UNIVERSITY OF EMBU

2017/2018 ACADEMIC YEAR

SECOND SEMESTER EXAMINATIONS

FIRST YEAR EXAMINATION FOR THE DEGREE OF MASTER IN SCIENCE (CHEMISTRY)

SCH 505 ADVANCED CHEMICAL THERMODYNAMICS

DATE: APRIL 3, 2018 **TIME: 2:00-5:00PM**

INSTRUCTIONS:

Answer Question ONE and any other THREE

QUESTION ONE (30 MARKS)

a) Using partialmolar volumes of two solvents, explain why the mixing of 20ml of water and 20 ml of ethanol would not give 40 ml of resultant solution (5 marks)

b) Given the following equations of fugacity

$$\Delta G = RT\ln\left(\frac{f_b}{f_a}\right)$$

Derive an expression for the dependence of fugacity on the pressure at constant Temperature (5 marks

c) Given the Gibbs Duheim equation

$X_1 d\ln a_1 + X_2 d\ln a_2 = 0$

Show that for the solvent

Given the Gibbs Duheim equation

$a_1 = 1 - X_2 = X_1$ as $X_2 \rightarrow 0$

(5 marks)

d) The fugacity of liquid water at 25°C is approximately 0.01313 atm. Calculate the fugacity of water liquid at 427 °C. The ideal heat of vaporization of water is 43.72 KJ mol^{-1} (5 marks)

e) The volume of $MgSO_4$ solution per 1000 g of water is given by

$V=55.51V^o +16.63\ M +0.1194M^2$ (M=Molal). Determine the $\overline{V}$ ($MgSO_4$) for the solution (5 marks)

f) The limiting law is given by $\log \gamma_+ = 0.509|Z_+\ Z_-|I^{\frac{1}{2}}$

In a plot of $\log \gamma_+$ against $I^{\frac{1}{2}}$ what would be the gradient for NaCl, $CuSO_4$ and $Al_2(SO4)_3$

(5 marks)

QUESTION TWO (20 MARKS)

a) From the defining equation of fugacity

$G_b - G_a = RT\ln\left(\frac{f_b}{f_a}\right)$ Where f_a and f_b are the fugacities of A and B respectively,

derive the dependence of fugacity on temperature $\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{\Delta Hm}{RT^2}$

Where ΔHm is the ideal enthalpy of vaporization (10 marks)

b) For a strong electrolyte

$A_V B_v \rightarrow V^+A^+ + V^-B^-$

Write down the expression for

i) The activity for the electrolyte
ii) The mean activity of the electrolyte
iii) The mean activity coefficient of the electrolyte (6 marks)

In very dilute solutions the Debye – Huckel equation becomes

$\log \gamma_\pm = A\ |Z^+Z^-|\sqrt{I}$

What do the various terms represent (4 marks)

QUESTION THREE (20 MARKS)

a) Discuss the use of apparent molar volume in determining the partial volume (10 marks)

b) The molar volume of an aqueous solution is given by

$V = 20(n_1+n_2) + 0.006T(n_1 + n_2) + 0.20n_1$

Where n_1 and n_2 are the number of moles of the solvent (1) and solute (2) respectively.

i) Determine an expression for $\bar{V}_1$ and $\bar{V}_2$ at constant temperature .

ii) Show that $\frac{\partial \bar{V}}{\partial T} = 0.006 cm^3 = \frac{\partial^2 V}{\partial T \partial n_2}$ (10 marks)

QUESTION FOUR (20 MARKS)

a) Given that $\bar{V}$ (ethanol) =38.622, V^Θ (ethanol)=40.727, $\bar{V}$ (H_2O)=17.76

and $V^{\Theta}(H_2O) = 18.068$, calculate the amount of H_2O that would be added to ethanol to make 2000cm3 of solution with 30 % ethanol (12 marks).

b) In a solution of compounds 1 and 2 with mole fractions X_1 and X_2 respectively. The activity of component 1 is given by $\ln a_1 = \ln X_1 + \frac{A}{R}X_2^2 + \frac{B}{R}X_2^3$

Where A and B are constants. Find an expression for the activity of component 2. (8 marks)

QUESTION FIVE (20 MARKS)

a) Define an equation of state and explain why it is sometimes useful to consider fugacity in such an equation. (4 marks)

b) Below is an equation of state

$$PV_m = RT + \frac{9R}{128}\frac{PT_c}{P_c}\left(1 - \frac{6T_c^2}{T^2}\right)$$

Where the subscript c denotes critical conditions.

i) What is critical temperature and how can it be represented mathematically? (4 marks)

ii) For this gas show that

$$f = p + \frac{9R}{128}\frac{PT_c}{P_c}\left(1 - \frac{6T_c^2}{T^2}\right)$$ (7 marks)

iii) Show that from this equation

$$p = \sqrt{fP_I}$$

Where P_I represents pressure of an ideal gas (5 marks)

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