



KIBABII UNIVERSITY

**UNIVERSITY EXAMINATIONS
2022/2023 ACADEMIC YEAR**

**FIRST YEAR SECOND SEMESTER
MAIN EXAMINATIONS**

FOR THE DEGREE OF MSc. (CHEMISTRY)

COURSE CODE: SCH 851E

COURSE TITLE: ADVANCED CHEMICAL THERMODYNAMICS

DATE: 14/12/2022

TIME: 9:00-11:00AM

INSTRUCTIONS TO CANDIDATES:

TIME: 2 HOURS

ANSWER ANY THREE QUESTIONS

THIS PAPER CONTAINS 3 PRINTED PAGES

KIBU OBSERVES ZERO TOLERANCE TO examination cheating

QUESTION ONE (20MARKS)

- (a) Distinguish between pressure and fugacity (3 marks)
 (b) To which volume must 1000ml of alcohol, containing 96.0 volume% ethanol, be diluted in order to make vodka with 64.0 volume % ethanol? The process at 15°C (5 marks)

| Partial molar volume | In 96% ethanol | In Vodka |
|----------------------|----------------|----------|
| Ethanol | 58.1 | 56.6 |
| Water | 14.5 | 17.1 |

- (c) The simple equation $PV_m = RT(1 + 6.4 \times 10^{-4}P)$ varied for hydrogen up to 1500 atmosphere. Calculate the fugacity of H₂ at 1000 atmosphere (5 marks)
 (d) Define the following terms (3marks)
 i. Fugacity coefficient
 ii. Activity
 iii. Mole fraction
 (e) Fugacity of water at 25°C is 0.0313 atm. Ideal heat of vaporization is 43.72kJ/mol. What is the fugacity at 27°C (4marks)

QUESTION TWO (20 MARKS)

- (a) Volume of MgSO₄ solution per 1000g of water is

$$V = 55.51V_1^0 + 16.6253M + 1.7738M^{\frac{3}{2}} + 0.1194M^2$$

Determine the partial molar volume of MgSO₄ (5 marks)

- (b) It is required to make 2 litres of solution methanol and water containing 30% mole methanol. How many litres of pure methanol and water should be mixed (5 marks)

$$\begin{aligned} \bar{V}_1 &= 38.632 \text{ cm}^3 & \bar{V}_2 &= 17.765 \text{ cm}^3 \\ V_1^0 &= 40.727 & V_2^0 &= 18.068 \end{aligned}$$

- (c) Starting with $V = f(n_1, n_2)$, show that the Gibbs-Duhein equation of partial volume is given by $X_1 d\bar{V}_1 + X_2 d\bar{V}_2 = 0$ (5 marks)
 (d) Using thermodynamic function, $\Delta G = \Delta H - T\Delta S$, show that $\left(\frac{d \ln f}{dT}\right)_p = \frac{\Delta H}{RT^2}$ (5 marks)

QUESTION THREE (20 MARKS)

- (a) Starting with $G_s = f(n_1, n_2, P, T)$, show that $\bar{G} = \left(\frac{dG}{dn_1}\right)_{n_2, PT}$ with an inside diameter (5 marks)

(b) At 60°C aniline and water mixtures form two liquids of composition 4.4 and 93.4% by weight aniline. Assuming Raoult's law holds for abundant component and Henry's law for dilute component in each phase. Calculate for each phase the activity coefficient of dilute component on the basis of solvent standard state ($M_{\text{aniline}} = 93.1$, $M_{\text{H}_2\text{O}} = 18$) (5 marks)

(c) In a solution, $R \ln a_1 = R \ln X_1 + AX_2^2 + BX_2^3$. Find the expression for activity of component 2 using Gibbs-Duhein equation $X_1 dU_1 + X_2 dU_2 = 0$ (5 marks)

(d) Using $\mu_2 + \mu_2^0 = RT \ln a_2^{\text{ideal}} + \mu_2^{\text{electrostatic interaction}}$, show that $\mu^{\text{electrostatic interaction}} = RT\gamma \pm$ (5marks)

QUESTION FOUR (20 MARKS)

(a) 1 mole of 50% solution of propanol in ethanol is distilled until the BP rises to 90°C. The vapour pressure of condensate after cooling is found to be 1066mmHg at 90°C. Vapour pressure of pure ethanol and propanol are 1190 and 574mmHg respectively at 90°C. Assuming the solutions and vapour to behave ideally, calculate;

- i. Mole fraction of ethanol at 90 in the boiling liquid (10 marks)
- ii. Mole fraction of ethanol in the distillate (5 marks)
- iii. Number of moles of ethanol distilled (5 marks)

QUESTION FIVE (20 MARKS)

- (a) Determine the activity and mean activity of $Al_2(SO_4)_3$
 - i. Activity (3 marks)
 - ii. Mean activity (2 marks)
- (b) Express change in chemical potential for NaCl as a function of molarity and mean activity coefficient $\mu = \mu^0 + \nu RT \ln \gamma_{\pm} M_{\pm}$ (3 marks)
- (c) In a 0,5m aqueous KCl mean activity coefficient 0.901 at 25 °C. What is the extra Gibbs free energy due to electrostatics interactions of the ions in solution (5 marks)
- (d) Determine the ionic strength of $MaCl_2$ (2marks)
- (e) Given that $\ln \gamma_i = -AZ_i^2 \sqrt{I}$, Prove that Debye Huckel limiting law at infinite dilution is $\ln \gamma_{\pm} = -A|Z_+ Z_-| I^{1/2}$ (5marks)