3 [30 points]:

Cyclopentane and tetrachloroethylene (TCE, C_2Cl_4) are mixed isothermally at 298K in equimolar amounts and kept in contact with air at 1 bar. The solubility of air in both components is negligible at all compositions.

The vapor pressure of cyclopentane at this temperature is 0.42 bar, and the vapor pressure of TCE is 0.03 bar.



The excess entropy at 298K is -2 J/mol K for a 50/50 mixture by mole fraction.

The excess enthalpy is given in the attached plot for 298K.

(a) Calculate the total entropy change of mixing associated with mixing one mole of pure cyclopentane and one mole of pure TCE at 298K.

$$\Delta \hat{S}_{mix} = \hat{S}^E - R \sum_i x_i \ln x_i = -\frac{2 \text{ J}}{\text{mol K}} - \frac{8.314 \text{ J}}{\text{mol K}} \cdot 2 \cdot 0.5 \ln 0.5$$

$$\Delta \hat{S}_{mix} = 3.76 \text{ J/mol K}$$

(b) Calculate the excess Gibbs free energy for an equimolar mixture of cyclopentane and TCE at 298K.

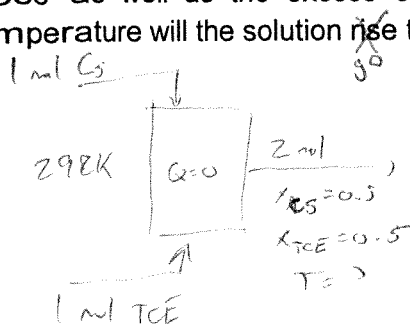
$$\hat{H}^E = 235 \text{ J/mol}$$

$$\hat{G}^E = \hat{H}^E - T \hat{S}^E$$

$$= 235 \text{ J/mol} - (298 \text{ K}) \left(\frac{-2.0 \text{ J/mol K}}{\text{mol K}} \right)$$

$$\hat{G}^E = 831 \text{ J/mol}$$

(c) Assuming the heat capacity of cyclopentane is 1 J/mol-K and the heat capacity of TCE is 1.5 J/mol-K, and these as well as the excess enthalpy, entropy, and free energy are independent of temperature, what temperature will the solution rise to when one mole of cyclopentane is added adiabatically to one mole of TCE?



Energy balance:

$$Q = 0 = \Delta \hat{H}$$

$$\Delta \hat{H} = \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in}$$

Ref: Pure components, 25°C, liquid

$$\therefore \Delta \hat{H} = \sum n_{out} \hat{H}_{out} = 0$$

$$n_{Cs} C_{p,Cs} \Delta T + n_{TCE} C_{p,TCE} \Delta T + \Delta \hat{H}_{mix} = 0$$

$$\Delta T = \frac{-\Delta \hat{H}_{mix}}{n_{Cs} C_{p,Cs} + n_{TCE} C_{p,TCE}}$$

$$= \frac{-235 \text{ J/mol} \cdot 2}{1 \text{ J/K} + 1.5 \text{ J/K}}$$

$$\Delta T = -94^\circ\text{C} = -128^\circ\text{C} \quad \hat{H}^E, \hat{S}^E, \hat{G}^E \neq f(T) \text{ is not a good assumption!!}$$

(d) Assume the mixture can be represented by the simple Margules model. Calculate the activity coefficients for cyclopentane and TCE in the equimolar mixture.

$$\frac{\hat{G}^E}{RT} = A x_1 x_2$$

$$@ x_1 = x_2 = 0.5 :$$

$$\frac{831 \text{ J/mol} \cdot \text{K}}{2.314 \text{ J/mol} \cdot \text{K} \cdot 298 \text{ K}} = A(0.5)^2$$

$$\Rightarrow A = 1.34$$

For single parameter Margules
 $@ x_1 = x_2 = 0.5 :$

$$\gamma_1 = \gamma_2 = \exp[1.34(0.5)^2] = 1.39$$

(e) What are the vapor phase compositions of each component at 298K?

$$y_{Cs} P = x_{Cs} \gamma_{Cs} P_{Cs}^{sat} = (0.5)(1.39)(0.42 \text{ bar}) = 0.29 \text{ bar}$$

$$y_{TCE} P = x_{TCE} \gamma_{TCE} P_{TCE}^{sat} = (0.5)(1.39)(0.03 \text{ bar}) = 0.02 \text{ bar}$$

$$P = 1 \text{ bar}$$

$$y_{Cs} = \frac{0.29}{1} = 0.29$$

$$y_{TCE} = 0.02$$

$$y_{Air} = 0.69$$