CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR AWARD OF DEGREE OF BACHELOR OF SCIENCE (CHEMISTRY)

CHEM 221: PHYSICAL CHEMISTRY

STREAMS: **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 07/07/2021 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS

- ***Answer question one and any two questions***
- ***Do not write on the question paper***

QUESTION ONE (30 MARKS)

1. A i) Explain the following terms:
   - I. Hydrolysis of a salt (1 mark)
   - II. Hydrolysis constant (1 mark)
   - III. Degree of hydrolysis (½ mark)

ii) Explain how hydrolysis of a salt can be minimized OR almost stopped. (½ mark)

iii) Derive an expression for the PH of an aqueous solution of weak acid and strong base. (3 marks)

iv) Calculate the hydrolytic constant, the degree of hydrolysis and the PH of an aqueous 0.01 M sodium acetate solution [Ka is 1.85×10^{-5} at 298K)

v) Predict whether the aqueous solutions of the following will be acidic, neutral or alkaline.

- I. HCOONa (1½ marks)
- II. Ammonium Propionate (1½ marks)
- III. Ammonium carbonate (1½ marks)

Propionic acid PKa = 4.87

Ammonia PKa = 9.24

Carbonic acid $PKa_1 = 6.27$, $PKa_2 = 10.33$

b) Calculate the solubility of $Zn(OH)_2$ in 1M NH_3 at 298K. Given Kinst. = 6.1×10^{-11} and KsP = 4.5×10^{-17} (21½ marks)

c) Discuss some of the applications of solubility product in qualitative analysis. (5 marks)

d i) Explain the following terms:

I. Critical temperature (½ marks)

II. Critical pressure (½ marks)

III. Critical volume (½ marks)

ii) Calculate the critical constants of a gas for which "a" equals 2.25 atm L2 Mol-2 and b equals 0.043L Mol-1 [r=0.0821L atm K^{-1} Mol^{-1}] (3 marks)

iii) Van der Waals Constant, b for CCl_4 gas is 0.1383L Mol^{-1}. Calculate the diameter of the CCl_4 molecule {Na = 6.023 x 1023} (½ marks)

iv) One mole of D at 76K and 4.2 atm and E at 628K and 20.2 atm occupy a volume of 1728cm^3 and 2914cm^3 respectively. Their critical constant values are shown below. Find the missing volume in the table and state which gas is more easily liquefiable and which is in one close to ideal behavior at STP?

Gas	TC	PC(atm)	VC(l)
Δ	43K	16.8	0.085
E	314	76.8	-

(4 marks)

QUESTION TWO (20 MARKS)

2. a i) 500ml of a saturated solution of $Ca(OH)_2$ is mixed with 500ml of 0.4M sodium hydroxide solution. Calculate the milligrams of $Ca(OH)_2$ which would be precipitated out. {KsP of $Ca(OH)_2 = 4.42 \times 10^{-5}$ Ca = 40, 0= 16, H = 1} (5 marks)

ii) Calculate the solubility of AgBr and AgScN when present together in a solution saturated with respect to both the salt at 298K. {KsP for AgBr = 5.0×10^{-13} and KsP for AgSCN = 1.0×10^{-12}} (4 marks)

b) i) Distinguish the following:

I. An ideal solution from a non ideal solution. (1½ marks)

II. Henry's law from Raoult's law. (1 mark)

III. An azeotrope from a zoetrope. (1 mark)

IV. Munual Solubility Temperature (MST) from Critical Solution Temperature (CST). (1 mark)

ii) At 20^0C the solubility of nitrogen gas in water is 0.0150g/L when the partial pressure of N2 is 580 torr. Find the solubility of N_2 in H2O at 20^0C when its partial pressure is 800 torr. (1 mark)

iii) Ethyl acetate and Ethyl Propionate form nearly ideal solution over the entire range of temperature at 20^0C vapour pressure of ethyl acetate is 72.8 MMHg and of ethyl propionate is 27.7mmHg. Calculate the vapour pressure of a liquid mixture containing 25g of ethyl acetate and 50g of ethyl propionate. What will be the mole fraction of each in the vapour phase?

(5½ marks)

iv) An immiscible liquid A when steam distilled with water gave a distillate 0.200dm^3 of which contained 0.0572 dm^3 of A. The observed boiling point for the distillation was 98.2^0C and the atmospheric pressure was 758mmHg. The vapour pressure of water at 98.20C was 712mmHg. The Relative density of liquid was found to be 1.83. Calculate the molar mass of the unknown liquid. (3 marks)

QUESTION THREE (20 MARKS)

3. a i) comment on the following statement "colligative properties are intensive" (1½ mark)

ii) Justify OR criticize the statement given below.

"Lowering of vapour pressure of a liquid by a non-volatile solute is due to the attraction of solvent molecule through salvation" (3 marks)

iii) Why is it necessary that the solid dissolved in the liquid solvent be non-volatile (in case of colligative properties) (1½ marks)

iv) Why is camphor more suitable than water as a solvent in determination of molecular weights of organic substances by cryoscopic method? (1½ mark)

v) Why is effervescence observed when a soda water bottle is opened. (1½ mark)

b i) A current of dry air was passed through a solution of 2.64g of benzoic acid in 30.0g of ether ($C_2H_5OC_2H_5$) and then through pure ether. The loss in weight of the solution was 0.645g and the ether 0.0345g. What is the molecular mass of benzoic acid? (3 marks)

ii) At 25^0C, 10.50 Liters of N2 at 760mm of Hg are passed through an aqueous solution of a non volatile solute, whereby the solution loses 0.246gm in weight. If the total pressure above the solution is also 760mm. What is the vapour pressure of the solution and mole fraction of the solute? Given that the vapour pressure of pure water at this temperature is 23.76mm of Hg. {R = 0.0821L atm K^{-1} mol^{-1}} (3 marks)

iii) In a Cottrell determination 22g of benzene was used as solvent. The readings on the differential thermometer before and after adding 0.586g of naphthalene (mol mass- 128) were 1.262 and 1.799 respectively. In a separate experiment, using the same amount of benzene but this time adding 0.627g of an organic compound X, the temperature readings were 1.269 and 1.963. Calculate the molecular mass of X. (2½ marks)

iv) Phenol (C_6H_5OH) associates in water to double molecules. When 0.6677g of Phenol is dissolved in 35.5g of water it depresses the freezing point by 0.215^0C. Calculate the Van't Hoff factor and the degree of association of Phenol molar depression constant of water = 1.85^0C Mol^{-1}. (2½ marks)

QUESTION FOUR (20 MARKS)

4. a) i) Explain the term osmotic pressure. (2 marks)

ii) Derive the relationship between lowering of vapour pressure and osmotic pressure of a solvent (5 marks)

iii) Consider a vertical tube with a cross-sectional are of $0.5cm^2$. The bottom of the tube is closed with a semipermeable membrane and 0.12gm of urea is placed in the tube. The closed end of the tube is just immersed in water. What will be the weight of water level in the tube in equilibrium? The final density of the solution is 1.01gm/cc and the temperature is 27^0c. What is the osmotic pressure of the solution in S.I unit?
(Molar mass of urea = 60)
R = 0.08206 Lit.atm K^{-1} Mol^{-1}
g = 980.665 CM Sec^{-2}
1 atm = 1.01325 x 10^6 dyne cm^{-2}
= 1.011235 x 10^5 pa,
1pa = 10 x $gmcm^{-1}$ sec^{-2} (5 marks)

iv) Using Van't Hoff equation, calculate the osmotic pressure of 0.865M sucrose solution at 200C and compare your result with the experimental value which is 26.64 atm. Explain the discrepancy. (R = 0.08206 Litre atm K^{-1} Mol^{-1}) (3 marks)

b) Draw a well labeled complete phase diagram of water system. (5 marks)

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