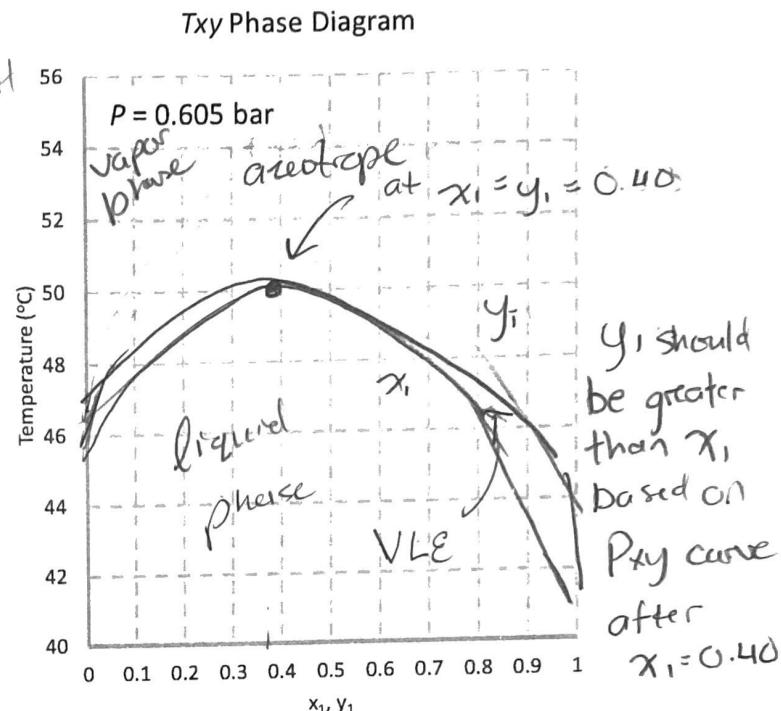
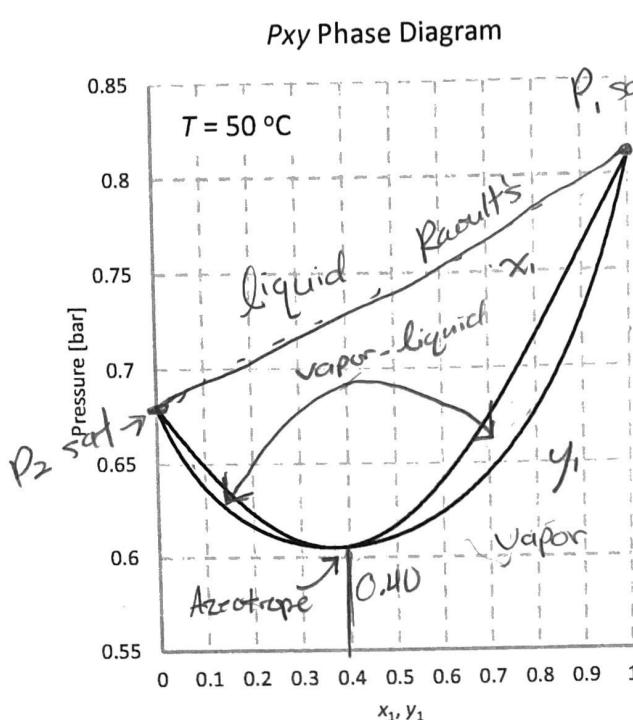


1. Consider a binary mixture of acetone (1) and chloroform (2). The P_{xy} phase diagram at 50°C is shown on the plot at the left below. Please answer the following questions.



- A. Label the azeotrope on the P_{xy} diagram. Label the liquid phase, the vapor phase, and the two-phase region.

- B. Are like interactions or unlike interactions stronger? Explain

P_{mix} is below Ideal Raoult's line, so $\gamma_i < 1$, this means g^{E} is negative so that the mixture is thermodynamically favored. Additionally, its T_{xy} azeotrope experiences a maximum in boiling point meaning it requires more energy to separate/vaporize the mixture.

- C. As carefully as you can, complete the corresponding T_{xy} diagram for acetone (1) and chloroform (2) at a constant pressure of 0.605 bar shown on the right. Identify at least two features that you have intentionally drawn.

D. From the data in the phase diagram, estimate the two-suffix Margules parameter, A , at 50°C .

assume ideal vapor $A = \underline{-2003 \text{ J/mol}}$

@ azeotrope: $x_i = y_i$

$$x_i y_i P_i^{\text{sat}} = y_i P$$

$$y_i P_i^{\text{sat}} = P$$

@ $x_1 = 1$, $P_1^{\text{sat}} = 0.8 \text{ bar}$

@ $x_2 = 1$ $P_2^{\text{sat}} = 0.67 \text{ bar}$

@ $x_1 = 0.40$, $P \approx 0.60 \text{ bar}$

for 2 components:

$$y_1 P_i^{\text{sat}} = P$$

$$y_1 = \frac{P}{P_i^{\text{sat}}} = \frac{0.60 \text{ bar}}{0.80 \text{ bar}} = 0.75$$

$$y_2 P_2^{\text{sat}} = P$$

$$y_2 = \frac{P}{P_2^{\text{sat}}} = \frac{0.60 \text{ bar}}{0.67 \text{ bar}} = 0.895$$

$$y_1 = 0.75$$

$$y_2 = 0.895$$

using 2-suffix:
 $RT \ln y_i = A x_i^2$

azeotrope occurs at

$$\begin{cases} x_1 = y_1 = 0.40 \\ x_2 = 0.60 \end{cases}$$

$$A = \frac{RT \ln y_1}{x_2^2} = \frac{(8.314 \text{ J/mol})(323 \text{ K}) \ln(0.75)}{(0.60)^2} = -2145 \text{ J/mol}$$

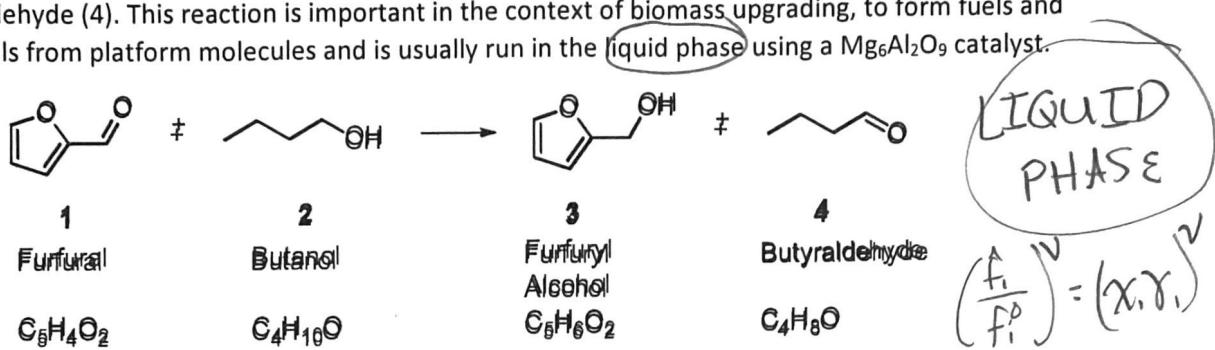
$$A = \frac{RT \ln y_2}{x_1^2} = \frac{(8.314 \text{ J/mol})(323 \text{ K}) \ln(0.895)}{(0.40)^2} = -1861 \text{ J/mol}$$

$$A = \frac{(-2145) + (-1861)}{2} = \boxed{-2003 \text{ J/mol}}$$

Average since
2-suffix

g^E is negative so unlike interactions
greater /

2. Consider the reaction of furfural (1) and butanol (2) reacting to form furfuryl alcohol (3) and butyraldehyde (4). This reaction is important in the context of biomass upgrading, to form fuels and chemicals from platform molecules and is usually run in the liquid phase using a $\text{Mg}_6\text{Al}_2\text{O}_9$ catalyst.



The enthalpies and entropies of formation of the liquid components and their saturation pressure at 413K are reported below.

	$\Delta h_{f,l,298}^\circ [\text{kJ mol}^{-1}]$	$\Delta s_{f,l,298}^\circ [\text{J mol}^{-1} \text{K}^{-1}]$	$P_i^{\text{sat}} \text{ at } 413 \text{ K [bar]}$
Furfural (1)	-200.2	218.0	0.52
Butanol (2)	-328.0	225.7	2.1
Furfuryl alcohol (3)	-276.4	215.7	0.37
Butyraldehyde (4)	-245.4	242.7	5.6

- A. Calculate the equilibrium constant for the liquid-phase reaction at 413 K. You may assume constant enthalpy of reaction.

Data at 298 K, need to find K_{298} first

$$K_{413} = 22$$

$$K_{298} = \exp\left(\frac{-\Delta g_{rxn}^{298}}{RT}\right)$$

$$K_{298} = \exp\left(\frac{+2019 \text{ J/mol}}{(8.314 \text{ J/mol})(298 \text{ K})}\right)$$

$$K_{298} = 0.4426$$

at 413 K assuming Δh_{rxn} constant

$$\ln\left(\frac{K_{413}}{K_{298}}\right) = -\left(\frac{6400 \text{ J/mol}}{8.314 \text{ J/mol K}}\right)\left(\frac{1}{413} - \frac{1}{298}\right)$$

$$K_{413} = 908$$

K_{413} should decrease for exothermic reaction at increased T ✓

$$\Delta g_{rxn} = \sum v_i g_f = \Delta h_{rxn} - T \Delta S_{rxn}$$

$$\Delta h_{rxn} = \sum v_i h_f^\circ =$$

$$= (-1)(-200.2) + (-1)(-328) + (1)(-276.4) + (1)(-245.4)$$

$$\Delta h_{rxn}^{298} = +6.4 \text{ kJ/mol} = +6400 \text{ J/mol}$$

$$\Delta S_{rxn}^{298} = \sum v_i S_f^\circ$$

$$= (-1)(218) + (-1)(225.7) + (1)(215.7) + (1)(242.7)$$

$$\Delta S_{rxn}^{298} = 14.7 \text{ J/K-mol}$$

$$\Delta g_{rxn} = \Delta h_{rxn} - T \Delta S$$

$$= (+6400 \text{ J}) - (413 \text{ K})(14.7 \text{ J/mole-K})$$

$$\Delta g_{rxn} = 2019.4 \text{ J/mol}$$

B. Calculate the extent of reaction at equilibrium for this reaction at 413 K for an initial mixture of 1 mol furfural and 1 mol butanol. You may assume the liquid mixture is ideal.

$$\xi = 0.824$$

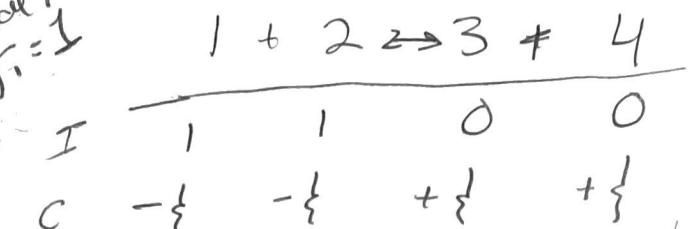
1:1 stoich

$$K_{413} = \prod_i (x_i \gamma_i)^{v_i}$$

ideal mix
 $\gamma_i = 1$

$$= \frac{(x_3 \gamma_3)(x_4 \gamma_4)}{(x_1 \gamma_1)(x_2 \gamma_2)}$$

$$K_{413} = \frac{x_3 x_4}{x_1 x_2}$$



$$\xi \quad (1-\xi) \quad (1-\xi) \quad (\xi) \quad (\xi)$$

$$x_i = \frac{1-\xi}{2} \quad \frac{1-\xi}{2} \quad \frac{\xi}{2} \quad \frac{\xi}{2}$$

$n_{\text{total}} = 2$

$$0.908 = \frac{(\xi/2)(\xi/2)}{(1-\xi/2)(1-\xi/2)} = \frac{(\xi)^2}{(1-\xi)^2}$$

$$\sqrt{0.908} = \sqrt{\frac{(\xi)^2}{(1-\xi)^2}}$$

$$0.952 = \frac{\xi}{(1-\xi)}$$

$$4908 = \frac{1}{(1-\xi)^2}$$

$$4908 = 1.952$$

$$\boxed{\xi = 0.4881}$$

solving...

C. In reality this liquid mixture is not ideal. Modify the expression from part B that you would need to solve for the extent of reaction (you do not need to solve it). What data would you need to find to for your solution?

$$K = \prod_i (x_i \gamma_i)^{v_i} = \prod_i \left(\frac{f_i}{f_i^0} \right)^{v_i}$$

$$\left(\frac{f_i}{f_i^0} \right)^{v_i} = (x_i \gamma_i)^{v_i}$$

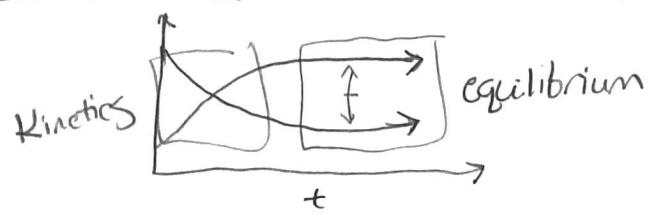
You would need
Moles

parameters
to solve
 γ_i

$$K_{413} = \frac{(x_3 \gamma_3)(x_4 \gamma_4)}{(x_1 \gamma_1)(x_2 \gamma_2)} = \frac{(\xi)^2 \gamma_3 \gamma_4}{(1-\xi) \gamma_1 \gamma_2}$$

D. Would your answer in Part B change if the catalyst were RuO₂ instead of Mg₆Al₂O₉? Explain.

No, catalysts only affect kinetics, not equilibrium. At equilibrium, reaction is purely driven by thermodynamics with a dependency on T, ΔG°rxn and ΔH°rxn only.



VLE

Consider the vapor phase that is in equilibrium above this reacting liquid mixture. You may assume that the gas phase and liquid phases are ideal and there is no reaction in the vapor phase.

E. What is the pressure in the reactor at equilibrium?

$$\varphi_i = 1$$

$$\gamma_i = 1 \quad , \quad \begin{matrix} \text{Ideal Raoult's VLE} \\ \varphi_i y_i P = x_i y_i P_{i,\text{sat}} \\ y_i P = x_i P_{i,\text{sat}} \end{matrix} \quad P_{i,\text{sat}} \text{ given in table}$$

$$\begin{aligned} P_{\text{tot}} &= \sum x_i P_{i,\text{sat}} \\ &= \left(\frac{1-\xi}{2} \right) \left(0.52 \text{ bar} \right) + \left(\frac{1-\xi}{2} \right) \left(2.1 \text{ bar} \right) + \left(\frac{\xi}{2} \right) \left(0.37 \text{ bar} \right) + \left(\frac{\xi}{2} \right) \left(5.6 \text{ bar} \right) \\ &\text{where } \xi = 0.488 \end{aligned}$$

$$P_{\text{tot}} = 0.52 + 1.05 + 0.185 + 1.44 = 2.80$$

$$P_{\text{tot}} = 2.13 \text{ bar}$$

F. What is the mole fraction of furfural in the gas phase?

$$y_i = \frac{x_i P_{i,\text{sat}}}{P} \quad x_i = \frac{1-\xi}{2} \quad \xi = 0.488 \quad y_1 = 0.0625$$

$$P_{i,\text{sat}} = 0.52 \text{ bar}$$

$$\underline{y_1 = 0.0170}$$

$$P_{\text{tot}} = 2.69 \text{ bar}$$

$$\underline{\gamma_1 = 1}$$

Final Exam 2022

Name Key

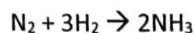
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Exam Guidelines:

- Non-graphing calculator and pencil/pens are permitted.
- One 8.5 x 11" sheet of paper with only your own handwriting is allowed (both sides ok).
- No textbook or other resources.
- All other materials, books, and cell phones should be zipped in your backpack.
- Show all your work and provide complete explanations to receive credit.
- Time = 110 minutes

Extra Space for your work below:

1. Production of ammonia (NH_3) takes place by the Haber-Bosch process. In this process, nitrogen reacts with hydrogen over a Fe catalyst to form ammonia. The reaction is shown below:



The standard enthalpy of formation of ammonia is -46.11 kJ/mol and its standard Gibbs free energy of formation is -16.45 kJ/mol at 298K.

- a. Calculate the equilibrium constant of the reaction at 298K as written above. (7pts)

$$\Delta h_{rxn} = 2(-46.11) = -9.2 \times 10^4 \text{ J/mol}$$

$$\Delta g_{rxn} = 2(-16.45) = -3.29 \times 10^4 \text{ J/mol}$$

$$K = \exp \frac{-\Delta g_{rxn}^{\circ}}{RT} = \exp \frac{-(-3.29 \times 10^4) \text{ J/mol}}{(8.3145 \text{ J/K})(298 \text{ K})}$$

$$K = 5.85 \times 10^6$$

- b. The reaction is sometimes written as $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$. Quickly calculate the equilibrium constant for the reaction as written here. (4pts)

$$K^{\frac{1}{2}} = (5.85 \times 10^6)^{\frac{1}{2}} = 765$$

- c. Write out the equilibrium condition for this reaction in terms of y and P . You may assume ideal gas (4pts)

$$K = \frac{y_{\text{NH}_3}^2 P^2}{y_{\text{N}_2}^3 y_{\text{H}_2}^3 P^4} = \frac{y_{\text{NH}_3}^2}{y_{\text{N}_2}^3 y_{\text{H}_2}^3 P^2}$$

- d. What set of conditions would give you the highest equilibrium yield for ammonia? (3pts)

- a. High temperature, high pressure
- b. Low temperature, low pressure
- c. High temperature, low pressure
- d. Low temperature, high pressure

- e. Why? (5 pts)

Increase P , increase y_{NH_3}

Exothermic so want to decrease T
more moles gas on reactants so
want to increase pressure

— Le Chatelier principle —

$$RP^2 = \frac{y_{\text{NH}_3}^2}{y_{\text{N}_2}^3 y_{\text{H}_2}^3}$$

- f. Why do you think that the industrial ammonia production process does not use the conditions you selected above? (4pts)

Low temperature, limits kinetics so at too low temperature, will not start reaction

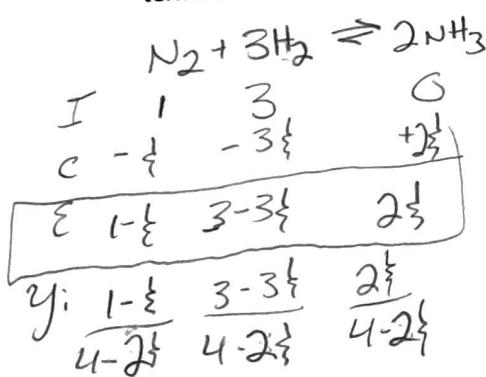
- g. Assume that the enthalpy of the reaction is constant with temperature. Calculate the equilibrium constant at 773K (8pts)

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{K_{773}}{5.85 \times 10^5} = - \left(\frac{-9.2 \times 10^4 \text{ J/mol}}{8.314 \text{ J/mol}} \right) \left(\frac{1}{773} - \frac{1}{298} \right)$$

$$K_{773} = 7.2 \times 10^{-5}$$

- h. A stream of 1 kmol/s of N₂ and 3 kmol/s of H₂ are fed into an isothermal reactor packed with Fe catalyst at 773K and 10 bar. Write out the mass balances for the three species in the reaction in terms of extent of reaction. (6 pts)



$$n_{tot} = 4 - 2\xi$$

$$K = \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3} \frac{P^2}{P^4}$$

$$K = \frac{(2\xi / 4 - 2\xi)^2}{(\frac{1-\xi}{4-2\xi})(\frac{3-3\xi}{4-2\xi})^3} \frac{1}{P^2}$$

- i. Write out the condition for equilibrium in terms of extent of reaction (4 pts)

$$K = \frac{(2\xi / 4 - 2\xi)^2}{(\frac{1-\xi}{4-2\xi})(\frac{3-3\xi}{4-2\xi})^3} \frac{1}{P^2}$$

2.

- a. Estimate the saturation pressure of furfuryl alcohol at 303K. Its normal boiling point is 445K and its enthalpy of vaporization is 53.6 kJ/mol (6 pts)

$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

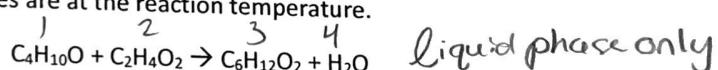
$$\ln\left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}\right) = \frac{-53.6 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol K}} \left(\frac{1}{303 \text{ K}} - \frac{1}{445 \text{ K}} \right)$$

$$P_2^{\text{sat}} = 0.001 \text{ bar}$$

- b. What assumptions did you have to make? (4pts)

Clausius Clapeyron equation: live
 assume basis 1 bar for P_1^{sat}
 $V^V \gg V^l$
 ideal gas
 constant ΔH_{vap}

3. The reaction of acetic acid with butanol to produce butyl-acetate processed to equilibrium at 308.15K. The reaction is shown below and it takes place in the liquid phase in an acetone solvent. The standard Gibbs free energies of formation and the activity coefficients for all reactive components in the system are shown in the table. All values are at the reaction temperature.



	1: butanol	2: acetic acid	3: butyl acetate	4: water
$\Delta g_f^\circ (\text{kJ/mol})$	-146.0	-381.3	-306.5	-228.1
γ_i	1.9	2.2	1.2	6.0

- a. Calculate the equilibrium constant of the reaction (7pts)

$$\Delta g_{\text{rxn}} = \sum \nu_i \bar{g}_F^\circ = (-1)(-146.0) + (-1)(-381.3) + (1)(-306.5) + (1)(-228.1)$$

$$\Delta g_{\text{rxn}} = -7.3 \text{ kJ/mol} = -7300 \text{ J/mol}$$

$$\ln K = -\frac{\Delta g_{\text{rxn}}}{RT} \quad K = \exp\left[\frac{(-7300 \text{ J/mol})}{(8.314 \text{ J/mol K})(308.15 \text{ K})}\right]$$

$$\underline{K = 17.28}$$

- b. A liquid mixture of 1 mol butanol and 1 mol acetic acid 18 mol acetone (solvent) reacts to equilibrium. Write out mass balances for each of the four components in terms of extent of reaction (6pts)

	(1)	(2)	\leftrightarrow	(3)	(4)	
I	1	1		0	0	
C	$-\xi$	$-\xi$		{	{	
E	$1-\xi$	$1-\xi$		{	{	

Liquid mixture

$$n_{\text{Tot}} = \frac{18}{1-\xi} + \frac{\xi}{1-\xi}$$

$$\underline{\underline{20}}$$

$$n_1 = 1-\xi \quad n_2 = 1-\xi \quad n_3 = \xi \quad n_4 = \xi$$

- c. Assuming that the solution is ideal, calculate the extent of reaction at equilibrium (6pts). You do not need to use an equation solver.

$$K_{298} = \frac{x_3 x_4}{x_1 x_2} \frac{P^2}{P^2} = \frac{\left(\frac{1}{20}\right) \left(\frac{1}{20}\right)}{\left(\frac{1-\xi}{20}\right) \left(\frac{1-\xi}{20}\right)} = \frac{\xi^2}{(1-\xi)^2}$$

$$\sqrt{17.28} = \sqrt{\frac{\xi^2}{(1-\xi)^2}} \rightarrow 4.16 = \frac{\xi}{1-\xi} \quad \boxed{\xi = 0.806}$$

$$4.16 = 5.16 \xi$$

- d. In reality, the mixture is not ideal. The activity coefficients of the compounds are shown in the table above. Calculate the extent of equilibrium (6pts) You do not need to use an equation solver.

$$K = \prod \left(\frac{f_i^\circ}{f_i} \right)^v = \left(\frac{f_1^\circ}{f_1} \right) \left(\frac{f_2^\circ}{f_2} \right) \left(\frac{f_3^\circ}{f_3} \right) \left(\frac{f_4^\circ}{f_4} \right)$$

$$R = (x_1 \gamma_1)^\circ (x_2 \gamma_2)^\circ (x_3 \gamma_3)^\circ (x_4 \gamma_4)^\circ$$

$$K_c = \frac{(x_3 x_4) \gamma_3 \gamma_4}{(x_1 x_2) \gamma_1 \gamma_2} = \frac{\xi^2 \gamma_3 \gamma_4}{(1-\xi)^2 \gamma_1 \gamma_2}$$

$$17.28 = \frac{(1-\xi)^2 (1.2 \times 60)}{(1-\xi)^2 (1.9 \times 2.2)}$$

$$\sqrt{10.03} = \sqrt{\frac{(\xi)^2}{(1-\xi)}}$$

$$3.167 - 3.167\xi = \xi$$

$$\boxed{\xi = 0.760}$$

4. Butanol is placed in a biological process, in which Clostridium acetobutylicum bacteria consume sugar and produce butanol. The butanol is extracted from the water by contacting the water stream with an organic solvent in a continuous extraction process at 308.15K. In one embodiment of this process, at the outlet of the extractor, the organic phase (phase β) has $x_B^\beta = 0.07$, while the aqueous phase (phase α) has $x_B^\alpha = 0.005$.

β - organic phase
$x_B^\beta = 0.07$
$x_H^\beta = 0.93$
$x_B^\alpha = 0.005$
$x_W^\alpha = 0.995$
α - aqueous phase

B: butanol
H: hexane
W: water

$$x_B^\alpha \gamma_B^\alpha = x_B^\beta \gamma_B^\beta$$

$$f_B^\alpha = f_B^\beta$$

$$RT \ln \gamma_B^\alpha = A(x_W^\alpha)^2$$

$$RT \ln \gamma_B^\beta = A(x_H^\beta)^2$$

- a. The 2-suffix Margules parameter for the butanol-hexane system is $A^{bh} = 4035 \text{ J/mol}$. Calculate the activity coefficient of butanol in the organic (hexane) phase. (8pts)

$$RT \ln \gamma_B^\beta = A x_H^\beta x_B^\beta$$

$$(8.314 \text{ J/Kelvin}) (308.15 \text{ K}) \ln \gamma_B^\beta = 4035 \frac{\text{J}}{\text{mol}} (0.93)^2$$

$$\gamma_B^\beta = 3.904$$

(alpha phase)

- b. Calculate the 2-suffix Margules parameter for the water butanol system. You may assume that the two streams exiting the extractor are in liquid-liquid equilibrium (12 pts)

LLE

$$x_B^\alpha \gamma_B^\alpha f_B^\alpha = x_B^\beta \gamma_B^\beta f_B^\beta$$

$$x_B^\alpha x_B^\beta = x_B^\beta \gamma_B^\beta$$

$$x_B^\beta \exp\left[\frac{A}{RT}(x_W^\alpha)^2\right] = x_B^\beta \exp\left[\frac{A}{RT}(x_H^\beta)^2\right]$$

-862.02

given: $x_B^\beta = 0.07$ $x_H^\beta = 0.93$
 $x_B^\alpha = 0.005$ $x_W^\alpha = 0.995$

$$\ln\left(\frac{x_B^\alpha}{x_B^\beta}\right) + \ln\exp\left[\frac{A}{RT}(x_W^\alpha)^2\right] = \exp\left[\frac{A}{RT}(x_H^\beta)^2\right]$$

$$A = RT \ln\left(\frac{x_B^\alpha}{x_B^\beta}\right) / \left((x_H^\beta)^2 - (x_W^\alpha)^2\right)$$

$$\ln\left(\frac{x_B^\alpha}{x_B^\beta}\right) = \frac{A}{RT} \left((x_H^\beta)^2 - (x_W^\alpha)^2\right)$$

$$A = 6889.3 \text{ J/mol}$$