UNIVERSITY OF
KWAZULU-NATAL

INYUVESI
YAKWAZULU-NATALI

SCHOOL OF ENGINEERING

MAIN EXAMINATION: JUNE 2023

COURSE AND CODE: THERMODYNAMICS 2 ENCH3TH

DURATION: 120 MINUTES **TOTAL MARKS:** 75

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EXTERNAL MODERATOR: DR MADISON LASICH

INSTRUCTIONS:

1. **ALL** questions should be attempted in the allocated time.

2. 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.

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

4. This examination question paper, together with all associated diagrams, **MUST BE HANDED IN TOGETHER WITH YOUR SCRIPT.**

Student Number:

QUESTION ONE

Ethyl acetate can be formed from ethanol and acetic acid, by the liquid phase reaction

$$C_2H_5OH_{(l)} + CH_3COOH_{(l)} \rightarrow H_2O_{(l)} + CH_3COOC_2H_{5(l)}$$

A liquid phase reactor with a constant temperature T = 298.15 K initially contains 5 moles each of ethanol, acetic acid, water, and ethyl acetate.

1.1 Construct the stochiometric table and calculate the equilibrium constant at 298.15 K. (10)

1.2 Find the molar composition of the reaction contents if the reaction is carried out at a constant pressure P = 50 bar. At this pressure, you cannot assume that the components form an ideal solution. But rather use the mixture fugacity expressed as $\hat{f}_i = \gamma_i x_i f_i$. (15)

The Poynting correction of the liquid fugacities to the fugacity at the reference pressure is given:

$$\frac{f_i}{f_i^0} = \exp\left[\frac{\bar{V}_i(P - P_0}{RT}\right]$$

DATA:

Compound	ΔH_f^0 [kJ/mol]	$S_{298.15}^0$ [J/mol]	$\bar{V}_i$ [cm³/mol]
Water	-285.83	69.95	18.07
Ethyl acetate	-479.86	259.4	98.59
Ethanol	-276.0	159.86	58.68
Acetic acid	-483.52	158	57.52

$$\Delta G_f^0 = \Delta H_f^0 - T\Delta S^0$$

$$K_{298.15} = \exp\left(\frac{-\Delta G_f^0}{RT}\right)$$

Total /25/

QUESTION TWO

An equimolar binary mixture of methyl ethyl ketone (MEK) (1) and toluene (2) is at 50°C and 25 kPa. Assuming that all binary interaction parameters k_{ij} are set to be zero,

2.1 Using the generalized correlations, calculate the fugacity coefficients $\widehat{\phi}_1$ and $\widehat{\phi}_2$. (22)

2.2 Calculate the compressibility factor Z and the molar volume at 50°C and 25 kPa. (3)

Data

Table 1: Pure component properties for methyl ethyl ketone (1) and toluene (2).

Component	T_c [K]	P_c [bar]	V_c [cm³/mol]	Z_c	ω
MEK	535.5	41.5	267	0.249	0.323
Toluene	591.8	41.1	316	0.264	0.264

For this system $k_{ij} = 0.0$

$$B_{ij} = \frac{RT_{c_{ij}}}{P_{c_{ij}}}(B^0 + \omega_{ij}B^1) \qquad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad T_{c_{ij}} = \left(T_{c_i}T_{c_j}\right)^{0.5}(1 - k_{ij}) \qquad P_{c_{ij}} = \frac{Z_{c_{ij}}RT_{c_{ij}}}{V_{c_{ij}}}$$

$$Z_{c_{ij}} = \frac{Z_{c_i} + Z_{c_j}}{2} \qquad V_{c_{ij}} = \left(\frac{V_{c_i}^{1/3} + V_j^{1/3}}{2}\right)^3$$

$$Z - 1 = \frac{BP}{RT} \qquad V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$$

$$\ln\hat{\phi}_1 = \frac{P}{RT}(B_{11} + y_2^2\delta_{12}) \qquad \ln\hat{\phi}_2 = \frac{P}{RT}(B_{22} + y_1^2\delta_{12}) \qquad \delta_{12} = 2B_{12} - B_{11} - B_{22}$$

$$R = 8314\ cm^3 \cdot kPa \cdot mol^{-1} \cdot K^{-1} = 8.314\ J \cdot mol^{-1} \cdot K^{-1}$$

Total /25/

QUESTION THREE

The laboratory division of your company has sent you the following data for the system n-propanol (1) and water (2) at 100 °C. A plot of the activity coefficients for this system at 100°C is given in Figure 1. The Lewis/Randall reference state is chosen for both species. The mole fraction of n-propanol in the liquid, x_1, is 0.3, and the temperature is 100°C. The saturation pressure of n-propanol at 100°C is 1.12 bar and 1.013 bar for water.

3.1 Describe in words the curve that corresponds to the activity coefficient for n-propanol, γ_1, and the curve that corresponds to the activity coefficient for water, γ_2. Explain your choices. (2)

3.2 What type of non-ideal behaviour does this system exhibit? What can be said about the molecular interactions? Please explain. (3)

3.3 Find the total pressure of the system. Clearly state the assumptions. (3)

3.4 Calculate the mole fraction of n-propanol in the vapour phase. (2)

3.5 Does this system exhibit an azeotrope? Explain. (2)

3.6 Estimate the value of the Henry's law constant of n-propanol in water. (3)

Total /15/

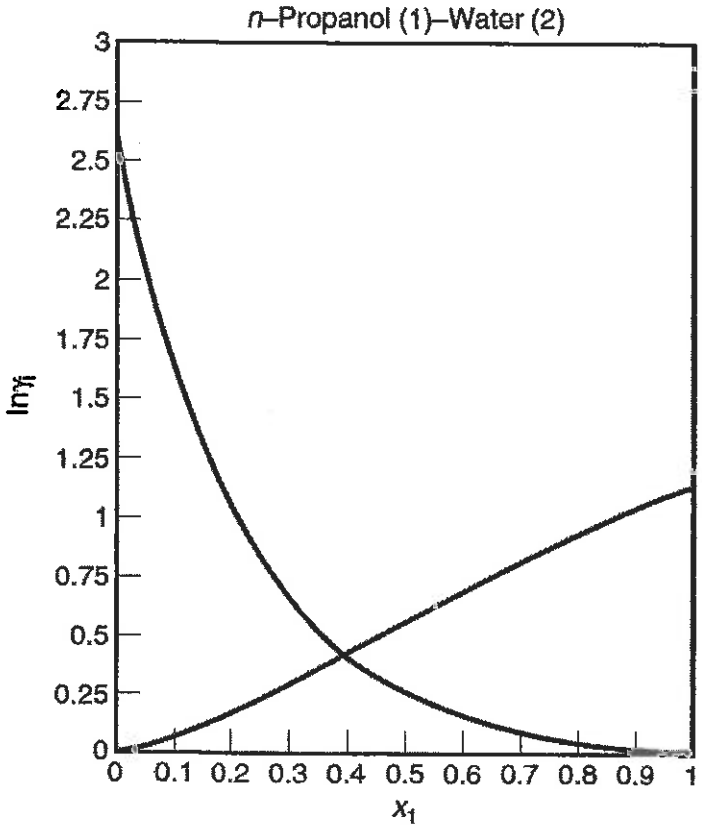

Figure 1: Plot of the activity coefficients for the system n-propanol (1) and water (2) at 100°C

QUESTION FOUR

4.1 State the instability criterion for a liquid phase. (2)

4.2 Use this to determine numerically the composition range of immiscibility for the methanol (1) + heptane (2) system at 35°C. (8)

The Margules 3-suffix parameters are A = 6500 J/mol and B = -450 J/mol

$$\frac{G^E}{RT} = x_1 x_2 [A + B(x_1 + x_2)]$$

Show all workings and state all assumptions. A solution must be found.

Total /10/

USEFUL RELATIONSHIPS

Universal Gas Constant

$R = 8.314\ J.mol^{-1}.K^{-1}$

$= 8.206 \times 10^{-2}\ L.atm.mol^{-1}.K^{-1}$

$= 8.314 \times 10^{-2}\ L.bar.mol^{-1}.K^{-1}$

$= 82.06\ cm^3.atm.mol^{-1}.K^{-1}$

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

$= 83.14\ cm^3.bar.mol^{-1}.K^{-1}$

$= 1.987\ cal.mol^{-1}.K^{-1}$

$= 8314\ cm^3.kPa.mol^{-1}.K^{-1}$

Raoult's Law

$$y_i P = x_i P_i^{sat}$$

Modified Raoult's Law

$$y_i P = x_i \gamma_i P_i^{sat}$$

Fugacity of liquids

$$\hat{f}_i^l = \phi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^l [P - P_i^{sat}]}{RT}\right)$$

Fugacity of liquids

$$\hat{f}_i^l = x_i \gamma_i P_i^{sat}$$

Henry's Law

$$\hat{f}_i = x_i H_i$$

Infinite dilution & Henry's Constant

$$\gamma_i^{\infty} = \frac{H_i}{f_i}$$

Van Laar

$$RT \ln \gamma_1 = A \left[\frac{Ax_2}{Ax_1 + Bx_2}\right]^2 \qquad RT \ln \gamma_2 = B \left[\frac{Ax_1}{Ax_1 + Bx_2}\right]^2$$

Gamma-Phi Method

$$y_i \Phi_i P = x_i \gamma_i P_i^{sat}$$

where

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \exp\left(\frac{-V_i^l [P - P_i^{sat}]}{RT}\right)$$

Phi-Phi Method

$$y_i \varphi_i^v = x_i \varphi_i^l$$