Quiz 12
Chemical Engineering Thermodynamics
April 16, 2020

Ephedrine (ephe) is a decongestant and stimulant (a regulated substance). It can be produce by extraction from green plants using ethanol at elevated temperatures followed by solvent exchange with water followed by phase separation. Assume that a liquid-liquid phase separation occurs at 25°C in pure water.
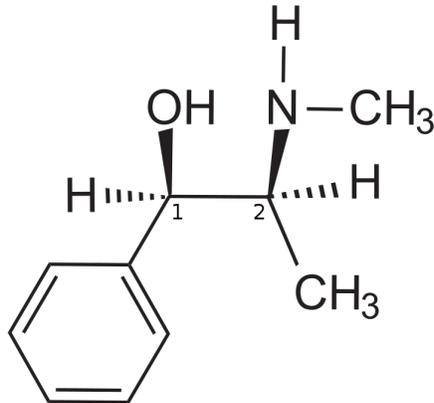
Ephedrine (Ephe) (1)

Consider **ephe (1)** in **water (2)** at **25°C**.
Assume that ephe can be approximated in UNIFAC LLEa tab in the Actcoeff.xls spreadsheet as:

CH3	2
CH	2
ACH	5
OH	1
ACNH2	1

(*For this problem you can use more than 3 digits where it seems necessary. Try to round to three digits or a minimum number of digits where possible for the sake of sanity.*)

a) What is the composition of the two liquid phases that will form at 25°C? (Assume initially that phase α is pure 2 and phase β is pure 1.
Iterate until convergence (4 or 5 iterations).
Use UNIFAC (LLEa) in the ActCoeff.xlsx sheet to calculate the γs.

b) Sketch T versus x_1 and show the 2-phase region with your two equilibrium points, as well as a curve demarking the 1- and 2-phase regions. Show a tie line between the α and β phases.

c) The binary water/ephe mixture is fed from the liquid extraction/solvent exchange process with a molar concentration of 0.25 ephe in water.

-After phase separation what fraction of this feed goes to the α and to the β phase? (Give α/F and β/F.)

-If the total feed is one mole, how many moles of ephe are in the β phase? (Show how this is calculated.)

-Add the input composition to the plot you made in part b with an arrow to the tie line.

d) Ephe is to be crystallized from the β phase.

-What is the crystallization temperature for ephe at this composition? For ephe: $\Delta H_f=$ 25kJ/mole $T_m = 313K$ $M_w = 165.2$g/mole. (This will require iteration of temperature beginning with 25°C to obtain γ_1 from UNIFAC LLEa sheet.)

-Add the crystallization curve to your plot from part b using the pure ephe crystallization temperature and your calculated crystallization temperature.

e) It is desired to obtain crystalline ephe that can be separated in a rotary decanter. Will this be possible in the proposed process of phase separation at 25°C. Explain how you expect this phase separation/crystallization to proceed at 25°C. Do you foresee problems with the process as described?

$R = 8.314$ J/(mol °K)

1. Assume that phase β is nearly pure 1, $x_1^\alpha = 1/\gamma_1^{\alpha,\infty}$, and α is nearly pure 2, $x_2^\beta = 1/\gamma_2^{\beta,\infty}$. These represent initialization of the iteration procedure. The procedure is most stable with an initial guess of mutual solubility outside the two-phase region.

2. Calculate $K_{i,old} = \gamma_i^\beta/\gamma_i^\alpha$ where the γ_i's are evaluated at the initial compositions.

3. Calculate $x_{1,new}^\beta = (1-K_{2,old})/(K_{1,old}-K_{2,old})$, $x_{2,new}^\beta = 1-x_{1,new}^\beta$.

4. Calculate $x_{i,new}^\alpha = K_{i,old}x_{i,new}^\beta$.

5. Determine $\gamma_{i,new}$ values for each liquid phase from the $x_{i,new}$ values.

6. Calculate $K_{i,new} = \gamma_i^\beta/\gamma_i^\alpha$.

7. Replace all $x_{i,old}$ and $K_{i,old}$ values with the corresponding new values.

8. Loop to step 3 until calculations converge. The calculations converge slowly.

$$\ln(x_i\gamma_i) = \frac{-\Delta H_i^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,i}}\right) \qquad\qquad 14.24$$

Answer Sheet (Please turn in this sheet with your work and one screen shot of the excel sheet that was used).

a)	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
c)	α/F	β/F	moles ephe in β	
d)	$T_{m,\beta}$, °C			

b) Sketch plot of T versus x_1 from part a. (Include the melting line and feed composition from parts c. and d.)

e) Feasibility of process:

Answer Sheet (Please turn in this sheet with your work and one screen shot of the excel sheet that was used).

a)	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
	0.000118	0.9999	0.464	0.536
c)	α/F	β/F	moles ephe in β	
	0.461	0.539	0.25	
d)	$T_{m,\beta}$, °C			
	31			

b) Sketch plot of T versus x_1 from part a. (Include the melting line and feed composition from parts c. and d.)
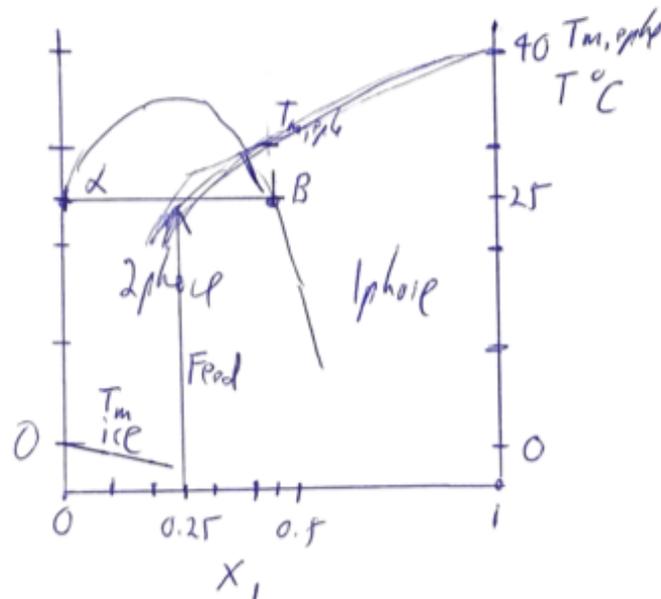
e) Feasibility of process:

The crystallization temperature is about 5°C above the phase separation temperature so the crystallization will occur slowly (rate depends on the quench depth, ΔT). It is feasible to produce ephe crystals that could be decanted but the process will be very slow.

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	x_1^α	x_2^α	x_1^β	x_2^β
0	0.000156	0.9998	0.2045	0.7955
1	0.000229	0.9998	0.356	0.644
2	0.000141	0.9999	0.449	0.551
3	0.000118	0.9999	0.464	0.536
4	0.000118	0.9999	0.464	0.536

1) $x_1^\alpha = \dfrac{1}{\gamma_1^{\alpha\infty}} = \dfrac{1}{6.392}$

$\qquad = 0.000156$

$x_2^\alpha = 0.9998$

$x_2^\beta = \dfrac{1}{\gamma_2^{\beta\infty}} = \dfrac{1}{1.217}$

$\qquad = 0.7955$

$x_1^\beta = 0.2045$

From UNIFAC LLEa

$\gamma_1^\alpha = 6261 \qquad \gamma_2^\alpha = 1 \qquad K_1 = \dfrac{\gamma_1^\beta}{\gamma_1^\alpha} = \dfrac{4.024}{6261} = 0.000643$

$\gamma_1^\beta = 4.024 \qquad \gamma_2^\beta = 1.553 \qquad K_2 = \dfrac{\gamma_2^\beta}{\gamma_1^\alpha} = \dfrac{1.553}{1} = 1.553$

$x_1^\beta = \left(\dfrac{1-k_2}{k_1 k_2}\right) = 0.356 \qquad x_2^\beta = 0.644$

$x_1^\alpha = x_1^\beta K_1 = 0.000229 \qquad x_2^\alpha = 0.9998$

From UNIFAC LLEa

$\gamma_1^\alpha = 6209 \qquad \gamma_1^\beta = 1.941 \qquad K_1 = 0.000313$

$\gamma_2^\alpha = 1 \qquad \gamma_2^\beta = 1.819 \qquad K_2 = 1.819$

$x_1^\beta = \dfrac{-0.819}{-1.819} = 0.449 \qquad x_1^\alpha = x_1^\beta K_1 = 0.000141$

$x_2^\beta = \dfrac{}{0.551} \qquad x_2^\alpha = 0.9999$

$\gamma_1^\alpha = 6277 \quad \gamma_1^B = 1.601 \qquad k_1 = 0.000255$

$\gamma_2^\alpha = 1 \qquad \gamma_2^B = 1.864 \qquad k_2 = 1.864$

$$x_1^B = \frac{(1-k_2)}{(k_1-k_2)} = \frac{-0.864}{-1.864} = 0.464 \quad x_2^B = 0.536$$

$x_1^\alpha = x_1^B k_1 = 0.000118$

$\gamma_1^\alpha = 6295 \quad \gamma_1^B = 1.565 \qquad k_1 = 0.000249$

$\gamma_2^\alpha = 1 \qquad \gamma_2^B = 1.865 \qquad k_2 = 1.865$

$$x_1^B = \left(\frac{1-k_2}{k_1-k_2}\right) = 0.464 \quad x_2^B = 0.536$$

$x_1^\alpha = 0.000118$

(b)

(c) For 1 mole of feed
Feed of ethe is $0.25\text{mole} = X_{ethe}^F \text{mole}$
0.539 goes to B

$X_{eth}^F = X_{eth}^B + X_{ethe}^\alpha$
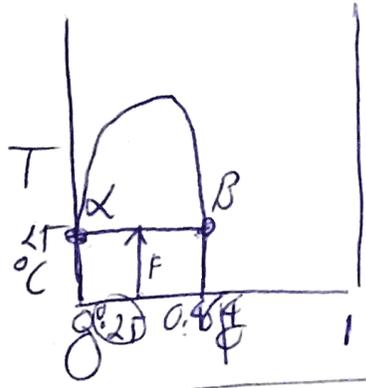
$(1\text{ mole})^F = (0.539\text{mole})^B + (0.461\text{mol})^\alpha$

B is 0.464 ethe
So 0.25 mols ethe (all of it)
are in the B phase

$\boxed{\dfrac{B}{F} = \dfrac{0.25-0.000118}{0.464-0.000118} = 0.539}$

$\dfrac{\alpha}{F} = 0.461$

d)

$$\ln(x_1 \gamma_1) = \frac{(-)\Delta H_f^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,1}}\right)$$

$$\left(\frac{-R \ln(x_1 \gamma_1)}{\Delta H_f^{fus}} + \frac{1}{T_{m,1}}\right)^{-1} = T$$

Use γ_1 at $25°C$ initially $= 1.941$

$$x_1 = 0.464$$

$$T = \frac{1}{\left(\frac{-8.315 \frac{J}{mol\, k}\,(\ln(0.464 \cdot 1.941))}{25,000 \, J/mol} + \frac{1}{313\, K}\right)}$$

$$= \left(0.000324 \frac{1}{K}\left(\ln(0.901)\right) + 0.00319\right)^{-1}$$

$$= 310 \, K$$

Set $T = 37°C$ in UNIFAC

$$\gamma_1 = 1.568$$

$$T = 303K \ (31\,°C)$$

$$\gamma_1 = 1.567$$

$$\boxed{T = 304K \ (31\,°C)}$$