CHUKA UNIVERSITY

UNIVERSITY EXAMINATION

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 221: PHYSICAL CHEMISTRY II

STREAMS: BSC CHEMISTRY **TIME: 2 HOURS**

DAY/DATE: FRIDAY 17/04/2020 **2.30 P.M. – 4.30 P.M.**

INSTRUCTIONS

1 Cal = 4.184 J

1 atm = 101.325 kpa =760 Torr

1ev= $1.60218 \times 10^{-19} J$

$\theta^0 c = TK - 273.15$

1J = 1Kg $m^2 s^{-2}$

1N = 1 Kg $m\ s^{-2}$

1 Pa =1 N $m^{-2} = 1 Kg m^{-1} s^{-2} = 1$ J m^{-3}

C = $3.0 \times 10^8\ m/s$

R=8.31447 J $k^{-1} mol^{-1} = 8.31447 \times 10^{-2}\ L\ bar k^{+} mol^{-1}$

R= $8.20574 \times 10^{-2}\ L\ atm\ L\ atm\ k^{+} mol^{-1}$

R= $6.23637 \times 10^{1}\ L\ Torr\ k^{-1} mol^{-1}$

h = 6.62608×10^{-34}JS

$N_A = 6.02214 \times 10^{23} mol^{-1}$

QUESTION ONE (30 MARKS)

1. (a) Comment on the following statements.

(i) Van der Waals equation takes into account only the attractive forces between molecules and repulsive interactions are not considered. (2 marks)

(ii) Compressibility factor of a real gas is greater than unity at high pressures and temperatures. (3 marks)

(b) Describe a condition under which a van der Waals gas will behave like an ideal gas at all temperatures? (1 mark)

(c) (i) Define and explain Raoult's law. (2 marks)

(ii) Calculate the vapour pressure of solvent above a solution containing 53.94g of a solute (molecular weight = 182.11) per 1000g of water at $25^0\ C$. At this temperature, the vapour pressure of water is 17.5/ mmHg. (1 mark)

(iii) Derive a relation for the elevation in boiling point of a solution with its molality. (4 marks)

(iv) A solution containing 2.44 g of a solute dissolved in 75 g of water boiled at 100.413 ^0C. Calculate the molecular weight of the solute $K_b = 0.52\ ^0C$ (1 mark)

(v) (I) Differentiate between osmotic pressure and osmosis.(1 mark)

(II) A 0.035M aqueous nitrous acid (HNO_2) has an osmotic pressure of 706.8 torr at 22.0 ^0C. Calculate the percent ionization of the acid $\{R = 0.08206 Latm\ mol^{-1}k^{-1}\}$ (3 marks)

(d) (i) Explain the meaning of the following:

(I) Phase ($\frac{1}{2}$ mark)

(II) Component ($\frac{1}{2}$mark)

(III) Degree of freedom (1 mark)

(ii) In the following systems calculate the number of phases, components and degrees of freedom

(I) $NH_4CI(s) \rightleftarrows NH_3g + HCI(g)$ when $P_{NH3} \neq P_{HCI}$
$P_{NH3} = P_{HCI}$ (3 marks)

(II) A dilute solution of sulphuric acid. ($1\frac{1}{2}$ marks)

(iii) The solubility product of CaF_2 at $25^0\ C$ is 1.6×10^{-10}

(I) Should precipitation occur when 50 ml of $5 \times 10^{-2} M Ca(N0_3)_2$ is mixed with 50ml of $4.0 \times 10^{-4} M\ NaF$ solution? (2 marks)

(II) If precipitation occurs (Q iii(I), how much CaF_2 will be precipitated? ($2\frac{1}{2}$ marks)

(iv) The solubility product of PI_2 is 7.47×10^{-9} at 15^0C and 1.39×10^{-8} at 25^0C. Calculate

(I) The molar heat of solution of PbI_2 (1 mark)

(II) The solubility in moles/litre at 75^0C. (1 mark)

QUESTION TWO (20 MARKS)

2 (a) (i) Calculate the pH of a 0.1 M K_3PO_4 solution. The third dissociation constant of ortho phosphoric acid is 1.3×10^{-12}. The hydrolysis proceeds only in the first step. Assume $kw = 1 \times 10^{-14}$. ($3\frac{1}{2}$ marks)

(ii) Show that the degree of ionization of a weak electrolyte HX which ionizes according to the equation

$HX \rightleftarrows H^+ + X^-$ is given by

$\alpha = \frac{Ka}{2C}[-1 + \sqrt{1 + \frac{4C}{K9}}]$ (3 marks)

(iii) Give the drawbacks in the Arrhenius theory of electrolytic dissociation. ($2\frac{1}{2}$ marks)

(iv) The value of equivalent conductance (Λ) of a 0.01M solution of a weak acid HA is 60 at 298K while the value of Λ^0 is 360 at the same temperature. Calculate P^{ka} of the acid considering the activities {A=0.51 for water at 25^0C) (5 marks)

(b) Gold melts at 1063^0C and Thallium at 302^0C. Cooling Gold/Thallium alloys at various composition gave the following results:

Gold by mass	80	60	40	25	20	10
Beginning of freezing ^0C	835	610	315	140	160	232
End of freezing ^0C	131	131	131	131	131	131

(i) Draw on graph paper, a phase diagram of the Gold/Thallium M. system. Labeling each area. (3 marks)

(ii) Sketch and explain the temperature against time curve obtained when cooling slowly an alloy containing 72% Gold. What would be the physical state of this alloy at 500^0C. ($1\frac{1}{2}$ marks)

(iii) Sketch and explain the temperature against time curve obtained when cooling slowly on alloy containing 4% Gold. ($1\frac{1}{2}$ marks)

QUESTION THREE (20 MARKS)

3. (a) (i) Derive the kinetic theory gas equation for an ideal gas. (5 marks)

(ii) Deduce the following gas laws from the kinetic gas equation

(I) Graham's law of Diffusion. (3 marks)

(II) Avogadro's law (2 marks)

(iii) Oxygen at 2.5 atmosphere pressure and 45^0C has a density of 0.7145 grams per litre. Determine root mean square velocity, average velocity and most probable velocity. (4 marks)

(b) How does the van der Waals equation explain the behaviour of gases at:

(i) Low pressure ($1\frac{1}{2}$ mark)

(ii) High pressures (1 mark)

(iii) Extremely low pressures (1 mark)

(c) A certain vapour obeys the Van der Waals equation with $a = 0.52\ m^6\ pa\ mol^{-2}$. It's volume is $4.99 \times 10^{-4} m^3 mol^{-1} at\ 300K\ and\ 3.20 \times 10^3 KPa$. Calculate the value of van der Waals constant. Find the temperature at this volume, when $P = 0$

QUESTION FOUR (20 MARKS)

4. (a) (i) Give a brief accounts of Henry's law. (3 marks)

(ii) The Henry law constant for $N_2(g)$ at 298K is $13.6 \times 10^{-6}\ mol\ L^{-1} atm^{-1}$. A diver descends to a depth where the pressure is 6 atm. If the diver's body contains about 6 L of blood. Calculate the maximum amount of nitrogen gas dissolved in the diver's

blood at 1 atm and 8 atm {assume solubility of nitrogen in water and blood to be the same} (2 marks)

(iii) An immiscible liquid A when steam distillate with water gave a distillate 0.2 dm^3 of which contained 0.0572 dm^3 of A. The observed boiling point of the distillation was $98.2^0\ C$ and the atmospheric pressure was 758 mmHg. The vapour pressure of water at $98.2^0\ C$ was 712 mmHg. The relative density of liquid was found to be 1.83. Calculate the molar mass of the unknown liquid. {Assume the density of water to be 1kg dm^{-3}} (3 marks)

(b) (i) Show that for a solution of a solute in a non-polar solvent at the particular concentration $\frac{\Delta T_B}{T_B}$ is independent of the nature of solvent {Assume Trouton's rule is valid} (2 marks)

(ii) Why is camphor more suitable than water as a solvent in determination of molecular weights of organic substances by cryoscopic method? (2 marks)

(iii) A solution containing 0.684 gm of cane sugar in 100 gm of water freezes at -0.037 ^0C, while a solution containing 0.585 gm of NaCI in 100 gm of water freezes at $-0.342^0\ C$. Calculate K_f for water, Van't Hoff factor i and % dissociation of NaCI {Molar mass of cane sugar = 342.3 g/mol} (3 marks)

(c) A solution of KI is isotonic with a 0.01 M solution of I_2 at $27^0\ C$. When equal volume of two solutions were mixed together, the osmotic pressure dropped by 18.5% of that of the individual solution. Calculate the percentage of conversion of I^- to I_3^-. Assume that the solutions behave ideally and the salts are completely dissociated. (5 marks)
