## Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING

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

1. (10) (T or F)
__ The UNIFAC model is based on local composition concepts.
Plotting $\ln \left(\mathrm{P}_{\mathrm{r}}{ }^{\text {sat }}\right)$ (y-axis) vs. $1 / \operatorname{Tr}$ ( x -axis) gives a line with a positive slope. The compressibility factor Z for liquids is always $\mathrm{Z}^{\mathrm{L}} \ll 1$.
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 65 C and 346 mm Hg . The vapor pressure of hexane at 65 C is 675 mmHg .
(b) Hexane is in an ideal gas vapor mixture with acetone at 65 C and 480 mmHg . The mole fraction of hexane is $y_{\text {hexane }}=0.4$. The vapor pressures are $\mathrm{P}^{\text {sat }}{ }_{\text {hexane }}=$ $675 \mathrm{mmHg}, \mathrm{P}^{\text {sat }}{ }_{\text {acetone }}=1020 \mathrm{mmHg}$.
(c) Hexane is a pure liquid at 65 C and 760 mmHg . The vapor pressure of hexane at 65 C is 675 mmHg .
3. (10) For the system 1-butanol (1) + 2-propanol (2) at 90 C , the vapor pressures are $P_{1}^{\text {sat }}=257 \mathrm{mmHg}$ and $P_{2}^{\text {sat }}=1026 \mathrm{mmHg}$. Using Raoult's law, estimate the dew pressure and coexisting phase compositions for an overall composition of $70 \mathrm{~mol} \%$ 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 $\mathrm{L} / \mathrm{F}$ for an overall composition $\mathrm{z}_{\mathrm{A}}=0.5$.
(b) (10) The phase compositions (use x for liquid, y for vapor) and calculated $\mathrm{L} / \mathrm{F}$ for an overall composition $\mathrm{z}_{\mathrm{A}}=0.5$ at 645 mm Hg .
5. The (1) $+(2)$ system exhibits vapor liquid equilibria at 24.95 kPa and 50 C . The compositions of the coexisting phases are $\mathrm{x}_{1}=0.36$ and $\mathrm{y}_{1}=0.62$ and $P_{1}^{s a t}=69.4 \mathrm{kPa}$, $P_{2}^{\text {sat }}=15.8 \mathrm{kPa}$.
(a) (5) Calculate $G^{E} /(R T)$ for the liquid phase at 50 C and composition $\mathrm{x}_{1}=0.36$. Note: $\bar{G}_{i}^{E} /(R T)=\ln \gamma_{i}$.
(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 $\mathrm{z}_{1}=0.8$ 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 $(\mathrm{A})+(\mathrm{B})$ exhibits $\mathrm{V}+\mathrm{L}$ 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 $P^{\text {sat }}{ }_{A} / P^{\text {sat }}{ }_{B}$ ?
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)

|  | A | B | C | D | E | F | G | H |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 6 | Current |  | Roots |  | Stable R | has a lo | fugacity |  |
| 7 | T (K) | 281.937592 | Z | V | fugacity | H | U | S |
| 8 | P (MPa) | 0.1 | $\mathrm{cm}^{3} / \mathrm{gmol}$ |  | MPa | $\mathrm{J} / \mathrm{mol}$ | $\mathrm{J} / \mathrm{mol}$ | J/molK |
| 9 | answers for three root region |  | 0.9806862 | 22988.876 | 0.0981 | -1177.73 | -3476.62 | -4.06066 |
| 10 |  |  | 0.0134429 | 315.12342 |  | -8169.21 | -8200.73 | -46.8466 |
| 11 |  |  | 0.0034694 | 81.327516 | 0.53412 | -17947.7 | -17955.9 | -77.6318 |
| 12 | \& fo | ot region | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! |

$\left[\begin{array}{llll|}\hline \text { Results- } \\ \text { PROPANE } & & \\ \text { T(K) } & 281.937 & \mathrm{P}(\mathrm{MPa}) & 0.1 \\ \mathrm{Z} & 0.980686 & 0.00346936 \\ \mathrm{~V}\left(\mathrm{~cm}^{\wedge} 3 / \mathrm{mol}\right) & 22988.4 & 81.3258 \\ \mathrm{U}(\mathrm{J} / \mathrm{mol}) & -3476.63 & -17955.9 \\ \mathrm{H}(\mathrm{J} / \mathrm{mol}) & -1177.74 & -17947.8 \\ \mathrm{~S}(\mathrm{~J} / \mathrm{mol}-\mathrm{K}) & -4.0607 & -77.6319 \\ \text { fugacity }(\mathrm{MPa}) & 0.0981002 & 0.534112 \\ \text { User Objecive } & 2.72848 \mathrm{e}-12 \\ & \\ & \\ \hline\end{array}\right.$
(state 2)


| Results |  |  |  |
| :--- | ---: | :--- | :--- |
| PROPANE |  |  |  |
| T(K) | 183.063 | $\mathrm{P}(\mathrm{MPa})$ | 0.1 |
| Z | 0.939524 | 0.00429792 |  |
| $\mathrm{~V}\left(\mathrm{~cm}^{\wedge} 3 / \mathrm{mol}\right)$ | 14299.9 | 65.4161 |  |
| $\mathrm{U}(\mathrm{J} / \mathrm{mol})$ | -8517.23 | -27272.4 |  |
| $\mathrm{H}(\mathrm{J} / \mathrm{mol})$ | -7087.2 | -27265.9 |  |
| $\mathrm{~S}(\mathrm{~J} / \mathrm{mol} \mathrm{K})$ | -29.524 | -117.774 |  |
| fugacity $(\mathrm{MPa})$ | 0.0942867 | 0.00670624 |  |
| User Objecive | $3.55271 \mathrm{e}-15$ |  |  |
|  |  |  |  |

Continued on next page...
(state 3)


| Results |  |  |  |
| :---: | :---: | :---: | :---: |
| PROPANE |  |  |  |
| T(K) | 230.61 | $\mathrm{P}(\mathrm{MPa})$ | 0.1 |
| Z |  | 0.96 | 0.00369706 |
| V (cr |  |  | 70.8858 |
| U (J/ |  |  | $-23234.7$ |
| H (J/ |  |  | -23227.6 |
| S (J/ |  |  | -98.2289 |
| fuga | Pa ) | 0.09 | 0.0967902 |
| User | cive |  | 78e-16 |

Identify the correct outlet state, and calculate the work done by the expander in $\mathrm{J} / \mathrm{mol}$.
$\qquad$

## Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

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

1. (10) A binary system (A) + (B) of $F$ total moles exists as $V$ moles vapor and $L$ moles liquid, where the overall composition is $60 \mathrm{~mol} \%$ (A) and the liquid composition is $47 \mathrm{~mol} \%(\mathrm{~A})$, and the vapor composition is $72 \mathrm{~mol} \%(\mathrm{~A})$. 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 $V+\mathrm{L}$ as shown. Pure heptane (C7) liquid is injected into the vapor at constant temperature and pressure. After injection the overall mixture is $10 \mathrm{~mol} \% \mathrm{C} 7$. What happens (circle the best answer)?
(a) All the C 7 goes to L and the V is only C 6 .
(b) The vapor is mostly C 6 with some C 7 .
(c) All the vapor condenses.
(d) All the liquid evaporates.
(e) None of the above. Explain


C6
4. (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
$\qquad$
5. The system chloroform (1) + 1,4-dioxane (2) exists as $\mathrm{V}+\mathrm{L}$ at 323.15 K and $\mathrm{P}=$ 19.89 kPa with $\mathrm{x}_{1}=0.2$ and $\mathrm{y}_{1}=0.3691$. At this temperature $P_{1}^{s a t}=69.31 \mathrm{kPa}$ and $P_{2}^{s a t}=15.78 \mathrm{kPa}$. Vapor pressures can be estimated at other temperatures using $\log _{10} P_{1}^{\text {sat }}=6.2983-1432.1 / T(K) ; \log _{10} P_{2}^{\text {sat }}=6.6074-1732.5 / T(K)$; (15) Fit the two-parameter Margules equation to this measurement.
(10) Determine the bubble temperature at 60 kPa and an overall composition of 40 $\mathrm{mol} \%(1)$. 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.

Name $\qquad$
6. A fluid is described by the following equation of state:

$$
Z=1+(a+b / T) \rho
$$

where $\mathrm{a}=500 \mathrm{~cm}^{3} / \mathrm{mol}, \mathrm{b}=-3.45 \mathrm{E} 5 \mathrm{~cm}^{3} \mathrm{~K} / \mathrm{mol}$ and the ideal gas heat capacity is Cp $=74.6 \mathrm{~J} / \mathrm{molK}$.
(a) (10) At 300 K and $\rho=4.5 \mathrm{E}-4 \mathrm{~mol} / \mathrm{cm}^{3}$, what is P (MPa)?
(b) (10) For this equation of state, derive $\left(U-U^{i g}\right) /(R T)$ in the fully integrated form. Leave the expression in terms of $a, b, Z$ and $\rho$.
7. (10) For benzene at the state $\mathrm{T}_{2}=290 \mathrm{~K}$ and $\mathrm{P}_{2}=0.1 \mathrm{MPa}$, the Peng-Robinson equation gives a value of $\left(S-S^{i g}\right)=-93.8886 \mathrm{~J} / \mathrm{molK}$. For benzene at the state $\mathrm{T}_{1}=$ 480 K and $\mathrm{P}_{1}=1 \mathrm{MPa}$, the Peng-Robinson equation gives $\left(\mathrm{S}-\mathrm{S}^{\mathrm{ig}}\right)=-2.1963 \mathrm{~J} / \mathrm{molK}$.
Cp is assumed to be constant and for benzene near these temperatures, $\mathrm{Cp}=100$ $\mathrm{J} / \mathrm{molK}$. Determine $\Delta \mathrm{S}$ 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. $\overline{(5)}$ Liquid exists in which region(s) of the diagram?
$\qquad$ only I II and III
$\qquad$ only II ___ I and III
__o only III

___ I and II

Name $\qquad$
9. Consider hexane at compressor inlet state I.

State I

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.

Name $\qquad$

$\qquad$

## Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers
Spring 2016
Exam 2A: April 08, 2015, Closed Book Portion (20 minutes)

1. (5) The fundamental relation for U is $\mathrm{dU}=\mathrm{TdS}-\mathrm{PdV}$. The definition of Helmholtz energy is $\mathrm{A} \equiv \mathrm{U}-\mathrm{TS}$. Derive the relation for dA.
2. At 320 K 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 320 K , such that $\mathrm{x}_{1}=$ 0.6 and $\mathrm{x}_{2}=0.4$. 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 320 K , such that $\mathrm{x}_{1}=$ 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 $\ln (\operatorname{Pr})(y$-axis) vs. $1 / \operatorname{Tr}$ ( x -axis) gives almost a straight line with a negative slope.
4. (10) A solution of $30 \mathrm{~mol} \%$ hexane and $70 \mathrm{~mol} \%$ 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.

Name $\qquad$
5. (5) The Soave-Redlich-Kwong equation is $Z=1 /(1-b \rho)-(a /(b R T)) b \rho /(1+$ $b \rho$ ). The parameters are made dimensionless using $A=a P /(R T)^{2}$ and $B=b P / R T$.
Rearrange the equation in the form $Z^{3}+a_{2} Z^{2}+a_{1} Z+a_{0}=0$, where $a_{2}, a_{1}$, and $a_{0}$ are functions of $A$ and $B$.
$\qquad$

## Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING

ChE 321: Thermodynamics for Chemical Engineers
6. The equation of state for a simple fluid has been correlated to the equation $Z=1+a P / R T$, where $a=-2360 \mathrm{~cm}^{3} / \mathrm{mol}$, and $\mathrm{C}_{\mathrm{P}}=43 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$.
(a) (10) Derive the Helmholtz departure for the fluid and calculate the numerical value ( $\mathrm{J} / \mathrm{mol}$ ) 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) $\left(\frac{\partial G}{\partial S}\right)_{V}=-\frac{S T}{C_{V}}-V\left(\frac{\partial T}{\partial V}\right)_{P}$ |  |
| (c) $\left(\frac{\partial G}{\partial T}\right)_{S}=-S+\frac{V T}{C_{V}}\left(\frac{\partial T}{\partial V}\right)_{P}$ |  |

Scratch area:

Name $\qquad$

1. The system methyl acetate (1) + hexane (2) forms an azeotrope at $\mathrm{x}_{1}=0.667$, $51.57^{\circ} \mathrm{C}$, and 1 bar. The component vapor pressures at $51.57^{\circ} \mathrm{C}$ are $\mathrm{P}_{1}{ }^{\text {sat }}=0.833$ bar, $\mathrm{P}_{2}{ }^{\text {sat }}=0.5736$ 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: $\qquad$

(5) Justify your choice:
2. (10) The system (1) + (2) can be modeled with Modified Raoult's law, using the one parameter Margules equation, $\ln \gamma_{1}=1.6 \mathrm{x}_{2}{ }^{2}, \ln \gamma_{2}=1.6 \mathrm{x}_{1}{ }^{2}$. The vapor pressures are $\log _{10} \mathrm{P}_{1}{ }^{\text {sat }}=8.4-1800 /(\mathrm{T}+230), \log _{10} \mathrm{P}_{2}{ }^{\text {sat }}=7.3-1300 /(\mathrm{T}+170)$, where T is in Celsius. Calculate the bubble pressure and coexisting phase compositions using Modified Raoult's Law for a mixture that is overall $75 \mathrm{~mol} \%$ (1) and $25 \mathrm{~mol} \%$ (2) at $60^{\circ} \mathrm{C}$. If an iterative solution is required, perform the first iteration, and indicate clearly the specific steps used to find the answers.
$\qquad$
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-Robinso | Equation of | Spreadsheet protected, but no password used. |  |  |  |  |  |  |  |  |  |
| 2 | Properties |  |  |  | Heat Capacity constants from Appendix |  |  |  | ideal gas values | $\begin{array}{\|cc} \hline H^{\mathrm{ig}}-\mathrm{H}^{\mathrm{ig}} & \mathrm{U}^{\mathrm{ig}}-\mathrm{U}_{\mathrm{R}}^{\mathrm{ig}} \\ \mathrm{~J} / \mathrm{mol} & \mathrm{~J} / \mathrm{mol} \\ \hline 19428.18 & 18576.03 \\ \hline \end{array}$ |  | $\begin{gathered} \mathrm{S}^{\mathrm{ig}}-\mathrm{S}_{\mathrm{R}}{ }^{\mathrm{g}} \\ \mathrm{~J} / \mathrm{mol} \mathrm{~K} \\ \hline 42.29261 \end{gathered}$ |
| 3 | Gas | $\mathrm{T}_{\mathrm{c}}(\mathrm{K})$ | $\mathrm{P}_{\mathrm{c}}(\mathrm{MPa})$ | $\omega$ | A | B | C | D |  |  |  |  |
| 4 | n-HEPTANE | 540.3 | 2.736 | 0.349 | -5.146 | 6.76E-01 | -3.65E-04 | 7.66E-08 |  |  |  |  |
| 5 |  |  |  |  |  |  |  |  |  |  |  |  |
| 6 | Current State |  | Roots |  | Stable Root has a lower fugacity |  |  |  |  |  |  |  |
| 7 | T (K) | 400.64 | Z | V | fugacity | H | U | s | $\mathrm{H}-\mathrm{H}^{\text {ig }}$ | U-U ${ }^{\text {ig }}$ | S-sig |  |
| 8 | P (MPa) | 0.5 |  | $\mathrm{cm}^{3} / \mathrm{gmol}$ | MPa | $\mathrm{J} / \mathrm{mol}$ | $\mathrm{J} / \mathrm{mol}$ | J/molk | J/mol | $\mathrm{J} / \mathrm{mol}$ | J/molk |  |
| 9 | answers for three root region |  | 0.7948996 | 5295.7962 | 0.414999 | 53426.05 | 50778.15 | 136.5684 | -1995.66 | -1312.45 | -3.43193 |  |
| 0 |  |  | 0.1600253 | 1066.1239 |  | 46617.49 | 46084.43 | 117.6609 | -8804.22 | -6006.17 | -22.3394 |  |
| 1 |  |  | 0.025902 | 172.5646 | 0.206904 | 24779.02 | 24692.74 | 70.85231 | -30642.7 | -27397.9 | -69.1481 |  |
| 2 | \& for 1 ro | oot region | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! |  |

The outlet pressure is 0.05 MPa . Possible outlet states are shown below.

## Case (a)

|  | A | B | c | D | E | F | G | H | 1 | J | K | L |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Peng-Robinson Equation of State (Pure Fluid)Properties |  |  |  | Spreadsheet protected, but no password used. |  |  |  |  |  |  |  |
| 2 |  |  |  |  | Heat Capacity constants from Appendix |  |  |  | ideal gas values | $\begin{array}{\|c} H^{i g}-H_{R}^{i g} \\ J / \mathrm{mol} \end{array}$ | $\begin{gathered} U_{U^{i g}}-U_{R}^{i^{i g}} \\ \mathrm{~J} / \mathrm{mol} \\ \hline 18586.62 \end{gathered}$ | $S^{i g}-S_{R}^{i g}$ <br> $\mathrm{J} / \mathrm{molK}$ <br> 61.4649 |
| 3 | Gas | $\mathrm{T}_{\mathrm{c}}(\mathrm{K})$ | $\mathrm{P}_{\mathrm{c}}(\mathrm{MPa})$ | $\omega$ | A | B | C | D |  |  |  |  |
|  | n-HEPTANE | 540.3 | 2.736 | 0.349 | -5.146 | $6.76 \mathrm{E}-01$ | -3.65E-04 | 7.66E-08 |  |  |  |  |
| 6 | Current State |  | Roots |  | Stable Root has a lower fugacity |  |  |  |  |  |  |  |
| 7 | T (K) | 400.692 | Z | V | fugacity | H | U | S | H- $\mathrm{H}^{\text {ig }}$ | U-U'9 | S-S ${ }^{\text {S }}$ |  |
| 8 | $\mathrm{P}(\mathrm{MPa})$ | 0.05 |  | $\mathrm{cm}^{3} / \mathrm{gmol}$ | MPa | $\mathrm{J} / \mathrm{mol}$ | J/mol | J/molk | $\mathrm{J} / \mathrm{mol}$ | $\mathrm{J} / \mathrm{mol}$ | $\mathrm{J} /$ molk |  |
| 9 | answers for three root region |  | 0.9825588 | 65468.726 | $\begin{aligned} & 0.049141 \\ & 0.202371 \end{aligned}$ | 55266.16 44868.5 24779.12 | 51992.73 | 158.901 | -166.575 | -108.469 | -0.27165 |  |
|  |  |  | 0.0129263 | 861.28717 |  |  | 44825.43 | 114.363 | -10564.2 | -7275.76 | -44.8097 |  |
|  |  |  | 0.0025979 | 173.09938 |  |  | 24770.47 | 71.04668 | -30653.6 | -27330.7 | -88.126 |  |
|  | \& for 1 ro | oot region | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! |  |

Case (b)

|  | A | B | C | D | E | F | G | H | 1 | J | K | L |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Peng-Robinson Equation of State (Pure Fluid) <br> Properties |  |  |  | Spreadsheet protected, but no password used. |  |  |  |  |  |  |  |
| 2 |  |  |  |  | Heat Capacity constants from Appendix |  |  |  | ideal gas values | $\begin{array}{\|c\|} \hline \mathrm{H}^{\mathrm{ig}}-\mathrm{H}_{\mathrm{R}}^{\mathrm{ig}} \\ \mathrm{~J} / \mathrm{mol} \end{array}$ | $\begin{gathered} U^{\mathrm{ig}}-U_{R}^{\text {ig }} \\ \mathrm{J} / \mathrm{mol} \\ \hline 18528.06 \\ \hline \end{gathered}$ | $\mathrm{S}^{\text {ig }}-\mathrm{S}_{\mathrm{R}}{ }^{\text {ig }}$$\mathrm{J} / \mathrm{molK}$ |
| 3 | Gas | $\mathrm{T}_{\mathrm{c}}(\mathrm{K})$ | $\mathrm{P}_{\mathrm{c}}(\mathrm{MPa})$ | $\omega$ | A | B | C | D |  |  |  |  |
| 4 | n-HEPTANE | 540.3 | 2.736 | 0.349 | -5.146 | $6.76 \mathrm{E}-01$ | -3.65E-04 | 7.66E-08 |  |  |  | 61.31273 |
| 5 |  |  |  |  |  |  |  |  |  |  |  |  |
| 6 | Current State |  | Roots |  | Stable Root has a lower fugacity |  |  |  |  |  |  |  |
| 7 | T (K) | 400.404537 | Z |  | fugacity | H | U | S | $\mathrm{H}-\mathrm{H}^{\text {ig }}$ | U-U ${ }^{\text {ig }}$ | S-S ${ }^{\text {ig }}$ |  |
| 8 | P (MPa) | 0.05 |  | $\mathrm{cm}^{3} / \mathrm{gmol}$ | MPa | $\mathrm{J} / \mathrm{mol}$ | J/mol | J/molk | $\mathrm{J} / \mathrm{mol}$ | J/mol | J/molk |  |
| 9 | answers for three root region |  | 0.9825223 | 65419.331 | $\begin{array}{\|l\|} \hline 0.049139 \\ 0.201039 \\ \hline \end{array}$ | 55205.02 | 51934.05 | 158.7484 | -166.763 | -108.577 | -0.27212 |  |
| 10 |  |  | 0.012961 | 862.98393 |  | 44821 | 44777.85 | 114.2444 | -10550.8 | -7264.78 | -44.7761 |  |
| 11 |  |  | 0.0025982 | 172.99644 |  | 24701.26 | 24692.61 | 70.8523 | -30670.5 | -27350 | -88.1682 |  |
| 12 | \& for 1 root region |  | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! ${ }^{\text {² }}$ | \#NUM! | \#NUM! ${ }^{\text { }}$ | \#NUM! | \#NUM! |  |

Case (c)

|  | A | B | C | D | E | F | G | H | 1 | J | K | L |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Peng-Robinson Equation of State (Pure Fluid) <br> Properties |  |  |  | Spreadsheet protected, but no password used. |  |  |  |  |  |  |  |
|  |  |  |  |  | Heat Capacity constants from Appendix |  |  |  | ideal gas values | $\begin{array}{\|c} \hline H^{\mathrm{ig}}-\mathrm{H}_{\mathrm{R}}{ }^{\mathrm{ig}} \mathrm{~J} / \mathrm{mol} \\ \hline 9084.403 \\ \hline \end{array}$ | $\begin{gathered} U^{i g}-U_{R}^{i g} \\ \mathrm{~J} / \mathrm{mol} \\ \hline 8660.074 \end{gathered}$ | $\begin{gathered} \hline S^{i g}-S_{R}{ }^{\mathrm{ig}} \\ \mathrm{~J} / \mathrm{molK} \end{gathered}$ |
|  | Gas | $\mathrm{T}_{\mathrm{c}}(\mathrm{K})$ | $\mathrm{P}_{\mathrm{c}}$ (MPa) | $\omega$ | A | B | C | D |  |  |  |  |
|  | n-HEPTANE | 540.3 | 2.736 | 0.349 | -5.146 | $6.76 \mathrm{E}-01$ | -3.65E-04 | $7.66 \mathrm{E}-08$ |  |  |  | 33.83935 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | Current State |  | Roots |  | Stable Root has a lower fugacity |  |  |  |  |  |  |  |
|  | T (K) | 349.185 | Z | V | fugacity | H | U | S | $\mathrm{H}-\mathrm{H}^{\mathrm{ig}}$ | U-U ${ }^{\text {ig }}$ | S-S ${ }^{\text {ig }}$ |  |
|  | $\mathrm{P}(\mathrm{MPa})$ | 0.05 |  | $\mathrm{cm}^{3} / \mathrm{gmol}$ | MPa | $\mathrm{J} / \mathrm{mol}$ | $\mathrm{J} / \mathrm{mol}$ | J/molk | $\mathrm{J} / \mathrm{mol}$ | $\mathrm{J} / \mathrm{mol}$ | J/molK |  |
|  | answers for three root region |  | 0.9741548 | 56565.057 | $\begin{array}{\|l\|} \hline 0.048738 \\ 0.048737 \\ \hline \end{array}$ | 44871.76 | 42043.51 | 131.1693 | -206.175 | -131.139 | -0.37784 |  |
|  |  |  | 0.0209134 | 1214.3522 |  | 36661.96 | 36601.24 | 92.46168 | -8415.97 | -5573.4 | -39.0854 |  |
|  |  |  | 0.002732 | 158.63335 |  | 11613.56 | 11605.63 | 35.92421 | -33464.4 | -30569 | -95.6229 |  |
| 2 | \& for 1 ro | oot region | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! | \#NUM! |  |

(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.

$\qquad$

## 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)

1. (5) The system (A) $+(\mathrm{B})$ where $P_{B}{ }^{\text {sat }}>P_{A}{ }^{\text {sat }}$ 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 $10 \mathrm{~mol} \%$ (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?
$\qquad$
2. We wish to use PreosProps.m to generate a n-pentane isotherm for a P-V chart at 375 K between 0.1 MPa and 6 MPa . For n-pentane, $\mathrm{Tc}=469.7 \mathrm{~K}, \mathrm{Pc}=3.369, \omega=$ 0.249 .

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

(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.
$\qquad$

Michigan State University
DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE
ChE321: Thermodynamics for Chemical Engineers
Spring 2015
Exam 2A: April 08, 2015, Equation Sheet Provided (85 minutes)
ANTOINE CONSTANTS for $\log _{10}\left(\mathrm{P}^{\text {sat }}(\mathrm{mmHg})\right)=\mathrm{A}-\mathrm{B} /(\mathrm{T}($ Celsuis $)+\mathrm{C})$.

|  | Component (1) | Component (2) |
| :--- | :--- | :--- |
| A | 7.2813 | 7.3205 |
| B | 1434.2 | 1465.2 |
| C | 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): $\mathrm{x}_{1}=0.65, \mathrm{y}_{1}=0.586, \mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)=70, \mathrm{P}=842 \mathrm{mmHg}$.
(a) (10) Fit the two-parameter Margules equation to the data.
(b) (10) Using the two-parameter Margules equation, predict the bubble pressure and $\mathrm{y}_{1}$ at $70^{\circ} \mathrm{C}$ for a mixture where $\mathrm{x}_{1}=0.3$. 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.

Name $\qquad$
(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 <br> Invalid |
| :---: | :---: | :--- |
| $d U=T d S-P d V$ | $\left(\frac{\partial U}{\partial T}\right)_{P}=C_{P}-P\left(\frac{\partial V}{\partial P}\right)_{T}\left(\frac{\partial P}{\partial T}\right)_{V}$ |  |
| $\left(\frac{\partial V}{\partial T}\right)_{S}$ | $-\frac{C_{V}}{T}\left(\frac{\partial P}{\partial T}\right)_{V}$ |  |

Scratch area:

Name $\qquad$
5. (10) A mixture of (1) + (2) follow Raoult's law. At $80^{\circ} \mathrm{C}$, the vapor pressures are $P_{1}{ }^{\text {sat }}$ $=1030 \mathrm{mmHg}$ and $P_{2}{ }^{\text {sat }}=620 \mathrm{mmHg}$. The mixture forms $V+L$ phases at an overall composition of $40 \mathrm{~mol} \%$ 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 $i=f i r s t v a l u e: l a s t v a l u e ; ~$ 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 $P V=R T-\left(\frac{a}{T}\right) P+b P$, where $a=385.2$ $\mathrm{cm}^{3}-\mathrm{K} / \mathrm{mol}$ and $b=15.23 \mathrm{~cm}^{3} / \mathrm{mol}$. Derive the formula for the enthalpy departure of a fluid that follows this equation of state. Possibly useful: $\int(1 / x) d x=\ln x$;

$$
\begin{aligned}
& \int(1 /(a x+b)) d x=(1 / a) \ln (a x+b) ; \int(x /(a x+b)) d x=x / a- \\
& \left(b / a^{\wedge} 2\right) \ln (a x+b) ; \int\left(1 /(a x+b)^{2}\right) d x=-1 /(a(a x+b))
\end{aligned}
$$

7. (10) Ideal gas state changes are given by $\Delta H^{i g}=\int C_{P} d T, \Delta U^{i g}=\int C_{V} d T, \Delta S^{i g}=$ $C_{P} \ln \frac{T_{2}}{T_{1}}-R \ln \frac{P_{2}}{P_{1}}$. For a fluid in at $\mathrm{P}_{1}=1 \mathrm{MPa}, \mathrm{T}_{1}=380 \mathrm{~K}$, the enthalpy departure is $-432 \mathrm{~J} / \mathrm{mol}$ and $\mathrm{Z}=0.75$. At $\mathrm{P}_{2}=0.15 \mathrm{MPa}, \mathrm{T}_{2}=400 \mathrm{~K}$, the enthalpy departure is $-120 \mathrm{~J} / \mathrm{mol}$ and $\mathrm{Z}=0.85$. For the fluid, $\mathrm{Cp}=77 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$ and can be considered temperature independent. Determine $\Delta H$ and $\Delta U$ in $\mathrm{J} / \mathrm{mol}$.
$\qquad$

Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers
Spring 2014
Exam 2: April 02, 2014, Closed Book Portion (35 minutes)
Note: 1 bar $=0.1 \mathrm{MPa}=750 \mathrm{mmHg} ; 1 \mathrm{~atm}=760 \mathrm{mmHg} . R=8.314 \mathrm{~cm}^{3} \mathrm{MPa} / \mathrm{mol}-\mathrm{K}$

1. (5) The system (A) $+(\mathrm{B})$ where $P_{A}{ }^{\text {sat }}>P_{B}{ }^{\text {sat }}$ 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) $d U=T d S-P d V ; H=U+P V ; G=H-T S$. Derive the relation for $d G$.
(5) (c) Describe what is meant by the 'combinatorial term' and the 'residual term' in UNIQUAC and UNIFAC.
$\qquad$
2. We wish to use PreosProps.m to generate an isobutane isotherm for a P-H chart at 280 K 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, $\mathrm{Tc}=408.1 \mathrm{~K}, \mathrm{Pc}=3.648, \omega=0.177$.

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

(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.
$\qquad$

Michigan State University
DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE
ChE321: Thermodynamics for Chemical Engineers
Spring 2014
Exam 2: April 02, 2014, Open Notes Portion (85 minutes)
ANTOINE CONSTANTS for $\log _{10}\left(\mathrm{P}^{\text {sat }}(\mathrm{mmHg})\right)=\mathrm{A}-\mathrm{B} /(\mathrm{T}($ Celsuis $)+\mathrm{C})$.

|  | Component $(1)$ | Component $(2)$ |
| :--- | :--- | :--- |
| A | 7.2807 | 7.8103 |
| B | 1434.2 | 1420 |
| C | 246.5 | 191.15 |

NOTE: the same T of $80^{\circ} \mathrm{C}$ is used throughout to minimize calculations.
3. Suppose component (1) and component (2) follow Raoult's Law. The temperature is $80^{\circ} \mathrm{C}$.
a. (10) What is the dew pressure ( mmHg ) and liquid composition when $\mathrm{y} 1=0.6$ ? What is x 1 at the dew point?
b. (10) At $80^{\circ} \mathrm{C}$ a mixture $F$ that is $48 \mathrm{~mol} \%$ component (1) is fed to a flash drum at 541.7 mmHg . The vapor composition is $\mathrm{y} 1=0.60$ and the liquid is $\mathrm{x} 1=0.42$.

What is the ratio of moles of vapor to moles of feed, $V / F$ ?
$\qquad$
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): $\mathrm{x}_{1}=0.30, \mathrm{y}_{1}=0.567, \mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)=80, \mathrm{P}=694.3$ 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 y 1 at $80^{\circ} \mathrm{C}$ for a mixture where $\mathrm{x}_{1}=0.6$. 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.
$\qquad$
5. The virial equation can be written, $Z=1+B P /(R T)$
(a) (10) For methane, $T_{c}=190.6 \mathrm{~K}, P_{c}=4.604, \omega=0.011$. What value is predicted for the virial coefficient at 120 K 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 $-100 \mathrm{~cm}^{3} / \mathrm{mol}$. 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 $a=187$ $\mathrm{cm}^{3} / \mathrm{mol}$. Derive the formula for the fugacity of a fluid that follows this equation of state. Possibly useful: $\int(1 \backslash x) d x=\ln x ; \int(1 /(a x+b)) d x=(1 / a) \ln (a x+b)$ $; \int(x /(a x+b)) d x=x / a-\left(b / a^{\wedge} 2\right) \ln (a x+b)$
$\qquad$

Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers
Exam 2: April 03, 2013, Closed Book Portion (40 minutes)
Note: 1 bar $=0.1 \mathrm{MPa}=750 \mathrm{mmHg} ; 1 \mathrm{~atm}=760 \mathrm{mmHg} . R=8.314 \mathrm{~cm}^{3} \mathrm{MPa} / \mathrm{mol}-\mathrm{K}$

1. (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 $P_{A}{ }^{\text {sat }}>P_{B}{ }^{\text {sat }}$. 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 $\mathrm{x}_{\mathrm{A}}$ (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.

$\qquad$
2. (10) The van der Waals equation is $Z=1 /(1-b \rho)-a \rho / R T$. The parameters are made dimensionless using $A=a P /(R T)^{2}$ and $B=b P / R T$. Rearrange the equation in the form $Z^{3}+a_{2} Z^{2}+a_{1} Z+a_{0}=0$, 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 .


Below are several possible outlet states. Calculate the work done by the expander $(\mathrm{J} / \mathrm{mol})$ 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.

Name $\qquad$

State 2a
$\left[\begin{array}{llll|}\text { Results } \\ \text { ETHANE } & & \\ \mathrm{T}(\mathrm{K}) & 239.669 & \mathrm{P}(\mathrm{MPa}) & 0.1 \\ \mathrm{Z} & 0.984784 & 0.00307039 \\ \mathrm{~V}\left(\mathrm{~cm}^{\wedge} 3 / \mathrm{mol}\right) & 19623.6 & 61.183 \\ \mathrm{U}(\mathrm{J} / \mathrm{mol}) & -4816.63 & -15636.1 \\ \mathrm{H}(\mathrm{J} / \mathrm{mol}) & -2854.24 & -15630 \\ \mathrm{~S}(\mathrm{~J} / \mathrm{mol}-\mathrm{K}) & -10.6238 & -81.3575 \\ \text { fugacity }(\mathrm{MPa}) & 0.0984977 & 0.801195 \\ \text { User Objecive } & 2.84217 \mathrm{e}-14 \\ & \\ & \\ \end{array}\right.$

State 2c
$\left[\begin{array}{llll|}\text { Results } \\ \text { ETHANE } & & \\ \mathrm{T}(\mathrm{K}) \quad 166.694 & \mathrm{P}(\mathrm{MPa}) & 0.1 \\ \mathrm{Z} & 0.960993 & 0.0035214 \\ \mathrm{~V}\left(\mathrm{~cm}^{\wedge} 3 / \mathrm{mol}\right) & 13318.8 & 48.8047 \\ \mathrm{U}(\mathrm{J} / \mathrm{mol}) & -7068.3 & -20896.9 \\ \mathrm{H}(\mathrm{J} / \mathrm{mol}) & -5736.39 & -20892 \\ \mathrm{~S}(\mathrm{~J} / \mathrm{mol}-\mathrm{K}) & -24.8503 & -107.257 \\ \text { fugacity }(\mathrm{MPa}) & 0.0962368 & 0.0345727 \\ \text { User Objecive } & -7.10543 \mathrm{e}-15 \\ & \\ & \\ \end{array}\right.$

State 2b

| - Results $\qquad$ ETHANE |  |  |
| :---: | :---: | :---: |
|  |  |  |
| T(K) | 184.206 | $\mathrm{P}(\mathrm{MPa}) \quad 0.1$ |
| Z |  | 0.9697660 .00331068 |
| $V\left(\mathrm{~cm}^{\wedge} 3 / \mathrm{mol}\right)$ |  | 14852.450 .7045 |
| $\mathrm{U}(\mathrm{J} / \mathrm{mol})$ |  | -6599.28-19792.4 |
| H (J/mol) |  | -5114.01-19787.3 |
| S ( $\mathrm{J} / \mathrm{mol}-\mathrm{K}$ ) |  | -21.3021-100.959 |
| fugacity ( MPa ) |  | 0.0970580 .097058 |
| User Objecive |  | $4.44089 \mathrm{e}-16$ |

State 2d

$\qquad$

Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers
Spring 2013
Exam 2: April 03, 2013, Open Notes Portion (80 minutes)
Note: 1 bar $=0.1 \mathrm{MPa}=750 \mathrm{mmHg} ; 1 \mathrm{~atm}=760 \mathrm{mmHg} . R=8.314 \mathrm{~cm}^{3} \mathrm{MPa} / \mathrm{mol}-\mathrm{K}$
4. The following data are available from an experiment with the system n-pentane(1) + acetone(2): $\mathrm{x}_{1}=0.292, \mathrm{y}_{1}=0.614, \mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)=34.35, \mathrm{P}=750 \mathrm{mmHg}$.

ANTOINE CONSTANTS for
$\log _{10}\left(P^{\text {sat }}(\mathrm{mmHg})\right)=A-B /\left(T\left({ }^{\circ} \mathrm{C}\right)+C\right)$

|  | n-pentane | acetone |
| :--- | :--- | :--- |
| $A$ | 6.85296 | 7.11714 |
| $B$ | 1064.84 | 1210.6 |
| $C$ | 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 $34.35^{\circ} \mathrm{C}$ for a mixture where $x_{1}=0.01$.
$\qquad$
(c) (15) Based on the parameters fitted above, provide Matlab code to solve for the bubble temperature of a binary mixture with overall composition $\mathrm{z}_{1}=0.8$ 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 $i=f i r s t v a l u e: l a s t v a l u e ; ~ s y n t a x ~ f o r ~ f z e r o: ~$ [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, ( $T_{c}=512.6 \mathrm{~K}, P_{c}=8.096 \mathrm{MPa}, \omega=0.566$ ). 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.

$\qquad$
6. A fluid is described by the following equation of state:

$$
Z=1+a \rho /(1-a \rho)
$$

where $a=-207 \mathrm{~cm}^{3} / \mathrm{mol}$, and the ideal gas heat capacity is $\mathrm{Cp}=65.3 \mathrm{~J} / \mathrm{molK}$.
(a) (10) Determine the fully integrated entropy departure function in terms of $a, T, \mathrm{Z}$ and $\rho$. Hints: $\int(1 \backslash x) d x=\ln x ; \int(1 /(a x+b)) d x=(1 / a) \ln (a x+b)$ $; \int(x /(a x+b)) d x=x / a-\left(b / a^{\wedge} 2\right) \ln (a x+b)$
(b) (5) At a pressure of 4 MPa and 400 K , what is the molar volume $\left(\mathrm{cm}^{3} / \mathrm{mol}\right)$ ?

Name $\qquad$

Michigan State University
DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE
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 $Z=1 /(1-b \rho)-a \rho / R T$. The parameters are made dimensionless using $A=a P /(R T)^{2}$ and $B=b P / R T$. Rearrange the equation in the form $Z^{3}+a_{2} Z^{2}+a_{1} Z+a_{0}=0$, where $a_{2}, a_{1}$, and $a_{0}$ are functions of $A$ and $B$.
$\qquad$
3. A P-x-y diagram is shown below for the system $A+B$ at $T=85^{\circ} \mathrm{C}$. From the diagram, mark the answers to the following questions, label them as '(a)', ' (b)', etc., and provide numerical values.

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

Michigan State University
DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers
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), $T=333.15, P=45.66 \mathrm{kPa}, \mathrm{x}_{1}=0.4, \mathrm{y}_{1}=0.827$. Pure component vapor pressures are $\mathrm{P}_{1}{ }^{\text {sat }}=82.66 \mathrm{kPa}, \mathrm{P}_{2}{ }^{\text {sat }}=12.8 \mathrm{kPa}$ at 333.15 K . Fit the two parameter Margules equation.
$\qquad$
(15) Based on the parameters fitted above, provide Matlab code to solve for the dew pressure of a binary mixture with overall composition $\mathrm{z}_{1}=0.8$ at 333.15 K . 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)).
$\qquad$
5. A fluid is described by the following equation of state:

$$
Z=1+(a+b / T) \rho
$$

where $\mathrm{a}=500 \mathrm{~cm}^{3} / \mathrm{mol}, \mathrm{b}=-4.8 \mathrm{E} 5 \mathrm{~cm}^{3} \mathrm{~K} / \mathrm{mol}$ and the ideal gas heat capacity is $\mathrm{Cp}=$ $79.3 \mathrm{~J} / \mathrm{molK}$.
(a) (10) Determine the internal energy departure function in terms of $a, b, T, \mathrm{Z}$ and $\rho$.
(b) (5) At a density of $2 \mathrm{E}-4 \mathrm{~mol} / \mathrm{cm}^{3}$ and 500 K , 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 $\mathrm{K}_{1}$ 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 $\mathrm{A}_{12}=$ 0.9 and $\mathrm{A}_{21}=3.3$. Is the plot consistent with these values? Explain using calculations.

## Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

ChE321: Thermodynamics for Chemical Engineers
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 $35^{\circ} \mathrm{C}$ and 103.1 mmHg (the vapor pressure) and a liquid molecule at $35^{\circ} \mathrm{C}$ 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. ${ }^{1}$

| $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)$ |  | $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0. | 0. | $82.4^{\mathrm{a}}$ |  | 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 | $76.7^{\mathrm{a}}$ |

a. (5) Does an azeotrope exist? If an azeotrope exists, between which two of the $\mathrm{x}_{1}$ 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 $x_{1}$ $\mathrm{y}_{1}$ diagram would look like for this system.

[^0]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 $\log _{10} \mathrm{P}(\mathrm{mmHg})=\mathrm{A}-\mathrm{B} /(\mathrm{T}+\mathrm{C})$. 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, ...)'

|  | A | B | C |
| :--- | :--- | :--- | :--- |
| 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 $\mathrm{P}=$ 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).

## Michigan State University

## DEPARTMENT OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

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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. ${ }^{2}$

| $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)$ |  | $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0. | 0. | $83.55^{\mathrm{a}}$ |  | 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 | $76.65^{\mathrm{a}}$ |

.(a) (10) Using only the data at $\mathrm{x}_{1}=0.37$, fit the van Laar equation. The vapor pressures at $76.62{ }^{\circ} \mathrm{C}$ are $\mathrm{P}_{1}{ }^{\text {sat }}=757.5 \mathrm{mmHg}$ and $\mathrm{P}_{2}{ }^{\text {sat }}=601.6 \mathrm{mmHg}$.

[^1](b) (10) Using the parameters fitted in part (a), set forth the procedure to determine bubble pressure for a mixture of $60 \mathrm{~mol} \%$ carbon tetrachloride at $80^{\circ} \mathrm{C}$ where the vapor pressures are $\mathrm{P}_{1}{ }^{\text {sat }}=838.6 \mathrm{mmHg}, \mathrm{P}_{2}{ }^{\text {sat }}=672.1 \mathrm{mmHg}$. Avoid unecessary 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 $70^{\circ} \mathrm{C}$ is 0.261 MPa , where $\mathrm{V}^{\text {satL }}=121$ $\mathrm{cm}^{3} / \mathrm{mol}, \mathrm{V}^{\text {satV }}=9974 \mathrm{~cm}^{3} / \mathrm{mol}$. Calculate the fugacity of n-pentane at $70^{\circ} \mathrm{C}$ 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 $\mathrm{mol} / \mathrm{h}$ 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 $Z=1+a P / R T$, where $a=-254 \mathrm{~cm}^{3} / \mathrm{mol}$, and $C_{P}=56 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$.
(a) (10) When the pressure is 5 MPa , what is the molar volume at 320 K ?
(b) (10) Evaluate the enthalpy departure for the fluid in terms of the EOS variables.


[^0]:    ${ }^{1}$ 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.

[^1]:    ${ }^{2}$ 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.

