UNIVERSITY OF
KWAZULU-NATAL
INYUVESI
YAKWAZULU-NATALI

SCHOOL OF ENGINEERING

MAIN EXAMINATIONS: JUNE 2019

COURSE AND CODE: THERMODYNAMICS 2 ENCH3TH

DURATION: 2 HOURS

TOTAL MARKS: 65

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INTERNAL MODERATOR(S): DR W. M. NELSON

EXTERNAL MODERATOR: DR A. T. KANIKI

INSTRUCTIONS:

1. **ALL** questions should be attempted. **Answer in ink.**
2. Answer ALL questions in the ONE BOOK provided.
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.

QUESTION 1

i) Perform a dew pressure calculation given the information for the binary system consisting of *n-pentanol and n-hexane, at a system temperature of 30 °C*. You need to only perform the calculation once, no iteration is required. State ALL assumptions.

(20)

ii) Considering the intermolecular forces between the system components, comment on the shape of the phase envelope and the system behavior.

(5)

TABLE 1: Data for the binary system.

	Component 1	Component 2
Chemicals	n-pentanol	n-hexane
vapour mole fraction, y_1	0.2	0.8
Molar mass, g/mol	88	86
Density, g/cm^3	0.8144	0.6603
Vapour pressure Antoine constants		
A_i	4.68277	4.00266
B_i	1492.549	1171.53
C_i	-91.621	-48.784
T range (K)	307.1 - 411	286.18 - 342.69
Wilson parameter, *cal/mol*	α_{12} = 1718	α_{21} = 166.8

Use the Wilson model.

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) + x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

$$\Lambda_{ij} = \frac{V_j}{V_i}\exp\left(\frac{-\alpha_{ij}}{RT}\right); \quad T \text{ in (K); } V_i\ (\tfrac{cm^3}{mol});$$

Antoine equation $\log_{10}P = A - \frac{B}{T+C}$ **P** in bar; **T** in K.

TOTAL /25/

QUESTION 2

Assuming **complete immiscibility** for the binary mixture of water (1) + toluene (2) at the constant pressure of 1 atm, answer the following questions. Use the following table of saturated vapor pressures.

t/°C	P_1^{sat}/kPa	P_2^{sat}/kPa
60	20.00	18.58
70	31.25	27.25
80	47.44	38.94
90	70.16	54.37

(a) What is the lowest temperature at which this binary mixture can exist entirely in the vapour phase? What is its composition?

(12)

(b) If the system in part a, is heated to 90 °C, find the composition of the components in the corresponding phases.

(6)

(c) Explain, using the concept of different phase equilibria, how VLLE behaviour would exist in a binary system.

(2)

TOTAL /20/

QUESTION 3

The following reaction reaches equilibrium at 500°C and atmospheric pressure:

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \qquad \text{(R1)}$$

Component	$\Delta H°_{298}$ (J/mol)	$\Delta G°_{298}$ (J/mol)
$CO(g)$	-110525	-137169
$H_2O(g)$	-241818	-228572
$CO_2(g)$	-393509	-394359
$H_2(g)$	0	0

Assume the mixture behaves as an ideal gas. The system initially contains 1 mol CO and 1 mol H_2O. Assume the following relationship is valid.

$$\ln\frac{K}{K'} = -\frac{\Delta H°}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

Answer the following questions:

(a) What is the composition of the system at equilibrium?

(12)

(b) What is the change in the Gibbs energy (nG) when the change in equilibrium reaction coordinate (ε_e) is less than 0.001. Explain your answer.

(2)

(c) As a process engineer, you wish to maximize the production of H_2. Discuss and elaborate on the implications of the following strategies:

I. Increasing the temperature. (2)

II. Increasing the pressure. (2)

III. Adding an inert component to the feed stream. (2)

TOTAL /20/

FORMULAE SHEET

Universal Gas Constant

R = 8.314 J. mol^{-1}. K^{-1} | 8.314 $Pa.m^3$. mol^{-1}. K^{-1}

8.206×10^{-2} L.atm. mol^{-1}. K^{-1} | 8.314 $Pa.m^3$. mol^{-1}. K^{-1}

8.314×10^{-2} L.bar. mol^{-1}. K^{-1} | 83.14 cm^3.bar. mol^{-1}. K^{-1}

82.06 cm^3.atm. mol^{-1}. K^{-1} | 1.987 cal. mol^{-1}. K^{-1}

Pressure 1 bar = 0.986293 atm = 14.5038 psia = 750.061 torr

Equations of State Virial: $Z = 1 + B/V + C/V^2 + \ldots$

van der Waals: $P = RT/(V - b) - a/V^2$

Pitzer correlation: $B^0 = 0.083 - \frac{0.422}{T_R^{1.6}}$; $B^1 = 0.139 - \frac{0.172}{T_R^{4.2}}$; $\frac{BP_c}{RT_c} = B^o + \omega B^1$

Rackett equation: $V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$;

Summation equation $\sum_{i=1}^{c} x_i = 1; \quad \sum_{i=1}^{c} y_i = 1;$

Isothermal Flash calculation $f(\Psi) = \sum_{i=1}^{c} \frac{z_i(1-K_i)}{1+\Psi(K_i-1)} = 0$

$$x_i = \frac{z_i}{1+\Psi(K_i-1)} \qquad y_i = \frac{z_i K_i}{1+\Psi(K_i-1)} = x_i K_i$$

Bubble point equation $\sum_{i=1}^{c} z_i K_i = 1$; Dew point equation $\sum_{i=1}^{c} z_i / K_i = 1$

Newton's method $\Psi^{(k+1)} = \Psi^{(k)} - \frac{f(\Psi^{(k)})}{f'(\Psi^{(k)})}$

Convergence criteria $\left|\frac{\Psi^{(k+1)} - \Psi^{(k)}}{\Psi^{(k)}}\right| < 0.0001$

$$\ln\phi_i = \frac{B_{ii}P}{RT}$$

Using the two term virial expansion in P:

$$ln\widehat{\varphi_1} = \frac{P}{RT}[B_{11} + y_2^2\delta_{12}] \quad ; \quad ln\widehat{\varphi_2} = \frac{P}{RT}[B_{22} + y_1^2\delta_{12}]$$

$$B = y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}\ ; \quad \delta_{ji} \equiv 2B_{ji} - B_{jj} - B_{ii};\ \delta_{ii} = 0;\ \delta_{jj} = 0;\ \delta_{ij}=\delta_{ji}$$

For a binary system: $P_1 = exp\frac{B_{11}(P-P_1^{sat})+Py_2^2\delta_{12}}{RT}$; $P_2 = exp\frac{B_{22}(P-P_2^{sat})+Py_1^2\delta_{12}}{RT}$

$$y_i\widehat{\varphi_i^v}P = x_i\gamma_i f_i^o$$

Gamma-Phi formulation $$y_i\theta_i P = x_i\gamma_i P_i^{sat}$$

$$\theta_i = \frac{\widehat{\varphi_i^v}}{\varphi_i^{sat}}\ exp\left[\frac{-V_i^L(P - P_i^{sat})}{RT}\right]$$

Equations for BUBBLE/DEW PT calculations from SVA:

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

$$y_i = \frac{x_i\gamma_iP_i^{sat}}{\theta_iP} \quad ; \quad x_i = \frac{y_i\theta_iP}{\gamma_iP_i^{sat}} \quad ; \quad \sum_i y_i = 1;\sum_i x_i = 1 \quad ;$$

$$P = \sum_i\frac{x_i\gamma_iP_i^{sat}}{\theta_i} \quad ; \quad P = \frac{1}{\sum y_i\theta_i/\gamma_iP_i^{sat}}$$

$$T_i^{sat} = \frac{B_i}{A_i - lnP} - C_i \quad ; \quad T = \frac{B_j}{A_j - lnP_j^{sat}} - C_j$$

$$P_j^{sat} = \frac{P}{\sum(\frac{x_i\gamma_i}{\theta_i})(P_i^{sat}/P_j^{sat})} \quad ; \quad P_j^{sat} = P\sum(\frac{y_i\theta_i}{\gamma_i})(P_j^{sat}/P_i^{sat})$$

$$K = \exp(-\frac{\Delta G^O}{RT})\ ; \quad ln\frac{K}{K'} = -\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T'}\right]$$