

Quiz 12
Chemical Engineering Thermodynamics
April 1, 2021

Yim et al.* studied the vapor liquid equilibria of 2,3-butanediol (2,3-BDO) in mixtures with 2-methyl-1-pentanol. 2,3-BDO is produced through bioconversion (fermentation) from agricultural waste. 2,3-BDO is seen as a promising carbon neutral feedstock for the chemical industry. It is separated from aqueous dispersions by liquid extraction using 2-methyl-1-pentanol and the binary mixture must be distilled under vacuum to produce pure 2,3-BDO. As an example of uses for 2,3-BDO, it can be easily converted to butadiene to make tires and other value added rubber products. Yim et al.* used UNIQUAC and NRTL (we will study these next week) to model the activity coefficients for this binary mixture with good results. In this quiz we will compare these results with a much simpler two-parameter Margules model for Lim et al.* 80kPa (0.8 bar) data using the Antoine parameters from the NIST webbook (given below for T in K and P in bar). You can use the *GammaFit.xls* spreadsheet for this calculation. **You will need to unprotect the tabs and delete cells not used as well as modify some of the calculations to include only the cells you are using.** Using these Margules coefficients we will recreate the 80kPa curves in Figure 3 below and compare with the data, reproducing the black lines shown in Figure 3 for 80kPa. We will also calculate the difference in y_1 values between calculated and measured based on the measured x_1 values and make a plot similar to Figure 6 below for the 80kPa data to assess the difference between UNIQUAC and the two-parameter Margules model.

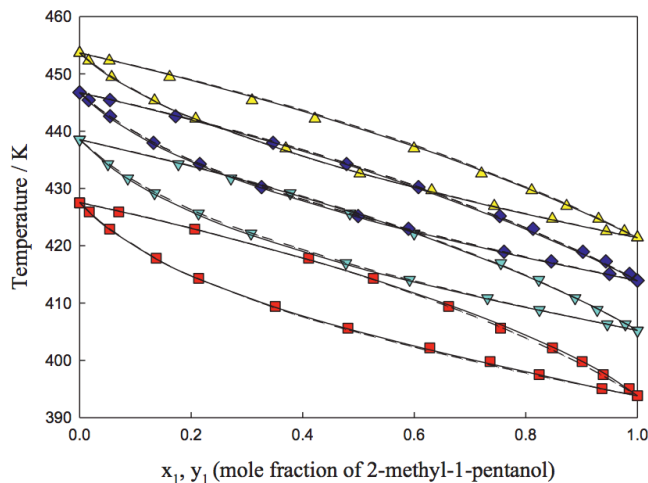


Fig. 3. Experimental and calculated T-x-y diagram for the 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system using NRTL and UNIQUAC: \blacktriangle , 101 kPa; \blacklozenge , 80 kPa; \blacktriangledown , 60 kPa; \blacksquare , 40 kPa; ---, calculated data by NRTL; —, calculated data by UNIQUAC.

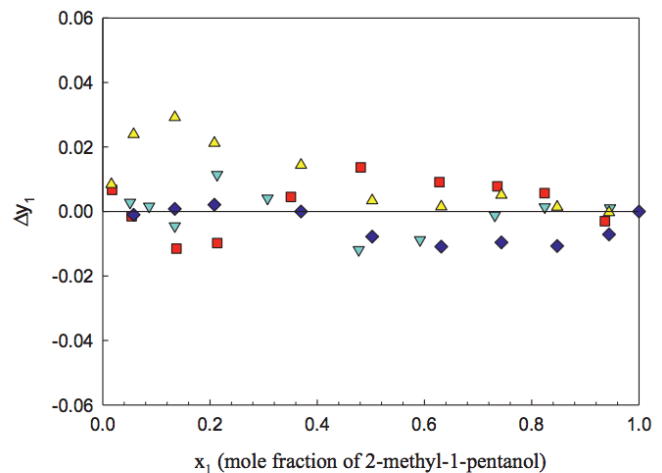


Fig. 6. Deviations of experimental vapor composition from calculated values using UNIQUAC model for 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system: \blacktriangle , 101 kPa; \blacklozenge , 80 kPa; \blacktriangledown , 60 kPa; \blacksquare , 40 kPa.

*Yim J-H, Kim H J, Oh JJ, Lim JS, Choi KY, *Isobaric vapor-liquid equilibria for two binary systems (2-methyl-1-pentanol + 2,3-butanediol and 3-methyl-1-butanol + 2,3-butanediol) at (40, 60, 80, and 101) kPa* Fluid Based Equilibria **530** 112897 (2021)

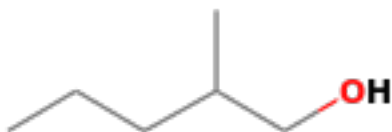
- a) Use the Yim et al.* data in the attached spreadsheet, the Antoine coefficients given below and the *GammaFit.xls* spreadsheet to calculate the two Margules coefficients, A_{12} and A_{21} . You will need to change the units in the spreadsheet to match the NIST Antoine equation and the Yim et al.* data. Note that **80 kPa = 0.8 bar**. Use the 'T-x-y fit P' tab. **Report**

A_{12} and A_{21} , give a **pdf of the spreadsheet**, and **explain how this tab operates** by listing the steps and giving the equations that it uses.

- b) Use the '*T-x-y Calc T*' tab in *GammaFit.xls* to calculate the bubble point composition and temperature. Explain how this tab works and give the equations it is using.
- c) Give the plot from the '*T-x-y Plot*' tab, explain what is being plotted (from which spreadsheets and what information) and compare it with Yim et al.* Figure 3.
- d) In a new tab (if you change cells much in existing tabs strange things can happen since some calculations are done in invisible cells) paste the x - and y -experimental and y -calculated parameters from the '*T-x-y Calc T*' tab and calculate Δy_1 . **Make a plot similar to Figure 6** of the difference between the experimental y_1 and the calculated y_1 for each of the temperatures. Provide a pdf of this plot.
- e) Glance at the Wikipedia pages for UNIQUAC and NRTL (or alternatively Chapters 12 and 13) and give a two to three sentence explanation for what is not accounted for in the two-parameter Margules model that improves the fit for the UNIQUAC and NRTL models used by Yim et al.* (Don't spend more than 10 minutes on this unless you find it compelling. In that case you should look for a job at Aspen or ChemCAD.)

Turn in a pdf of your excel spread sheets and the plots of parts c and d. As well as answers to the questions.

Component (1)



2-methyl-1-Pentanol
Formula: C₆H₁₄O
Molecular weight: 102.1748

Antoine Equation Parameters

$$\log_{10}(P) = A - (B / (T + C))$$

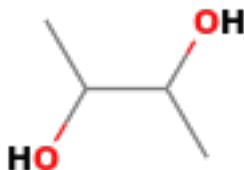
P = vapor pressure (bar)

T = temperature (K)

[View plot](#) Requires a JavaScript / HTML 5 canvas capable browser.

Temperature (K)	A	B	C	Reference	Comment
298. - 423.	6.198	2625.143	3.181	Hovorka, Lankelma, et al., 1938	Coefficients calculated by NIST from author's data.

Component (2)



2,3-Butanediol
Formula: C₄H₁₀O₂
Molecular weight: 90.1210

Antoine Equation Parameters

$$\log_{10}(P) = A - (B / (T + C))$$

P = vapor pressure (bar)

T = temperature (K)

[View plot](#) Requires a JavaScript / HTML 5 canvas capable browser.

Temperature (K)	A	B	C	Reference	Comment
317. - 455.	6.07439	2616.746	-24.565	Stull, 1947	Coefficients calculated by NIST from author's data.

ANSWERS: Quiz 11
Chemical Engineering Thermodynamics
March 25, 2021

- a) Use the Yim et al.* data in the attached spreadsheet, the Antoine coefficients given below and the *GammaFit.xls* spreadsheet to calculate the two Margules coefficients, A_{12} and A_{21} . You will need to change the units in the spreadsheet to match the NIST Antoine equation and the Yim et al.* data. Note that **80 kPa = 0.8 bar**. Use the '*T-x-y fit P*' tab. **Report A_{12} and A_{21} , give a pdf of the spreadsheet, and explain how this tab operates by listing the steps and giving the equations that it uses.**

System Components		Parameters to adjust			Antoine Coefficients			Calculated				
		A_{12}	A_{21}	P(Bar)	A	B	C	$T^{sat}(K)$				
(1) 2-methyl-1-Pentanol				1	6.198	2625.143	3.181	413.85				
(2) 2,3-Butanediol		0.4554661	0.0553139	0.8	6.07439	2612.746	-24.565	447.94				
<---optional---->												
x_1	x_2	$y_{1,calc}$	$y_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	P_1^{sat}	P_2^{sat}	P_{calc}	$(P_{error})^2$
0	1	1.5769082	1	0	1	0	1	446.8	2.31	0.77	0.77	0.00
0.0164	0.9836	1.5341114	1.0002266	0.0545	0.9455	0.0716907	0.9283093	445.4	2.22	0.73	0.78	0.00
0.0547	0.9453	1.4446722	1.0024321	0.1723	0.8277	0.2029654	0.7970346	442.6	2.04	0.67	0.79	0.00
0.1325	0.8675	1.300778	1.0132467	0.347	0.653	0.3789127	0.6210873	438	1.77	0.57	0.80	0.00
0.2156	0.7844	1.1901463	1.032261	0.4787	0.5213	0.5003553	0.4996447	434.3	1.58	0.50	0.81	0.00
0.3263	0.6737	1.0922059	1.0653413	0.6074	0.3926	0.6149627	0.3850373	430.2	1.38	0.43	0.80	0.00
0.4994	0.5006	1.0140802	1.1204307	0.7533	0.2467	0.7480909	0.2519091	425.2	1.17	0.36	0.80	0.00
0.5896	0.4104	0.9972427	1.1427131	0.8129	0.1871	0.8064034	0.1935966	423	1.09	0.33	0.80	0.00
0.7609	0.2391	0.9912638	1.1535133	0.9024	0.0976	0.9025107	0.0974893	419	0.95	0.28	0.80	0.00
0.8456	0.1544	0.9947389	1.1364472	0.9434	0.0566	0.9423973	0.0576027	417.3	0.90	0.26	0.80	0.00
0.9499	0.0501	0.9992354	1.0899029	0.9858	0.0142	0.9835963	0.0164037	415.1	0.84	0.24	0.81	0.00
1	0	1	1.0568723	1	0	1	0	413.9	0.80	0.23	0.80	0.00

This tab calculates the bubble point temperature and compositions y_i , using the x_i values, P^{sat} (calculated from the Antoine equation using the generated T_{bp}) and P . It calculates P_{calc} from

$$P_{calc} = \sum_i x_i \gamma_i P_i^{sat}$$

and adjusts A_{12} and A_{21} until $(P_{calc} - P)^2$ reaches a minimum. γ_i is calculated from

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1] ; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$$

- b) Use the '*T-x-y Calc T*' tab in *GammaFit.xls* to calculate the bubble point composition and temperature. **Explain how this tab works and give the equations it is using.** Turn in a **pdf of the spreadsheet.**

This is a bubble point temperature calculation. It uses the A_{12} and A_{21} parameters determined in part a to calculate γ_i from

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1] ; \text{ similarly } \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$$

These values are used with

$$P_{calc} = \sum_i x_i \gamma_i P_i^{sat}$$

To calculate P_{calc} . Rather than compare the square of the difference with P, a better minimization is found using $\sum \log(P_{calc}/P)$ which equals 0 when $P_{calc}/P = 1$ and varying $1/T$ rather than T . These are used since P^{sat} is related to $\exp(-E_a/kT)$ by the Arrhenius Equation, so $\ln(P)$ should be linear in $1/T$ with $-E_a$ as the slope.

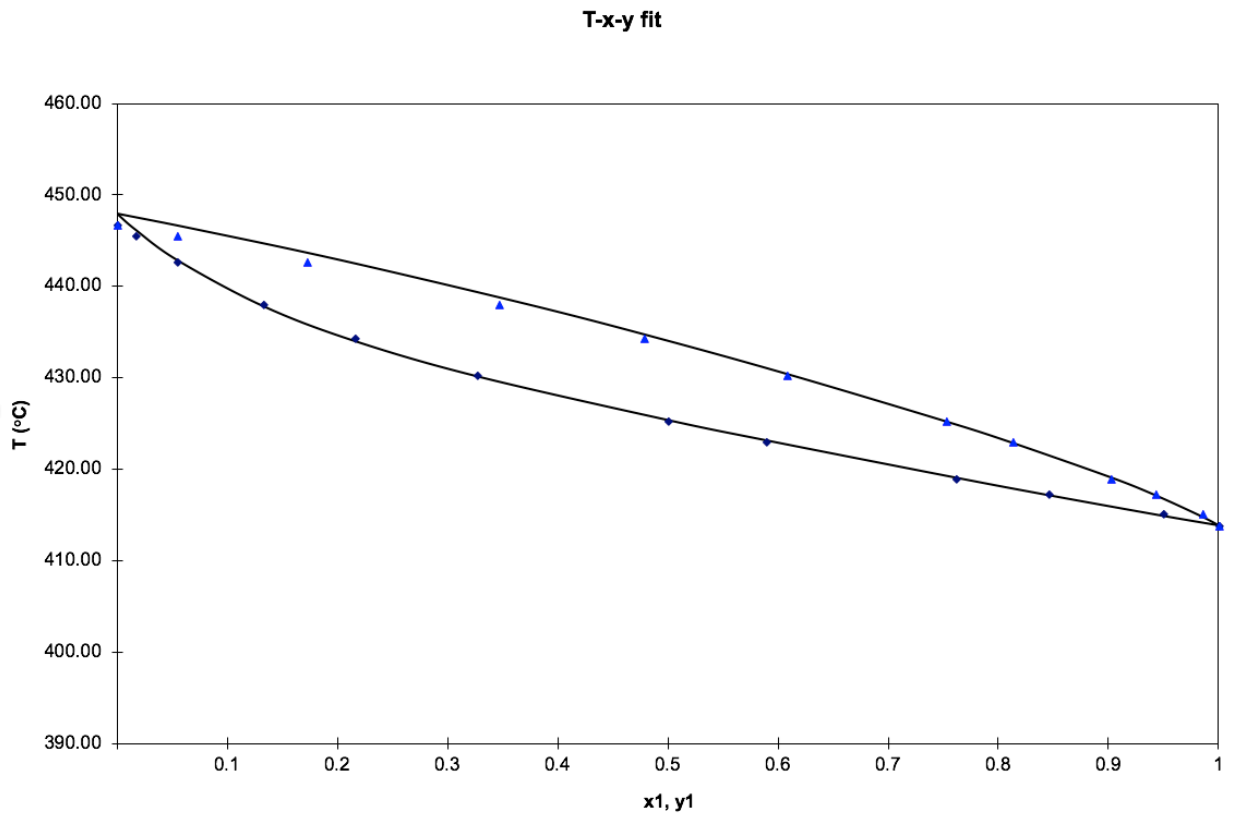
This yields T_{bp} . y_i are calculated using $y_i = x_i \gamma_i P^{sat}/P$.

System Components		Parameters to use			Antoine Coefficients			Calculated	
		A_{12}	A_{21}	P(bar)	A	B	C	T^{sat} (K)	
(1) 2-methyl-1-Pentanol		0.4554861	0.0553139	0.8	1.00	6.198	2625.143	3.181	413.85
(2) 2,3-Butanediol					2.00	6.07439	2612.746	-24.565	447.94

<---optional--->															
x_1	x_2	$\gamma_1, calc$	$\gamma_2, calc$	$y_1, expt$	$y_2, expt$	$\gamma_1, calc$	$\gamma_2, calc$	T_{expt}	T_{calc}	$1/T$	P_i^{sat}	P_2^{sat}	P_{calc}	$\log(P_{calc})$	$\log(P_{calc}/P_e)$
1	0	1.5769082	1	1	0	1	0	446.80	447.93573	0.0013868	2.39	0.80	0.80	0.0969058	1.805E-11
0.0164	0.9836	1.5341114	1.0002266	0.0545	0.9455	0.0714774	0.9285226	445.40	446.2186	0.00139011	2.27	0.76	0.80	0.0969132	1.001E-11
0.0547	0.9453	1.4446722	1.0024321	0.1723	0.8277	0.2028047	0.7971953	442.60	442.84803	0.00139665	2.05	0.67	0.80	0.0969092	7.319E-13
0.1325	0.8675	1.300778	1.0132467	0.347	0.653	0.3790809	0.6209191	438.00	437.82759	0.00140651	1.76	0.57	0.80	0.0969021	6.217E-11
0.2156	0.7844	1.1901463	1.032261	0.4787	0.5213	0.5006673	0.4993327	434.30	434.00683	0.00141411	1.56	0.49	0.80	0.0969114	2.012E-12
0.3263	0.6737	1.0922059	1.0653413	0.6074	0.3926	0.6150065	0.3849835	430.20	430.15778	0.00142185	1.38	0.43	0.80	0.0969043	3.25E-11
0.4994	0.5006	1.0140802	1.1204307	0.7533	0.2467	0.7479413	0.2520587	425.20	425.37485	0.00143159	1.18	0.36	0.80	0.096903	4.946E-11
0.5896	0.4104	0.9972427	1.1427131	0.8129	0.1871	0.8063075	0.1936925	423.00	423.13307	0.0014362	1.10	0.33	0.80	0.09691	1.494E-18
0.7609	0.2391	0.9912638	1.1535133	0.9024	0.0976	0.9024804	0.0975196	419.00	419.07241	0.00144462	0.96	0.28	0.80	0.0969057	1.882E-11
0.8456	0.1544	0.9947389	1.1364472	0.9434	0.0566	0.9424384	0.0575616	417.30	417.14318	0.00144866	0.90	0.26	0.80	0.0968988	1.265E-10
0.9499	0.0501	0.9992354	1.0899029	0.9858	0.0142	0.9836141	0.0163859	415.10	414.87406	0.00145344	0.83	0.24	0.80	0.0968983	1.368E-10
1	0	1.0568723	1	1	0	1	0	413.90	413.84598	0.00145561	0.80	0.23	0.80	0.0968996	1.075E-10

For each x_1 the correct T is found to make sum $x \gamma P^{sat}$ equal to 0.8 b
This finds the bubble point temperature and composition which are used in th
Dew point is this temperature and the experimental x_1 values

- c) Give the plot from the '*T-x-y Plot*' tab, explain what is being plotted (from which spreadsheets and what information) and compare it with Yim et al.* Figure 3.



The points are the input data for x and y . The top line is the bubble point temperature and composition from part b. The bottom line is the bubble point temperature from part b versus the experimental x_1 values for the dewpoint.

- d) In a new tab (if you change cells much in existing tabs strange things can happen since some calculations are done in invisible cells) paste the x - and y -experimental and y -calculated parameters from the '*T-x-y Calc T*' tab and calculate Δy_1 . **Make a plot similar to Figure 6** of the difference between the experimental y_1 and the calculated y_1 for each of the temperatures.

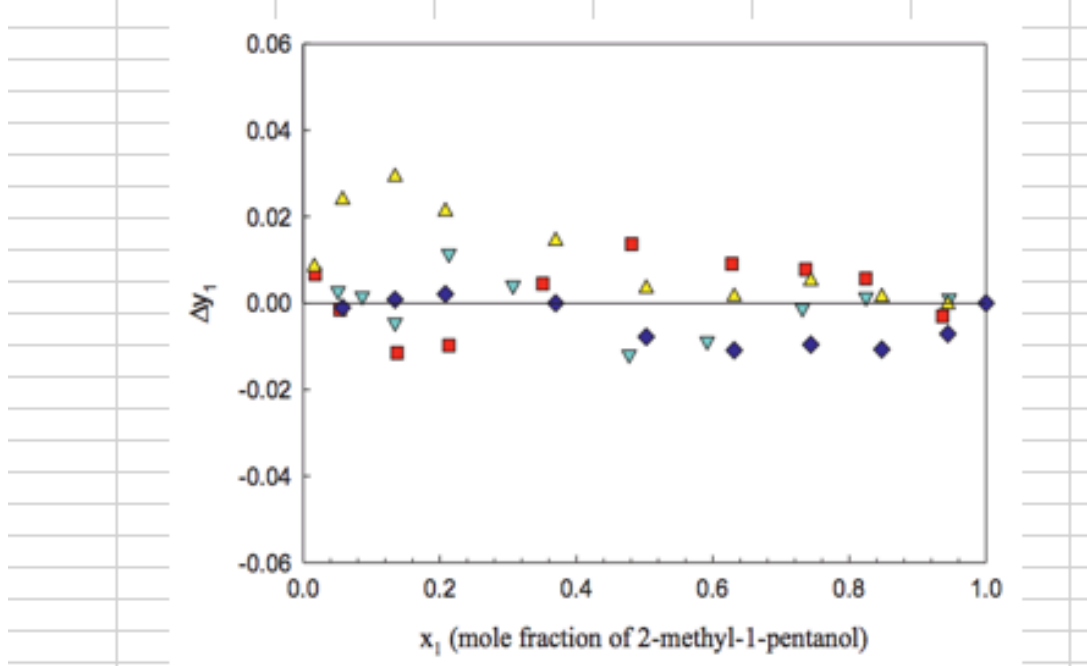
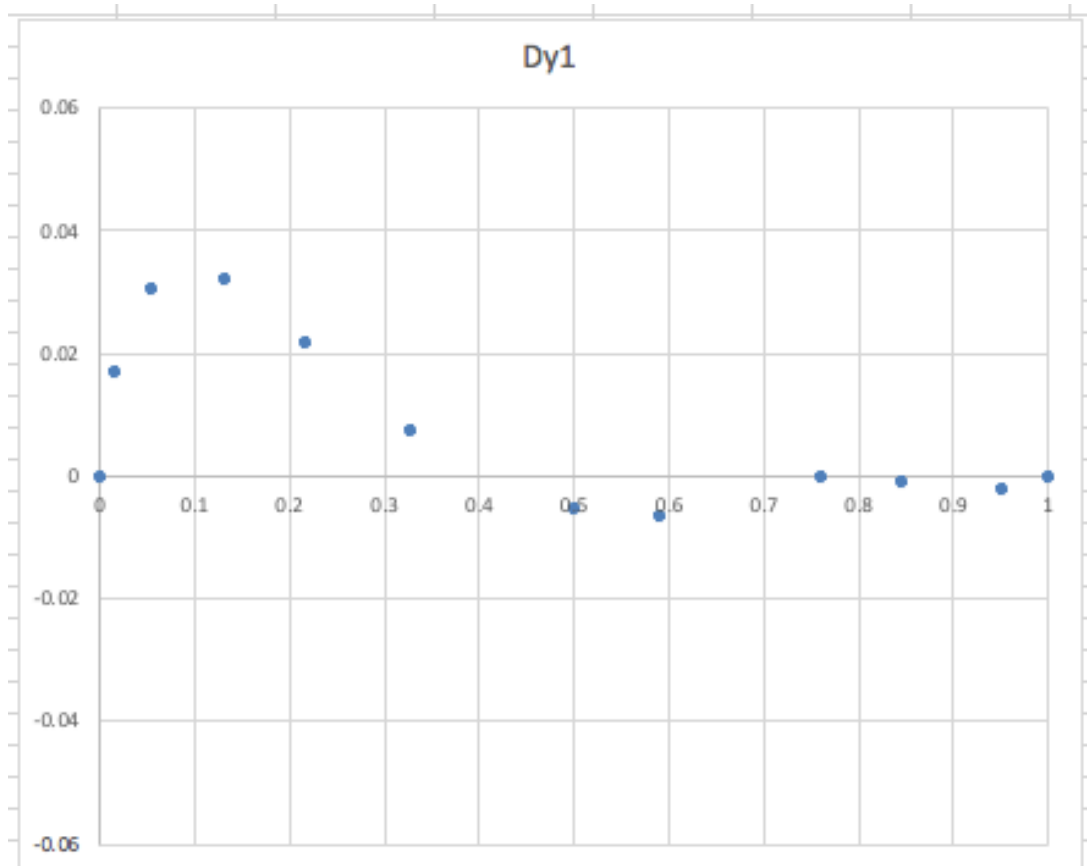


Fig. 6. Deviations of experimental vapor composition from calculated values using UNIQUAC model for 2-methyl-1-pentanol (1) + 2,3-butanediol (2) system: \blacktriangle , 101 kPa; \blacklozenge , 80 kPa; \blacktriangledown , 60 kPa; \blacksquare , 40 kPa.

- e) Glance at the Wikipedia pages for UNIQUAC and NRTL (or alternatively Chapters 12 and 13) and give a two to three sentence explanation for what is not accounted for in the two-parameter Margules model that improves the fit for the UNIQUAC and NRTL models used by Yim et al.* (Don't spend more than 10 minutes on this unless you find it compelling. In that case you should look for a job at Aspen or ChemCAD.)

UNIQUAC and NRTL include local clustering of species that impacts the entropy of mixing. They also include specific chemical group contributions and differences between interactions in the vicinity of chemical species. They use many more than two parameters to describe the miscibility.