Michigan State University

DEPARTMENT OF CHEMICAL ENGINEERING

ChE 321: Thermodynamics for Chemical Engineers Exam 2A: April 4, 2018, Equation Sheet

Spring 2018

1. (10) (T or F)

- ____ The UNIFAC model is based on local composition concepts.
- Plotting $\ln(P_r^{sat})$ (y-axis) vs. 1/Tr (x-axis) gives a line with a positive slope.
- _____ The compressibility factor Z for liquids is always $Z^L \ll 1$.
- 2. (10) Estimate with minimum calculations the values of fugacity for hexane under the following conditions. Include units. Your answer should be of the type provided by a quick estimation.
 - (a) Hexane is a pure vapor at 65C and 346 mm Hg. The vapor pressure of hexane at 65C is 675 mmHg.
 - (b) Hexane is in an ideal gas vapor mixture with acetone at 65C and 480 mmHg. The mole fraction of hexane is $y_{hexane} = 0.4$. The vapor pressures are $P^{sat}_{hexane} = 675 \text{ mmHg}$, $P^{sat}_{acetone} = 1020 \text{ mmHg}$.
 - (c) Hexane is a pure liquid at 65C and 760 mmHg. The vapor pressure of hexane at 65C is 675 mmHg.

3. (10) For the system 1-butanol (1) + 2-propanol (2) at 90C, the vapor pressures are $P_1^{sat} = 257$ mmHg and $P_2^{sat} = 1026$ mmHg. Using Raoult's law, estimate the dew pressure and coexisting phase compositions for an overall composition of 70 mol% butanol. Avoid unnecessary calculations. If an iterative solution is required, perform the first iteration, and indicate clearly the specific steps needed to efficiently find the answers.

4. A P-x-y diagram is shown below for the system A+B. From the diagram, mark the answers to the following questions, label them as '(a)', ' (b)', etc., and provide numerical values.



- (a) (10) The dew pressure and coexisting phase compositions (use x for liquid, y for vapor) and L/F for an overall composition $z_A = 0.5$.
- (b) (10) The phase compositions (use x for liquid, y for vapor) and calculated L/F for an overall composition $z_A = 0.5$ at 645 mm Hg.

5. The (1) + (2) system exhibits vapor liquid equilibria at 24.95 kPa and 50C. The compositions of the coexisting phases are $x_1 = 0.36$ and $y_1 = 0.62$ and $P_1^{sat} = 69.4$ kPa, $P_2^{sat} = 15.8$ kPa.

(a) (5) Calculate $G^{E}/(RT)$ for the liquid phase at 50C and composition $x_1 = 0.36$. Note: $\overline{G}_i^E/(RT) = \ln \gamma_i$.

(b) (10) Fit the two parameter Margules equation to the experimental data.

(c) (10) Use the results of part (b) to calculate the bubble pressure and coexisting phase compositions for a mixture of overall composition at $z_1 = 0.8$ at 50C. Avoid unnecessary calculations. If an iterative solution is required, perform the first iteration, and indicate clearly the specific steps needed to efficiently find the answers.

6. (10) The system (A) + (B) exhibits V + L phase equilibria and at a particular temperature and pressure the coexisting compositions are $y_A = 0.6$ and $x_A = 0.25$. Using Raoult's law to model the system, what is P^{sat}_A/P^{sat}_B ?

7. (15) Propane passes through an adiabatic expander with an efficiency of 85%. The inlet conditions are 380 K and 5 MPa.



Continued on next page...

Several possible outlet states are given below (note that one state is on the next page). (state 1)

· ·	/									
	Α	В		С	D		E	F	G	Н
6	Current Stat	e	Ro	ots		:	Stable Roc	ot has a low	er fugacity	
7	T (K)	281.937	592	Z	V		fugacity	Н	U	S
8	P (MPa)		0.1		cm ³ /gmo		MPa	J/mol	J/mol	J/molK
9	answer	s for three	0.9	9806862	22988.8	376	0.0981	-1177.73	-3476.62	-4.06066
10	root	region	0.0	0134429	315.123	342		-8169.21	-8200.73	-46.8466
11			0.0	0034694	81.3275	516	0.53412	-17947.7	-17955.9	-77.6318
12	& for 1	root region	#	[‡] NUM!	#NUM	!	#NUM!	#NUM!	#NUM!	#NUM!
	Results									
	PROPANE									
	T(K) 281.	937 P(MPa	a)	0.1						
	z	0.9	980686 0	.00346936						
	V (cm^3/mol)		22988.4	81.3258						
	U (J/mol)		-3476.63	-17955.9						
	H (J/mol)		-1177.74	-17947.8						
	S (J/mol-K)		-4.0607 -	77.6319						
	fugacity (MPa)	0	.0981002	0.534112						
	User Objecive		2.7284	8e-12						
(sta	ate 2)									
	Á	В	С)	Е	F	G	Н	
6	Current State		Roots		Stat	le R	oot has a lov	ver fugacity		
7	T (K)	183.062959	z	V	/ fua	acitv	, н	U	S	

0	Ourient State		Roots		Stable Root has a lower rugacity				
7	Т (К)	183.062959	Z	V	fugacity	н	U	S	
8	P (MPa)	0.1		cm ³ /gmol	MPa	J/mol	J/mol	J/molK	
9	answers	for three	0.9395241	14300.231	0.094287	-7087.2	-8517.23	-29.524	
10	root re	egion	0.0524794	798.77434		-10557.7	-10637.6	-57.1507	
11			0.0042979	65.417476	0.006707	-27265.8	-27272.3	-117.774	
12	& for 1 ro	ot region	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	

- Results

T(K)	183.063	P(MPa)	0.1			
z		0.93952	4 0.00429792			
V (cm ⁴	3/mol)	1429	9.9 65.4161			
U (J/mo	0	-8517.23 -27272.4				
H (J/mo	0	-7087.2 -27265.9				
S (J/mo	I-K)	-29.524 -117.774				
fugacity	(MPa)	0.09428	67 0.00670624			
User O	bjecive	3.5	5271e-15			

Continued on next page...

(sta	ate 3)							
	А	В	С	D	E	F	G	Н
6	Current State		Roots		Stable Roc	ot has a low	er fugacity	
7	Т (К)	230.608998	Z	V	fugacity	н	U	S
8	P (MPa)	0.1		cm ³ /gmol	MPa	J/mol	J/mol	J/molK
9	answers	for three	0.9669301	18539.842	0.09679	-4522.42	-6376.4	-17.1171
10	root r	egion	0.0264368	506.8964		-9511.23	-9561.92	-52.1002
11			0.0036971	70.887138	0.09679	-23227.6	-23234.6	-98.229
12	& for 1 ro	ot region	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
	PROPANE T(K) 230.6 Z V (cm^3/mol) U (J/mol) H (J/mol) S (J/mol-K) fugacity (MPa) User Objecive	1 P(MPa) 0.966 185 -637 -452 -17. 0.0967 -8	0.1 93 0.00369706 39.5 70.8858 6.37 -23234.7 2.38 -23227.6 117 -98.2289 7902 0.096790 .88178e-16	2				

Identify the correct outlet state, and calculate the work done by the expander in J/mol.

Michigan State University

DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers Exam 2A: April 05, 2017, Equation sheet

Spring 2017

(10) A binary system (A) + (B) of F total moles exists as V moles vapor and L moles liquid, where the overall composition is 60 mol% (A) and the liquid composition is 47 mol% (A), and the vapor composition is 72 mol% (A). What is V/F?

- 2. Which of the following constraint(s) are NOT required to apply Raoult's law: (I) ideal gas in the vapor; (II) $U = \sum x_i U_i$ in liquid; (III) $G = \sum x_i G_i$ in liquid; (IV) components similar in size; (V) components similar in functionality; (VI) $S = \sum x_i S_i$
- 3. (5) Pure hexane (C6) exists as V + L as shown. Pure heptane (C7) liquid is injected into the vapor at constant temperature and pressure. After injection the overall mixture is 10 mol% C7. What happens (circle the best answer)?
 - (a) All the C7 goes to L and the V is only C6.
 - (b) The vapor is mostly C6 with some C7.
 - (c) All the vapor condenses.
 - (d) All the liquid evaporates.
 - (e) None of the above. Explain



- (5) Select all that are true. This model is used frequently in polymer modeling.
 _____ Flory
 - ____ van Laar
 - None of these models
 - Scatchard-Hildebrand
 - ____ Flory-Huggins

5. The system chloroform (1) + 1,4-dioxane (2) exists as V + L at 323.15K and P = 19.89 kPa with $x_1 = 0.2$ and $y_1 = 0.3691$. At this temperature $P_1^{sat} = 69.31$ kPa and $P_2^{sat} = 15.78$ kPa. Vapor pressures can be estimated at other temperatures using $\log_{10} P_1^{sat} = 6.2983 - 1432.1/T(K)$; $\log_{10} P_2^{sat} = 6.6074 - 1732.5/T(K)$; (15) Fit the two-parameter Margules equation to this measurement.

(10) Determine the bubble temperature at 60 kPa and an overall composition of 40 mol% (1). If an iterative calculation is required, perform the first iteration and specify values for the next iteration. If an iterative calculation is not required, provide the bubble temperature and composition of the other phase.

- 6. A fluid is described by the following equation of state: Z = 1 + (a + b/T)ρ where a = 500 cm³/mol, b = -3.45E5 cm³K/mol and the ideal gas heat capacity is Cp = 74.6 J/molK. (a) (10) At 300K and ρ = 4.5E-4 mol/cm³, what is P (MPa)?
 - (b) (10) For this equation of state, derive $(U U^{ig})/(RT)$ in the fully integrated form. Leave the expression in terms of *a*, *b*, *Z* and ρ .

- 7. (10) For benzene at the state $T_2 = 290$ K and $P_2 = 0.1$ MPa, the Peng-Robinson equation gives a value of (S S^{ig}) = -93.8886 J/molK. For benzene at the state $T_1 = 480$ K and $P_1 = 1$ MPa, the Peng-Robinson equation gives (S S^{ig}) = -2.1963 J/molK. Cp is assumed to be constant and for benzene near these temperatures, Cp = 100 J/molK. Determine Δ S for moving from state 1 to state 2.
- 8. Select the best answer. For the A + B system shown in the right,
 - a. (5) At 200 mmHg
 - _____ boiling T of pure *A* < boiling T of pure *B*
 - _____ boiling T of pure *A* > boiling T of pure *B*
 - _____ boiling T of pure $A \approx$ boiling T of pure B
 - can't tell without Antoine coefficients
 - b. (5) Liquid exists in which region(s) of the diagram? (mm
 - ____ only I ____ II and III
 - ____ only II _____ I and III
 - ____ only III
 - ____ I and II



х_А, у_А



- a. (5) Is hexane one or two phases at the inlet state I? Use cell references or mark the Matlab output to provide the inlet enthalpy. Explain.
- b. (5) Hexane is compressed to 2 MPa in a reversible adiabatic compressor. Two possible outlet states are shown below. What is the outlet temperature? Is the outlet one or two phases? If the outlet is two phases, give the quality. Explain your answer. If neither of the given alternatives is correct, explain how you would find the reversible outlet state using cell references or Matlab selectors.



Michigan State University

DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers Exam 2A: April 08, 2015, Closed Book Portion (20 minutes)

Spring 2016

- 1. (5) The fundamental relation for U is dU = TdS PdV. The definition of Helmholtz energy is $A \equiv U$ -TS. Derive the relation for dA.
- At 320K pure component (1) is a liquid with a vapor pressure of 0.3 MPa and a saturation fugacity coefficient of 0.85 and pure component (2) is a liquid with a vapor pressure of 0.25 MPa and a saturation fugacity coefficient of 0.95.
 (a) (5) Liquid components (1) and (2) are mixed at 0.8 MPa and 320K, such that x1 = 0.6 and x2 = 0.4. Provide the values of the component fugacities in the liquid mixture if the mixture is assumed to follow Raoult's Law.

(b) (5) Liquid components (1) and (2) are mixed at 0.8 MPa and 320K, such that $x_1 = 0.6$ and $x_2 = 0.4$. Provide the values of the component fugacities in the mixture if the mixture is assumed to be an ideal solution of liquids, ignoring the Poynting correction.

- 3. (10) (T or F)
- ____ The compressibility factor Z for a real fluid is always less than unity
- _____ Plotting Z vs. Pr gives identical curves for all fluids at the same Tr.
- _____ Plotting ln(Pr) (y-axis) vs. 1/Tr (x-axis) gives almost a straight line with a negative slope.
- 4. (10) A solution of 30 mol% hexane and 70 mol% ethanol exists in the vapor phase at 80 C and 0.1 MPa. The conditions are changed at constant pressure until the mixture is totally condensed. What type of calculation should be performed to calculate the conditions for complete condensation? (e.g. bubble temperature, dew temperature, bubble pressure, dew temperature, isothermal flash?) For a complete answer, provide constraint *values* needed for the calculation.

5. (5) The Soave-Redlich-Kwong equation is $Z = 1/(1 - b\rho) - (a/(bRT))b\rho/(1 + b\rho)$. The parameters are made dimensionless using $A = aP/(RT)^2$ and B = bP/RT. Rearrange the equation in the form $Z^3 + a_2Z^2 + a_1Z + a_0 = 0$, where a_2 , a_1 , and a_0 are functions of *A* and *B*.

Michigan State University

DEPARTMENT OF CHEMICAL ENGINEERING

ChE 321: Thermodynamics for Chemical Engineers Exam 2A. EQUATION SHEET PORTION Spring 2016

6. The equation of state for a simple fluid has been correlated to the equation Z = 1 + aP/RT, where $a = -2360 \text{ cm}^3/\text{mol}$, and $C_P = 43 \text{ J/mol-K}$.

(a) (10) Derive the Helmholtz departure for the fluid and calculate the numerical value (J/mol) at 300 K and 0.2 MPa.

7. (10) Indicate if each of the following equations is correct (T) or incorrect (F). Valid work in the scratch area is required for full credit.

Expression	Indicate T or F
(a) $\left(\frac{\partial G}{\partial S}\right)_P = -S\left(\frac{\partial T}{\partial S}\right)_P + V$	
(b) $\left(\frac{\partial G}{\partial S}\right)_V = -\frac{ST}{C_V} - V \left(\frac{\partial T}{\partial V}\right)_P$	
$(c) \left(\frac{\partial G}{\partial T}\right)_{S} = -S + \frac{VT}{C_{V}} \left(\frac{\partial T}{\partial V}\right)_{P}$	

Scratch area:

•

1. The system methyl acetate (1) + hexane (2) forms an azeotrope at $x_1 = 0.667$, 51.57° C, and 1 bar. The component vapor pressures at 51.57° C are $P_1^{sat} = 0.833$ bar, $P_2^{sat} = 0.5736$ bar. Fit the two parameter Margules equation parameters.

(5) Pick which diagram represents the qualitative behavior that you expect for the system based on the information given above. The expected shape of the phase behavior is: _____



(5) Justify your choice:

2. (10) The system (1) + (2) can be modeled with Modified Raoult's law, using the one parameter Margules equation, $\ln \gamma_1 = 1.6 x_2^2$, $\ln \gamma_2 = 1.6 x_1^2$. The vapor pressures are $\log_{10}P_1^{sat} = 8.4 - 1800 / (T + 230)$, $\log_{10}P_2^{sat} = 7.3 - 1300 / (T + 170)$, where T is in Celsius. Calculate the bubble pressure and coexisting phase compositions using Modified Raoult's Law for a mixture that is overall 75 mol% (1) and 25 mol% (2) at 60 °C. If an iterative solution is required, perform the first iteration, and indicate clearly the specific steps used to find the answers.

3. The state below is the inlet to a throttle valve.

A B C D E F G H I J K L

1	Peng-Robinson Equation of State (Pure Fluid)				Spreadsheet protected, but no password used.							
2	Properties				Heat Capacity constants from Appendix				ideal gas	H ^{ig} - H _R ^{ig}	U ^{ig} - U _R ^{ig}	S ^{ig} -S _R ^{ig}
3	Gas	T _c (K)	P _c (MPa)	ω	Α	В	С	D	values	J/mol	J/mol	J/molK
4	n-HEPTANE	540.3	2.736	0.349	-5.146	6.76E-01	-3.65E-04	7.66E-08		19428.18	18576.03	42.29261
5	5											
6	6 Current State Roots		Stable Root has a lower fugacity									
7	T (K)	400.64	Z	V	fugacity	н	U	S	H-H ^{ig}	U-U ^{ig}	S-S ^{ig}	
8	P (MPa)	0.5		cm ³ /gmol	MPa	J/mol	J/mol	J/molK	J/mol	J/mol	J/molK	
9	answers	for three	0.7948996	5295.7962	0.414999	53426.05	50778.15	136.5684	-1995.66	-1312.45	-3.43193	
10				1000 1000		40047 40	40004 40	447 0000	0004 00	C00C 47	22 2204	
10	root r	region	0.1600253	1066.1239		46617.49	40004.43	117.6609	-0004.22	-6006.17	-22.3394	
11	root r	region	0.1600253	1066.1239 172.5646	0.206904	24779.02	46084.43 24692.74	70.85231	-8604.22	-27397.9	-69.1481	

The outlet pressure is 0.05 MPa. Possible outlet states are shown below. Case (a)

	A	В	C	D	E	F	G	н	1	J	К	L
1	Peng-Robins	on Equation of	State (Pure	Fluid)		Spreadshe	et protecte	d, but no p	assword us	sed.		
2	Properties		22		Heat Capa	city consta	nts from A	ppendix	ideal gas	H ^{ig} - H _R ^{ig}	U ^{ig} - U _R ^{ig}	S ^{ig} -SR ^{ig}
3	Gas	T _c (K)	P _c (MPa)	ω	A	В	С	D	values	J/mol	J/mol	J/molK
4	n-HEPTANE	540.3	2.736	0.349	-5.146	6.76E-01	-3.65E-04	7.66E-08		19439.21	18586.62	61.46491
5												
6	Current State		Roots		Stable Roc	ot has a low	er fugacity					8
7	T (K)	400.692	Z	V	fugacity	н	U	S	H-H ^{ig}	U-U ^{ig}	S-S ^{ig}	
8	P (MPa)	0.05		cm ³ /gmol	MPa	J/mol	J/mol	J/molK	J/mol	J/mol	J/molK	
9	answers	for three	0.9825588	65468.726	0.049141	55266.16	51992.73	158.901	-166.575	-108.469	-0.27165	
10	root	region	0.0129263	861.28717		44868.5	44825.43	114.363	-10564.2	-7275.76	-44.8097	
11			0.0025979	173.09938	0.202371	24779.12	24770.47	71.04668	-30653.6	-27330.7	-88.126	
12	& for 1 ro	oot region	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	
\mathbf{C}	$ace(\mathbf{h})$											
	ase(0)											
	A	В	С	D	E	F	G	Н	1	J	K	L
1	Peng-Robinso	on Equation of	State (Pure	Fluid)		Spreadshee	et protecte	d, but no p	assword us	ed.		
2	Properties				Heat Capa	city constar	nts from A	opendix	ideal gas	H ^{ig} - H _R ^{ig}	U ^{ig} - U _R ^{ig}	S ^{ig} -S _R ^{ig}
3	Gas	T _c (K)	P _c (MPa)	ω	Α	В	С	D	values	J/mol	J/mol	J/molK
4	n-HEPTANE	540.3	2.736	0.349	-5.146	6.76E-01	-3.65E-04	7.66E-08		19378.25	18528.06	61.31273
5												
6	Current State		Roots		Stable Roo	t has a low	er fugacity					
7	T (K)	400.404537	Z	V	fugacity	н	U	S	H-H ^{ig}	U-U ^{ig}	S-S ^{ig}	
8	P (MPa)	0.05		cm ³ /gmol	MPa	J/mol	J/mol	J/molK	J/mol	J/mol	J/molK	
9	answers	for three	0.9825223	65419.331	0.049139	55205.02	51934.05	158.7484	-166.763	-108.577	-0.27212	
10	root r	egion	0.012961	862.98393		44821	44777.85	114.2444	-10550.8	-7264.78	-44.7761	
11			0.0025982	172.99644	0.201039	24701.26	24692.61	70.8523	-30670.5	-27350	-88.1682	
12	& for 1 ro	ot region	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	
Ca	ase (c)											
	A	В	С	D	E	F	G	Н	1	J	K	L
1	Peng-Robins	on Equation of	f State (Pur	e Fluid)		Spreadsh	eet protec	ted, but no	password	used.		
2	Properties				Heat Cap	acity const	ants from	Appendix	ideal ga	s H ^{ig} - H _R	^{ig} U ^{ig} - U _R	^{ig} S ^{ig} -S _R ^{ig}
3	Gas	T _c (K)	P _c (MPa)	ω	Α	В	С	D	values	J/mo	l J/mol	I J/molK
4	n-HEPTANE	540.3	2.736	0.349	-5.146	6.76E-01	-3.65E-0	4 7.66E-0	8	9084.4	03 8660.0	74 33.83935
5					_							
6	Current State)	Roots		Stable Ro	oot has a lo	wer fugac	ity				
7	T (K)	349.185	Z	V	fugacity	н	U	S	H-H ^{ig}	U-U ^{ig}	S-S ^{ig}	
8	P (MPa)	0.05	5	cm ³ /gmol	MPa	J/mol	J/mol	J/molK	J/mol	J/mo	I J/molł	<
9	answers	for three	0.9741548	56565.05	0.048738	3 44871.76	6 42043.5	1 131.169	-206.1	75 -131.1	39 -0.377	84
10	root	region	0.0209134	1214.352	2	36661.96	36601.2	4 92.4616	68 -8415.9	97 -5573	3.4 -39.08	54
11			0.002732	2 158.6333	5 0.048737	7 11613.56	5 11605.6	3 35.9242	21 -33464	.4 -305	69 -95.62	29
12	& for 1 r	oot region	#NUM!	#NUM!	#NUM!	Ź#NUM!	É #NUM!	Ś#NUM	É #NUM	! ´ #NUN	1!	1!

⁽⁵⁾ Which of the above cases represents the outlet condition (with reasonable roundoff error)? If none of the cases are reasonable, indicate.

(5) Justify your selection.

Michigan State University

DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers Exam 2A: April 08, 2015, Closed Book Portion (25 minutes) Spring 2015

1. (5) The system (A) + (B) where $P_B^{sat} > P_A^{sat}$ forms a maximum pressure azeotrope at $x_A = 0.22$. The system is in a piston-cylinder at $x_A = 1$, where both vapor and liquid coexist and V/F = 0.45. Some component *B* is injected into the system at constant *T* and *P* until the overall composition is 10 mol% (A). What happens to the coexisting phases? Be specific about the changes and compositions.

(5) (b) Discuss how/why KE and PE depend on density at a fixed pressure.

(5) (c) Besides temperature and pressure, what property(ies) are the same in both phases when two binary phases are in phase equilibrium?

2. We wish to use PreosProps.m to generate a n-pentane isotherm for a P-V chart at 375K between 0.1 MPa and 6 MPa. For n-pentane, Tc = 469.7K, Pc = 3.369, $\omega = 0.249$.

Fluid Specifications n-PENTANE			
Reference T(K) 298.15 Refere	ence Pressure (MPa)	0.1	
	For Matching,	For Matching U, H, S,	
T(K) 375 P(MPa) 1	Root to use:	or Saturation	
	Iarge Z	adjust T	
Run Type	Small Z	Value to match:	
No Matching, use specified T,P	Results		-
Match U Match S	n-PENTANE		
Match H Match V	T(K) 375	P(MPa) 1	
Find Saturation	z	0.72413 0.0426456	
	V (cm^3/mol)	2257.74 132.963	
User Objective, Adjust 1 and P	U (J/mol)	31973.7 13810.4	
The fluid is specified by editing PreosProps.m.	H (J/mol)	34231.5 13943.4	
Save the file, and then fill in the information here.	S (J/mol-K)	92.1847 41.1158	
	fugacity (MPa)	0.785191 0.545209	
Calculate	User Objecive	0	

(a) (5) make a qualitative sketch of the shape you expect for the isotherm.



 $V (\text{cm}^3/\text{mol})$

(b) (10) Describe how you would use the GUI to generate the data you need to plot an isotherm. Be specific about how you would find endpoints for any abrupt changes in your isotherm, and how to interpret multiple values from the GUI such as those above. Add a dot to your plot to indicate the approximate location of the state given in the above GUI. Add values to the x- and y-axis for your dot.

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DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers Exam 2A: April 08, 2015, Equation Sheet Provided (85 minutes) Spring 2015

ANTOINE CONSTANTS for $log_{10}(P^{sat}(mmHg)) = A - B/(T(Celsuis) + C)$.

-		
	Component (1)	Component (2)
Α	7.2813	7.3205
В	1434.2	1465.2
С	254.2	264.3

- 3. Some experiments have shown that components (1) and (2) do not follow Raoult's Law. The following data are available from an experiment with component (1) + component (2): $x_1 = 0.65$, $y_1 = 0.586$, $T(^{\circ}C) = 70$, P = 842 mmHg.
 - (a) (10) Fit the two-parameter Margules equation to the data.

(b) (10) Using the two-parameter Margules equation, predict the bubble pressure and y_1 at 70°C for a mixture where $x_1 = 0.3$. If an iterative calculation is required, perform the first iteration and specify values for the next iteration. If an iterative calculation is not required, provide the bubble pressure and vapor composition.

(c) (10) Based on your calculations, sketch the behavior you expect for the Pxy and Txy diagrams. Make the Pxy semi-quantitative by labeling known quantities from parts (a) and/or (b). The Txy can be left qualitative.

4. (10) A simple derivative manipulation is applied to each of the starting expressions in the left column below. Some of the manipulations may involve errors. Indicate whether the ending expression in each row is valid or invalid. Valid work in the scratch area is necessary for full credit.

Starting Expression	Ending Expression	Indicate Valid or
		Invalid
dU = TdS - PdV	$\left(\frac{\partial U}{\partial T}\right)_{P} = C_{P} - P\left(\frac{\partial V}{\partial P}\right)_{T}\left(\frac{\partial P}{\partial T}\right)_{V}$	
$\left(\frac{\partial V}{\partial T}\right)_{S}$	$-\frac{C_V}{T}\left(\frac{\partial P}{\partial T}\right)_V$	

Scratch area:

5. (10) A mixture of (1) + (2) follow Raoult's law. At 80°C, the vapor pressures are P_1^{sat} = 1030 mmHg and P_2^{sat} = 620 mmHg. The mixture forms V + L phases at an overall composition of 40 mol% component (1) and 750 mmHg. Write a Matlab function that will find the V/F for this condition. For full credit, use an fzero call properly in your code. Use programming syntax and variable names, not hand-written algebra or pseudo-code. (If needed, syntax of a for loop: for i =firstvalue:lastvalue; syntax for fzero: [varValueFinal] = fzero(@objName, varValueGuess))The first statements are given.

```
function LOF
Psat = [1030 620]; %mmHg
P = 750; mmHg
```

6. (10) A fluid follows the equation of state $PV = RT - \left(\frac{a}{T}\right)P + bP$, where a = 385.2 cm³-K/mol and b = 15.23 cm³/mol. Derive the formula for the enthalpy departure of a fluid that follows this equation of state. Possibly useful: $\int (1/x)dx = \ln x$; $\int (1/(ax + b))dx = (1/a)\ln(ax + b); \int (x/(ax + b))dx = x/a - (b/a^2)\ln(ax + b); \int (1/(ax + b)^2)dx = -1/(a(ax + b))$

7. (10) Ideal gas state changes are given by $\Delta H^{ig} = \int C_P dT$, $\Delta U^{ig} = \int C_V dT$, $\Delta S^{ig} = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$. For a fluid in at P₁ = 1 MPa, T₁ = 380K, the enthalpy departure is -432 J/mol and Z = 0.75. At P₂ = 0.15 MPa, T₂ = 400 K, the enthalpy departure is -120 J/mol and Z = 0.85. For the fluid, Cp = 77 J/mol-K and can be considered temperature independent. Determine ΔH and ΔU in J/mol.

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ChE321: Thermodynamics for Chemical EngineersSpring 2014Exam 2: April 02, 2014, Closed Book Portion (35 minutes)Spring 2014

Note: 1 bar = 0.1 MPa = 750 mmHg; 1 atm = 760 mmHg. $R = 8.314 \text{ cm}^3 \text{MPa/mol-K}$

1. (5) The system (A) + (B) where $P_A^{sat} > P_B^{sat}$ forms a maximum pressure azeotrope at $x_A = 0.73$. The system is in a piston-cylinder at the azeotropic conditions $x_A = 0.73$, where both vapor and liquid coexist and V/F = 0.45. More component *A* is injected into the system at constant *T* and *P*. What happens to the coexisting phases? Be specific about the changes.

(5) (b) dU = TdS - PdV; H = U + PV; G = H - TS. Derive the relation for dG.

(5) (c) Describe what is meant by the 'combinatorial term' and the 'residual term' in UNIQUAC and UNIFAC.

2. We wish to use PreosProps.m to generate an isobutane isotherm for a P-H chart at 280K between 0.1 MPa and 6 MPa. (The y-axis is usually a log scale, which is shown linearly below using logarithms of values, so the shape should look the same as P-H charts you have used.) For isobutane, Tc = 408.1K, Pc = 3.648, $\omega = 0.177$.

PreosPropsMenu		
Fluid Specifications ISOBUTANE Reference T(K) 200 Referen	ce Pressure (MPa)	0.1
T(K) 280 P(MPa) 0.1 Run Type No Matching, use specified T,P Match II. Match S	For Matching, Root to use: Iarge Z Small Z Results	For Matching U, H, S, or Saturation adjust T value to match: 0
Match B Match V Match H Match V Find Saturation User Objective, Adjust T and P The fluid is specified by editing PreosProps.m. Save the file, and then fill in the information here.	T(K) 280 Z V (cm ⁴ 3/mol) U (J/mol) H (J/mol) S (J/mol-K) fugacity (MPa) User Objecive	P(MPa) 0.1 0.969613 0.00410454 22572.6 95.5537 27314.1 9268.39 29571.4 9277.95 116.736 38.7377 0.0970419 0.188521 0

(a) (5) make a qualitative sketch of the shape you expect for the isotherm.



H(J/mol)

(b) (10) Describe how you would use the GUI to generate the data you need to plot an isotherm. Be specific about how you would find endpoints for any abrupt changes in your isotherm, and how to interpret multiple values from the GUI such as those above. Add a dot to your plot to indicate the approximate location of the state given in the above GUI. Add values to the x- and y-axis for your dot.

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ChE321: Thermodynamics for Chemical Engineers Exam 2: April 02, 2014, Open Notes Portion (85 minutes) Spring 2014

ANTOINE CONSTANTS for $log_{10}(P^{sat}(mmHg)) = A - B/(T(Celsuis) + C)$.

	Component (1)	Component (2)
Α	7.2807	7.8103
В	1434.2	1420
С	246.5	191.15

NOTE: the same T of 80 °C is used throughout to minimize calculations.

- 3. Suppose component (1) and component (2) follow Raoult's Law. The temperature is 80 °C.
 - a. (10) What is the dew pressure (mmHg) and liquid composition when $y_1 = 0.6$? What is x1 at the dew point?

b. (10) At 80 °C a mixture *F* that is 48 mol% component (1) is fed to a flash drum at 541.7 mmHg. The vapor composition is y1 = 0.60 and the liquid is x1 = 0.42. What is the ratio of moles of vapor to moles of feed, *V/F*?

- 4. Some experiments have shown that components (1) and (2) do not follow the results predicted by problem 3. The following data are available from an experiment with the system component (1) + component (2): $x_1 = 0.30$, $y_1 = 0.567$, $T(^{\circ}C) = 80$, P = 694.3 mmHg.
 - (a) (10) Fit the two-parameter Margules equation to the data.

(b) (10) Using the two-parameter Margules equation, predict the bubble pressure and y1 at 80°C for a mixture where $x_1 = 0.6$. If an iterative calculation is required, perform the first iteration and specify values for the next iteration. If an iterative calculation is not required, provide the bubble pressure and vapor composition.

- 5. The virial equation can be written, Z = 1 + BP/(RT)
- (a) (10) For methane, $T_c = 190.6$ K, $P_c = 4.604$, $\omega = 0.011$. What value is predicted for the virial coefficient at 120K using the generalized virial coefficient correlation?

(b) (10) Write a Matlab function that will find the temperature where the virial coefficient has a value of -100 cm³/mol. For full credit, use an fzero call properly in your code. Use programming syntax and variable names, not hand-written algebra or pseudo-code. (If needed, syntax of a for loop: for i =firstvalue:lastvalue; syntax for fzero: [varValueFinal] = fzero(@objName, varValueGuess))The first statements are given.

function virial
Tc = 190.6; %K
Pc = 4.604; %MPa
w = 0.011;

6. (10) A fluid follows the equation of state $Z = 1 + a\rho/(1 - a\rho)$, where a = 187 cm³/mol. Derive the formula for the fugacity of a fluid that follows this equation of state. Possibly useful: $\int (1 \setminus x) dx = \ln x$; $\int (1/(ax + b)) dx = (1/a) \ln(ax + b)$; $\int (x/(ax + b)) dx = x/a - (b/a^2) \ln(ax + b)$

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ChE321: Thermodynamics for Chemical Engineers Sp Exam 2: April 03, 2013, Closed Book Portion (40 minutes)

Spring 2013

Note: 1 bar = 0.1 MPa = 750 mmHg; 1 atm = 760 mmHg. R = 8.314 cm³MPa/mol-K

 (5) (a) Describe the easiest procedure (bubble, dew, flash, etc.) to create a complete T-x-y diagram for a binary system at a specified *P*, where the activity coefficient expression and parameters are known. Be specific about how each line on the diagram is calculated.

(5) (b) The binary system A + B follows Raoult's law, and at a specified temperature $P_A^{sat} > P_B^{sat}$. The system is closed in a piston/cylinder. The system is equimolar and initially at a low pressure where only vapor exists. The pressure is to be raised until only a trace of vapor exists. What type of calculation (bubble, dew, flash) is best and quickest to use to find this pressure? Explain your choice.

(5) (c) For the process described in 1(b), it is desired to create a qualitative plot of y_A and x_A (both on y-axis) as a function of *P* (on x-axis) starting from the initial state where everything is totally vapor to a state where everything is totally liquid. Sketch the shape of the two curves/lines for each composition. Omit the lines for y_A and x_A in the region where the respective phase does not exist.



2. (10) The van der Waals equation is $Z = 1/(1-b\rho) - a\rho/RT$. The parameters are made dimensionless using $A = aP/(RT)^2$ and B = bP/RT. Rearrange the equation in the form $Z^3 + a_2Z^2 + a_1Z + a_0 = 0$, where a_2 , a_1 , and a_0 are functions of A and B.

3. (15) Ethane enters a reversible adiabatic expander at the following conditions. The outlet of the expander is to be at 0.1 MPa.

Reference T(K) 298.15	eference Pressure (MPa)	0.1	
K) 240 P(MPa) 0. Run Type Image: Constraint of the system 0. Image: Constraint of the system Image: Constraint of the system 0. Image: Constraint of the system Image: Constraint of the system 0. The fluid is specified by editing Preosp Save the file, and then fill in the information Calculate	For Matching, Root to use: Small Z Results ETHANE T(K) 240 Z V (cm^3/mol) U (J/mol) h (J/mol) h (J/mol) S (J/mol-K) fugacity (MPa) User Objecive	For Matching U, H, S or Saturation adjust T Value to match: 0 P(MPa) 0.5 0.920616 0.0153033 3674.06 61.0734 -5017.83 -15636.1 -3180.77 -15605.5 -24.8503 -81.3575 0.462899 0.818334 0.522723	

Below are several possible outlet states. Calculate the work done by the expander (J/mol) after selecting the correct outlet state. If none of the provided states is correct, indicate how you would use the buttons/boxes on the GUI to find the outlet state.

P(MPa) 0.1		
0.984784 0.00307039		
19623.6 61.183		
-4816.63 -15636.1		
-2854.24 -15630		
-10.6238 -81.3575		
0.0984977 0.801195		
2.84217e-14		

State 2c

State 2b

- Results ETH/	ANE	
T(K)	184.206	P(MPa) 0.1
Z		0.969766 0.00331068
V (cm	^3/mol)	14852.4 50.7045
U (J/m	ol)	-6599.28 -19792.4
H (J/m	ol)	-5114.01 -19787.3
S (J/m	ol-K)	-21.3021 -100.959
fugacity (MPa)		0.097058 0.097058
User (Objecive	4.44089e-16

State 2d

ETHANE		ETHANE	
T(K) 166.694	P(MPa) 0.1	T(K) 232.277	P(MPa) 0.1
Z	0.960993 0.0035214	Z	0.983461 0.00306018
V (cm^3/mol)	13318.8 48.8047	V (cm [^] 3/mol)	18992.8 59.0989
U (J/mol)	-7068.3 -20896.9	U (J/mol)	-5080.09 -16270.9
H (J/mol)	-5736.39 -20892	H (J/mol)	-3180.77 -16265
S (J/mol-K)	-24.8503 -107.257	S (J/mol-K)	-12.0076 -84.0483
fugacity (MPa)	0.0962368 0.0345727	fugacity (MPa)	0.0983692 0.650831
User Objecive	-7.10543e-15	User Objecive	4.54747e-13

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ChE321: Thermodynamics for Chemical Engineers Exam 2: April 03, 2013, Open Notes Portion (80 minutes) Spring 2013

Note: 1 bar = 0.1 MPa = 750 mmHg; 1 atm = 760 mmHg. $R = 8.314 \text{ cm}^3 \text{MPa/mol-K}$

4. The following data are available from an experiment with the system n-pentane(1) + acetone(2): $x_1 = 0.292$, $y_1 = 0.614$, T(°C) = 34.35, P=750 mmHg.

ANTOINE CONSTANTS for $log_{10}(P^{sat}(mmHg)) = A - B/(T(^{\circ}C) + C)$

<u> </u>		
	n-pentane	acetone
Α	6.85296	7.11714
В	1064.84	1210.6
С	232.012	229.664

(a) (10) Fit the two-parameter van Laar equation to the data.

(b) (10) Using the two-parameter van Laar equation, predict the bubble pressure at 34.35° C for a mixture where $x_1 = 0.01$.

(c) (15) Based on the parameters fitted above, provide Matlab code to solve for the bubble temperature of a binary mixture with overall composition z₁ = 0.8 at 760 mmHg. For full credit, your method must work, avoid unnecessary calculations, and provide all constants. Half credit is for the logic and half credit is for Matlab syntax. (If needed, syntax of a for loop: for i =firstvalue:lastvalue; syntax for fzero: [varValueFinal] = fzero(@objName, varValueGuess)).

5. (10) Below is a plot for Z^0 given by the Lee Kesler charts. We would like to generate a predicted curve Z vs. P_r at $T_r = 0.5$ using the Peng-Robinson equation for methanol, $(T_c = 512.6 \text{ K}, P_c = 8.096 \text{ MPa}, \omega = 0.566)$. Write a Matlab script to generate and plot the line. The syntax of the PreosProps.m function line is function [Z H S U phi info] = PreosProps(Tref, Pref, T, P, match). Half the credit is for the logic and half credit is for the syntax. See problem 4 for syntax hints. Also 'match' is a row vector of four zeros.



6. A fluid is described by the following equation of state: $Z = 1 + a\rho/(1 - a\rho)$

where $a = -207 \text{ cm}^3/\text{mol}$, and the ideal gas heat capacity is Cp = 65.3 J/molK.

- (a) (10) Determine the fully integrated entropy departure function in terms of *a*, *T*, Z and ρ . Hints: $\int (1 \setminus x) dx = \ln x$; $\int (1/(ax + b)) dx = (1/a) \ln(ax + b)$; $\int (x/(ax + b)) dx = x/a - (b/a^2) \ln(ax + b)$
- (b) (5) At a pressure of 4 MPa and 400K, what is the molar volume (cm^3/mol) ?

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ChE321: Thermodynamics for Chemical Engineers

Exam 2: April 11, 2012, Closed Book Portion

1. (5) Explain the differences in particle motions for the following types of simulations at the same temperature and density: ideal gas particles, purely repulsive particles, square-well particles.

(5) The van Laar and Scatchard-Hildebrand models are both derived from van der Waals models. What did Scatchard-Hildebrand do differently than van Laar to make the model less empirical?

(5) The acentric factor is a parameter used frequently in equations of state. Describe the origin of the parameter.

2. (10) The van der Waals equation is $Z = 1/(1-b\rho) - a\rho/RT$. The parameters are made dimensionless using $A = aP/(RT)^2$ and B = bP/RT. Rearrange the equation in the form $Z^3 + a_2Z^2 + a_1Z + a_0 = 0$, where a_2 , a_1 , and a_0 are functions of A and B.

3. A P-x-y diagram is shown below for the system A+B at $T = 85^{\circ}C$. From the diagram, mark the answers to the following questions, label them as '(a)', ' (b)', etc., and provide numerical values.



 x_A, y_A

- (a) (5) The dew pressure and coexisting phase compositions (use x for liquid, y for vapor) and V/F for an overall composition $z_A = 0.5$.
- (b) (5) The phase compositions (use x for liquid, y for vapor) and calculated V/F for an overall composition $z_A = 0.5$ at 645 mm Hg.
- (c) (5) Sketch the y-x diagram qualitatively for this system.

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Spring 2012

Exam 2: April 11, 2012, Open Book Portion

4. (15) Isobutanol is of interest as a fermentation product as a potential chemical intermediate or biofuel. Literature studies (Udovenko, V.V.; Frid, Ts.B.; Zh. Fiz. Khim. 1948, 22, 1135-1145) report the following data for methanol(1) + isobutanol(2), T = 333.15, P = 45.66 kPa, $x_1 = 0.4$, $y_1 = 0.827$. Pure component vapor pressures are $P_1^{sat} = 82.66$ kPa, $P_2^{sat} = 12.8$ kPa at 333.15K. Fit the two parameter Margules equation.

(15) Based on the parameters fitted above, provide Matlab code to solve for the dew pressure of a binary mixture with overall composition z₁ = 0.8 at 333.15K. For full credit, your method must work, avoid unnecessary calculations, and provide all constants. Half credit is for the logic and half credit is for Matlab syntax. (If needed, syntax of a for loop: for i =firstvalue:lastvalue; syntax for fzero: [varValueFinal] = fzero(@objName, varValueGuess)).

- 5. A fluid is described by the following equation of state: $Z = 1 + (a + b/T)\rho$ where a = 500 cm³/mol, b = -4.8E5 cm³K/mol and the ideal gas heat capacity is Cp = 79.3 J/molK.
 - (a) (10) Determine the internal energy departure function in terms of a, b, T, Z and ρ .

- (b) (5) At a density of 2E-4 mol/cm³ and 500K, what is the system pressure?
- 6. A curve for a binary (1) + (2) system is shown below.



- (a) (5) Beginning with 1 mole of pure (1), how many moles of (2) can be added before the system forms two liquid layers?
- (b) (5) When two liquid layers form, what is the approximate LLE K₁ for component 1? Answers are accepted for either phase as the extract phase.
- (c) (5) The student who generated the curve got confused about which Margules parameters were used to generate the plot. The student thinks that values were $A_{12} = 0.9$ and $A_{21} = 3.3$. Is the plot consistent with these values? Explain using calculations.

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ChE321: Thermodynamics for Chemical Engineers Spring 2011

Exam 2: April 13, 2011, Closed Book Portion

1. (5) Explain why the total kinetic energy of the sites of a molecule is different than the kinetic energy of the center of mass.

(5) Explain why the temperature fluctuates in a simulation with attractive and repulsive potential energy.

(5) Compare in magnitude the kinetic energy of a ethanol vapor molecule at 35°C and 103.1 mmHg (the vapor pressure) and a liquid molecule at 35°C and 103.1 mmHg.

2. VLE data for the system carbon tetrachloride (1) and 1,2-dichloroethane (2) are given below at 760 mm Hg, as taken directly from the literature.¹

X1	y 1	$T(^{o}C)$	X1	y ₁	$T(^{o}C)$
0.	0.	82.4 ^a	0.506	0.557	75.78
0.040	0.141	81.59	0.880	0.831	75.71
0.091	0.185	80.39	0.900	0.848	75.86
0.097	0.202	80.27	0.923	0.875	75.95
0.185	0.310	78.73	0.960	0.907	76.20
0.370	0.473	76.62	1.0	1.0	76.7 ^a

- a. (5) Does an azeotrope exist? If an azeotrope exists, between which two of the x_1 entries in the table does the azeotrope exist? If an azeotrope does not exist, explain why the data indicate that conclusion.
- b. (5) To the right of the table above, sketch a schematic of what you think a $P-x_1-y_1$ diagram would look like for this system.

¹ Yound, H.D., Nelson, O.A., Ind. Eng. Chem. Anal. Ed. 4, 67 (1932), except for normal boiling points marked with superscript a, from Perry's 5th edition, p. 3-49ff.

- c. (5)Does the system exhibit positive or negative deviations from Raoult's law? (you may neglect gas phase non-idealities). Justify your answer.
- 3. Antoine coefficients for ethanol (1) + 1-propanol (2) are provided below. The Antoine equation is log₁₀P(mmHg) = A B/(T + C). This problem involves setting up Matlab code for a bubble temperature calculation. The problem is divided into two parts. If needed, the syntax for an fzero statement is '[varValueFinal] = fzero(@objName,varValueGuess).' The syntax for a function statement is '[result] = functname(input1,...)'

	А	В	С
ethanol	8.1122	1592.864	226.184
1-propanol	8.37895	1788.02	227.438

- (a) (5) Provide Matlab code that will establish vectors A, B, C to hold the Antoine coefficients given above, and set the pressure P to 760 mmHg, and the binary composition, represented by vector x to 70% ethanol.
- (b) (10) Add to your code a procedure to find the bubble temperature at pressure P = 760 mmHg using Raoult's law at the composition available in the vector x. Your code statements should use valid Matab syntax. (Note: half the credit for this section is for properly setting up the bubble temperature logic and half the credit is for the Matlab programming).

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Exam 2: April 13, 2011, Open Book Portion

4. VLE data for the system carbon tetrachloride (1) and 1,2-dichloroethane (2) are given below at 760 mm Hg, as taken directly from the literature.²

X1	y ₁	T(°C)	X ₁	y ₁	T(°C)
0.	0.	83.55 ^a	0.506	0.557	75.78
0.040	0.141	81.59	0.880	0.831	75.71
0.091	0.185	80.39	0.900	0.848	75.86
0.097	0.202	80.27	0.923	0.875	75.95
0.185	0.310	78.73	0.960	0.907	76.20
0.370	0.473	76.62	1.0	1.0	76.65 ^a

.(a) (10) Using only the data at $x_1 = 0.37$, fit the van Laar equation. The vapor pressures at 76.62 °C are $P_1^{sat} = 757.5$ mmHg and $P_2^{sat} = 601.6$ mmHg.

² Yound, H.D., Nelson, O.A., Ind. Eng. Chem. Anal. Ed. 4, 67 (1932), except for normal boiling points marked with superscript a, from NIST WebBook.

(b) (10) Using the parameters fitted in part (a), set forth the procedure to determine bubble pressure for a mixture of 60 mol% carbon tetrachloride at 80°C where the vapor pressures are $P_1^{sat} = 838.6$ mmHg, $P_2^{sat} = 672.1$ mmHg. Avoid unceessary calculations in your procedure. If an iterative calculation is required, perform the first interation and specify values for the next iteration. If an iterative calculation is not required, provide the bubble pressure and vapor composition. 5. (10) The vapor pressure of n-pentane at 70°C is 0.261 MPa, where $V^{satL} = 121$ cm³/mol, $V^{satV} = 9974$ cm³/mol. Calculate the fugacity of n-pentane at 70°C and 2 MPa. Use the virial equation to represent vapor phase non-idealities.

6. (5) An equilmolar mixture of water (1) + MEK (2) exits a distillation column at 100 mol/h as vapor and is condensed into a decanter at 298K. LLE has been modeled for the two components using UNIFAC in Example 14.3 and 14.5. What are the flow rates of the two liquid streams exiting the decanter?

- 7. The equation of state for a simple fluid has been correlated to the equation Z = 1 + aP/RT, where $a = -254 \text{ cm}^3/\text{mol}$, and $C_P = 56 \text{ J/mol-K}$.
 - (a) (10) When the pressure is 5 MPa, what is the molar volume at 320K?
 - (b) (10) Evaluate the enthalpy departure for the fluid in terms of the EOS variables.