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DR S BABAE

INTERNAL MODERATOR(S): DR WM NELSON

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INSTRUCTIONS:

1. **ALL** questions should be attempted. *Answer in ink.*

2. Two books are provided: Book 1 and Book 2. Answer Section A in Book 1 (PN) and Section B in Book 2 (SB).

3. Any programmable or non-programmable calculator may be used provided it has been cleared of any information that would subvert the purpose of the examination.

4. Calculations must be shown in sufficient detail to illustrate your understanding of the procedure.

5. State all assumptions clearly.
SECTION A [BOOK 1 – PN]

QUESTION 1

Chen et al. [1] reported the results of their predictive model (Low Pressure Mixing Rule – LPMR) using a new excess free energy mixing rule coupled with the original UNIFAC method and the Soave-Redlich Kwong (SRK) Equation of State (EoS), against other EoS/G^B predictive models. These include the following thermodynamic model combinations:

- Predictive Soave-Redlich Kwong (PSRK)
- Chen-modified Predictive Soave-Redlich Kwong (MPSRK)
- Volume-translated Peng Robinson group contribution (VTPR)
- Linear Combination of the Vidal and Michelsen rules (LCVM)

1.1 Discuss the approach used in the UNIFAC method.

1.2 Explain what is a “symmetric” and an “asymmetric” system?

1.3 Consider Figures 1 and 2 provided on PAGE 3. Describe the phase behaviour for the systems, \{ethanol + water\}, and \{ethane + 1-decanol\} at the conditions provided.

*Note. An interpretation of the phase equilibrium data is necessary and not just a comparison of the various models.*

1.4 Consider Table 1 provided on PAGE 4 and the model fits presented in Figures 1 & 2. With respect to ALL of the models presented, discuss the results for the two systems, \{ethanol + water\}, and \{ethane + 1-decanol\}. Comment on the suitability of the different model/s, especially whether the LPMR model is an acceptable predictive method for these systems.


QUESTION 1 cont. on next page...
QUESTION 1 cont.

1.5 Define the fugacity coefficient, $\phi_1$.

1.6 For the ethane (1) + 1-decanol (2) system at 448.2 K, given the data in Tables 2-3 on Page 5, at $T = 448.2$ $K$ and vapour mole fraction of ethane of 0.9801, use the Peng-Robinson equation of state with the van der Waals mixing rule, to calculate, $\phi_2$.

DATA

ALL THE NECESSARY DATA FOR QUESTION 1 IS PROVIDED ON PAGES 3-5.
FIGURE 1. Vapour-Liquid equilibrium results for the ethanol + water system. Experimental data from reference 2.

FIGURE 2. Vapour-Liquid equilibrium results for the ethane + 1-decanol system. Experimental data from reference 3.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature range (K)</th>
<th>Pressure range (bar)</th>
<th>NP</th>
<th>PSRK</th>
<th>MPSRK</th>
<th>VTPR</th>
<th>LCVM</th>
<th>this work</th>
<th>PSRK</th>
<th>MPSRK</th>
<th>VTPR</th>
<th>LCVM</th>
<th>this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol/water</td>
<td>293.2−442.2</td>
<td>1.1−30.93</td>
<td>25</td>
<td>3.2</td>
<td>15.1</td>
<td>10.2</td>
<td>3.8</td>
<td>4.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethanol/water</td>
<td>423.2−523.2</td>
<td>5.6−189.7</td>
<td>77</td>
<td>2.1</td>
<td>8.3</td>
<td>7.9</td>
<td>1.4</td>
<td>4.4</td>
<td>0.8</td>
<td>4.5</td>
<td>6.4</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>2-propanol/water</td>
<td>423.2−549.2</td>
<td>5.2−93.4</td>
<td>66</td>
<td>2.2</td>
<td>12.6</td>
<td>7.0</td>
<td>3.3</td>
<td>7.5</td>
<td>1.1</td>
<td>8.3</td>
<td>9.0</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>propane/ethanol</td>
<td>313.6−449.8</td>
<td>3.2−238.3</td>
<td>22</td>
<td>9.4</td>
<td>12.1</td>
<td>7.2</td>
<td>7.2</td>
<td>5.9</td>
<td>0.6</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>ethane/1-decanol</td>
<td>418.2</td>
<td>5.8−143.2</td>
<td>14</td>
<td>8.0</td>
<td>9.4</td>
<td>9.1</td>
<td>26.6</td>
<td>4.6</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>n-pentane/acetone</td>
<td>373.2−449.8</td>
<td>4.7−179.9</td>
<td>27</td>
<td>1.1</td>
<td>1.8</td>
<td>4.0</td>
<td>1.6</td>
<td>3.3</td>
<td>0.9</td>
<td>1.0</td>
<td>1.9</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>dimethyl ether/ethanol</td>
<td>352.2−373.6</td>
<td>1.9−31.66</td>
<td>43</td>
<td>9.8</td>
<td>9.8</td>
<td>9.3</td>
<td>8.1</td>
<td>11.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>dimethyl ether/2-propanol</td>
<td>323.2−373.7</td>
<td>1.29−26.21</td>
<td>29</td>
<td>11.1</td>
<td>12.4</td>
<td>11.7</td>
<td>9.6</td>
<td>13.2</td>
<td>1.4</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(\Delta P (\%) = (\frac{1}{NP}) \sum \Delta P_j \times 100\)  
\(\Delta V = (\frac{1}{NP}) \sum \Delta V_j \times 100\)
TABLE 2. Experimental Pxy data for the ethane and 1-decanol system at 448.2 K [4]

<table>
<thead>
<tr>
<th>Liquid mole fraction ETHANE</th>
<th>Vapor mole fraction ETHANE</th>
<th>Total pressure bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0275</td>
<td>0.96483</td>
<td>5.38</td>
</tr>
<tr>
<td>0.0406</td>
<td>0.97584</td>
<td>8.10</td>
</tr>
<tr>
<td>0.0803</td>
<td>0.98671</td>
<td>16.58</td>
</tr>
<tr>
<td>0.1166</td>
<td>0.99023</td>
<td>25.06</td>
</tr>
<tr>
<td>0.166</td>
<td>0.99173</td>
<td>35.89</td>
</tr>
<tr>
<td>0.2185</td>
<td>0.99216</td>
<td>48.44</td>
</tr>
<tr>
<td>0.2731</td>
<td>0.9923</td>
<td>62.84</td>
</tr>
<tr>
<td>0.3077</td>
<td>0.99081</td>
<td>75.65</td>
</tr>
<tr>
<td>0.3595</td>
<td>0.98892</td>
<td>90.56</td>
</tr>
<tr>
<td>0.3828</td>
<td>0.98908</td>
<td>95.56</td>
</tr>
<tr>
<td>0.3992</td>
<td>0.98816</td>
<td>102.5</td>
</tr>
<tr>
<td>0.4615</td>
<td>0.98584</td>
<td>117.00</td>
</tr>
<tr>
<td>0.4963</td>
<td>0.98267</td>
<td>130.50</td>
</tr>
<tr>
<td>0.535</td>
<td>0.98013</td>
<td>143.20</td>
</tr>
</tbody>
</table>


TABLE 3. Physical properties and parameters (PREOS) for ethane and 1-decanol

<table>
<thead>
<tr>
<th>Formulae</th>
<th>ethane</th>
<th>1-decanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (g/mol)</td>
<td>C₂H₆</td>
<td>C₁₀H₂₂O</td>
</tr>
<tr>
<td>Tc (K)</td>
<td>30.07</td>
<td>158.28</td>
</tr>
<tr>
<td>Pc (bar)</td>
<td>184.55</td>
<td>687.3</td>
</tr>
<tr>
<td>Vc (m³/mol)</td>
<td>48.72</td>
<td>23.15</td>
</tr>
<tr>
<td>Zc</td>
<td>145.5</td>
<td>649</td>
</tr>
<tr>
<td>θ</td>
<td>0.279</td>
<td>0.263</td>
</tr>
<tr>
<td>y (vapour mole fraction)</td>
<td>0.100</td>
<td>0.622</td>
</tr>
<tr>
<td>k</td>
<td>0.98013</td>
<td>0.01987</td>
</tr>
<tr>
<td>α(Tc)</td>
<td>0.5262</td>
<td>1.2439</td>
</tr>
<tr>
<td>a(Tc)</td>
<td>0.4987</td>
<td>5.0353</td>
</tr>
<tr>
<td>a₁ (bar.cm⁶/mol²)</td>
<td>2209430.408</td>
<td>64491310.15</td>
</tr>
<tr>
<td>b₁ (cm³/mol)</td>
<td>1101840.577</td>
<td>324732525.2</td>
</tr>
<tr>
<td>kₘ</td>
<td>24.5</td>
<td>192.0</td>
</tr>
<tr>
<td>kₘ</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
QUESTION 2

a) Consider a binary liquid mixture of hexane (1) and acetone (2). At 15°C and 300 bar, this mixture forms two partially miscible liquid phases. Phase α has 20 total moles with \( x_1^α = 0.2 \), while phase β has 10 total moles with \( x_1^β = 0.8 \).

The following data are available at 15°C:

<table>
<thead>
<tr>
<th>Species</th>
<th>( M_w ) [g/mol]</th>
<th>( \nu \left[ cm^3/mol \right] )</th>
<th>( P_0^{sat} ) [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>86</td>
<td>130.5</td>
<td>12.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>58</td>
<td>73.4</td>
<td>19.5</td>
</tr>
</tbody>
</table>

i. Draw a schematic of the system, labelling it with all the information that you have. Make your schematic as accurate as possible; for example, consider which phase α or β is at the top. [3]

ii. Are the like interactions stronger or weaker than the unlike interactions? Explain. [2]

iii. Calculate the value of \( f_1 \). [2]

iv. Using the two-suffix Margules equation to describe this system, determine the \( A \) parameter for the two-suffix Margules model.

\[ (G^E = Ax_1x_2) \] [3]

QUESTION 2 continued on next page.
QUESTION 2 cont.

v. Estimate at what temperature would you need to heat the system described in (a) to make it completely miscible.

*State the assumptions made.*

[2]

b) A binary mixture of solids, \( a \) and \( b \), is known to form three distinct solid phases: \( \alpha \), \( \beta \), and \( \gamma \). The Gibbs energy vs. mole fraction \( a \), is plotted at constant temperature and pressure in the diagram below.

Describe the phases that are present and their composition for the entire range of mole fraction \( a \). Explain.

[3]

TOTAL /15/
QUESTION 3

Consider the following reaction:

\[ A(g) + 2B(g) \rightarrow 2C(g) \]

...R1

with a stoichiometric feed of \( A \) and \( B \). At 200°C and 1 bar, 25 mol% of the species in the reactor is the product \( C \). At 300°C and 1 bar, 53.9 mol% \( C \) is produced.

3.1 Using a basis of one mole of \( A \) and 2 moles of \( B \) reacting at 250°C and 2 bar, estimate the equilibrium compositions. State any assumptions.

[14]

3.2 As a process engineer, you wish to maximize the production of \( C \). Discuss the implications of the following strategies:

i. Increasing the temperature.

ii. Increasing the pressure.

iii. Addition of an inert to the feed stream.

[6]

State ALL assumptions and show all working.

TOTAL /20/
FORMULAE SHEET

Universal Gas Constant
R = 8.314 J mol⁻¹ K⁻¹
8.314 Pa m³ mol⁻¹ K⁻¹
8.206 x 10⁻² L atm mol⁻¹ K⁻¹
8.314 Pa m³ mol⁻¹ K⁻¹
8.314 cm³ bar mol⁻¹ K⁻¹
8.314 cm³ bar mol⁻¹ K⁻¹
8.206 cm³ atm mol⁻¹ K⁻¹
1.987 cal mol⁻¹ K⁻¹

Equations of State
Virial: Z = 1 + B/V + C/V² + ...
Van der Waals: P = RT/(V – b) – a/V²
Peng-Robinson:
\[ P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \]

Pitzer correlation:
\[ B^0 = 0.083 - \frac{0.422}{T_R^{1.6}} \]
\[ B^1 = 0.139 - \frac{0.172}{T_R^{4.2}} \]
\[ \frac{B_P}{RT_c} = B^0 + \omega B^1 \]

Rackett equation:
\[ V_{sat} = V_c Z_c (1 - T_f)^{0.2857} \]

Using the two term virial expansion in P:
\[ \ln \frac{f_i}{f_i^{sat}} = \frac{V_i^L (P - P_i^{sat})}{RT} \]
\[ \ln \phi_i = \frac{B_i^0 P}{RT} \]

For a binary system:
\[ P_1 = \exp \frac{B_{11} (P - P_1^{sat}) + p y_2^2 \delta_{12}}{RT} \]
\[ P_2 = \exp \frac{B_{22} (P - P_2^{sat}) + p y_1^2 \delta_{12}}{RT} \]
Equations for calculations from SVA:

\[ \theta_i = \theta(T, P, y_1, y_2, \ldots, y_{N-1}) \]
\[ \gamma_i = \gamma(T, P, x_1, x_2, \ldots, x_{N-1}) \]
\[ p_i^{\text{sat}} = f(T) \]

\[ y_i = \frac{x_i y_i p_i^{\text{sat}}}{x_i p_i^{\text{sat}}} \quad (14.8) \]
\[ x_i = \frac{y_i \theta_i}{y_i p_i^{\text{sat}}} \quad (14.9) \]

\[ \Sigma_i y_i = 1; \Sigma_i x_i = 1 \]

\[ p = \Sigma_i \frac{x_i y_i p_i^{\text{sat}}}{x_i} \quad (14.10) \]
\[ p = \Sigma_i \frac{1}{y_i \theta_i / y_i p_i^{\text{sat}}} \quad (14.11) \]

\[ T_i^{\text{sat}} = \frac{B_i}{A_i - \ln p_i} - C_i \quad (14.12) \]

\[ p_j^{\text{sat}} = \frac{p}{\Sigma_i (x_i y_i p_i^{\text{sat}} / p_i^{\text{sat}})} \quad (14.13) \]
\[ p_j^{\text{sat}} = p \Sigma_i (\frac{y_i \theta_i}{y_i})(p_j^{\text{sat}} / p_i^{\text{sat}}) \quad (14.14) \]

\[ T = \frac{B_j}{A_j - \ln p_j^{\text{sat}}} - C_j \quad (14.15) \]

\[ K = \exp \left( -\frac{\Delta G^0}{RT} \right) \]

\[ \ln \frac{K}{K'} = -\frac{\Delta H}{R} \left[ \frac{1}{T} - \frac{1}{T'} \right] \]
FOR THE PR EOS:

\[ a(T) = a(T_C) \alpha(T) \; ; \; a(T_C) = 0.457235 \frac{(RT_C)^2}{P_C} \; ; \; \alpha(T_C) = \left[ 1 + \alpha \left( 1 - \sqrt{\frac{T}{T_C}} \right) \right]^2 \]

\[ b = 0.077796 \frac{RT}{P_C} \]

\[ k = 0.378893 + 1.4897153\omega - 0.1713848\omega^2 + 0.0196554\omega^3 \]

mixing rules:

\[ a = \sum_i \sum_j z_i z_j a_{ij} \]

\[ a_{ij} = \sqrt{a_i a_j (1 - k_{ij})} \]

\[ b = \sum_i z_i b_i \]

With

\[ A_m \equiv \frac{aP}{(RT)^2} \]

\[ B_m \equiv \frac{bP}{RT} \]

PREOS is re-written in terms of the compressibility factor as

\[ Z^2 - (1 - B_m)Z + Z(A_m - 3B_m - 2B_m^2) - (A_mB_m - B_m^2 - B_m^3) = 0 \]

\[ RT\ln \left( \frac{f_i}{y_i P} \right) = RT\ln(\phi_i) = \int_{\omega}^{V} \left[ \frac{RT}{V} - \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} \right] dV - RT\ln(Z) \]

\[ \ln \phi_i = \frac{b_i}{b_m} (Z - 1) - \ln(Z - B_m) - \frac{A_m}{2\sqrt{2}B_m} \left[ \sum_{j=1}^{i-1} \frac{z_j a_{ij}}{a_m} - \frac{b_j}{b_m} \right] \ln \left( \frac{Z + (1 + \sqrt{2})B_m}{Z (1 + \sqrt{2})B_m} \right) \]