CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

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

CHEM 221: PHYSICAL CHEMISTRY III

STREAMS: **TIME: 2 HOURS**

DAY/DATE:

INSTRUCTION:

Answer Question **ONE** and any other **TWO** Questions

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	$m\ s^{-1}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^{4}	$C\ mol^{-1}$
Boltzmann's constant	k	1.380 65	10^{-23}	$J\ K^{-1}$
Gas constant	$R = N_A k$	8.314 47		$J\ K^{-1}\ mol^{-1}$
		8.314 47	10^{-2}	$dm^3\ bar\ K^{-1}\ mol^{-1}$
		8.205 74	10^{-2}	$dm^3\ atm\ K^{-1}\ mol^{-1}$
		6.236 37	10	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	$J^{-1}\ C^2\ m^{-1}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$J^{-1}\ C^2\ m^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$J\ s^2\ C^{-2}\ m^{-1}\ (= T^2\ J^{-1}\ m^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	$J\ T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	$J\ T^{-1}$
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	$W\ m^{-2}\ K^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 37	10^{5}	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		$m\ s^{-2}$
Gravitational constant	G	6.673	10^{-11}	$N\ m^2\ kg^{-2}$

Exact value

QUESTION ONE (30 MARKS)

1a (i). Describe the distribution of molecular speeds in an ideal gas (5 Marks)

(ii). A gas bulb of 1 litre capacity contains 2.0 x 10^{21} molecules of nitrogen exerting a pressure of 7.57 x 10^{3} N/m^3 . Calculate the root mean square speed and temperature of the gas molecules if the ratio of most probable speed to the room mean square speed is 0.82. Calculate the most probable speed of these molecules at this temperature. (2 Marks)

(iii) In a sample of nitrogen N_2 with a molar mass of 28.0 g/mol at a temperature of 273°C. Find the ratio of the number of molecules with a speed very close to 300m/s to the number with a speed very close to 100m/s (2 Marks)

b (i) Van der Waals constant b of Ar is 3.22×10^{-5} mol^{-1}. Calculate the molecular diameter of Ar. ($1\frac{1}{2}$ Marks)

(ii) The compression factor (compressibility factor) of 1 mole of a Van der Waals as at 0^oC and 100 ^oC atmospheric pressure is found to be 0.5. Assuming that the volume of a as molecule is negligible, calculate the Van der Waals constant 'a'. ($1\frac{1}{2}$ Marks)

(iii) Gases NO and CH_4 obeying Van der Waals equation have Tc and Pc values given below.

	Tc K	Pc (atm)
NO	177	64
CH_4	550	45

Which gas has

(I) Smaller value of a
(II) smaller value of b
(III) larger value of Vc
(IV) Is nearly ideal in behavior at 300k and 10atm pressure? give a reason (4 Marks)

(iv) Explain in terms of kinetic theory why an automobile pump get heated while pumping air into a tire. (1 Marks)

(v) Hydrogen will dissociate into atoms at high enough temperature that is $H_2 = 2H$. Assuming ideal as behavior of H_2 and H atom, what would be the density of hydrogen at 2000^0C, If 35% dissociates into atoms? The pressure is 1 atm. ($1\frac{1}{2}$ Marks)

(vi) Two gases N_2 and C_2H_6 obeying Van der Waals equation have the following Tc and Pc

	Tc	Pc
N_2	126K	34 atm
C_2H_6	305K	48 atm

Which gas has/ is

(I) Smaller value of a (2 Marks)
(II) smaller value of b (2 Marks)
(III) larger value of Vc (2 Marks)
(IV) Nearly ideal in behavior at 300k and 10atm pressure? give a reason ($1\frac{1}{2}$ Marks)
(V) Calculate the temperature below which N_2 would be (1 Mark)

c(i) Calculate the degree of hydrolysis of ammonium acetate, if the dissociation constant of ammonium hydroxide is $1.8x10^{-5}$ that for acetic acid is $1.8x10^{-5}$ and the ionic product of water is $1.0x10^{-14}$ ($1\frac{1}{2}$ Marks)

(ii) Calculate the pH of 0.15M solution of ammonium chloride if the dissociation constant for ammonium is $1.8x10^{-5}$ ($1\frac{1}{2}$ Marks)

QUESTION TWO (20 MARKS)

2(a) Calculate the solubility of $Mg(OH)_2$ in

(i) pure water (1 Mark)
(ii) 0.01M NaOH (1 Mark)
(iii) 0.01M $Ba(OH)_2$, ksp for $Mg(OH)_2 = 1.2x10^{-11}$ (1 Mark)

b(i) Calculate the solubility of AgBr and AgScN when present together in a solution saturated with respect to both the salt at 298K. Ksp (AgBr) = $5.0x10^{-13}$ and Ksp (AgScN) = $1.0x10^{-12}$

(3 Marks)

(ii) Calculate the stability of $Zn(OH)_2$ in 1M NH3 at 298K. Given $K_{inst} = 6.1 \times 10^{-11}$ and Ksp = 4.5×10^{-17} (2 Marks)

(iii) Write short notes on the drawbacks in the Arrhenius theory of electrolyte dissociation (2 Marks)

c. Briefly discuss the following

(i) Henry's law ($2\frac{1}{2}$ Marks)

(ii) Raoult's law ($2\frac{1}{2}$ Marks)

d (i) At 20°C the solubility of nitrogen gas in water is 0.015g/L when the partial pressure of N_2 is 580 torr. Find the solubility of N_2 in H_2O at 20°C when its partial pressure is 800 torr. (1 Mark)

(ii) Air was passed through a solution containing $2x10^{-2}$ kg of a substance in 0.1kg of water and ten trou pure water. The loss in mass of the solution was $2.945x10^{-3}$kg and that of pure water was 5.9×10^{-5}kg. Calculate the molar mass of the substance. ($2\frac{1}{2}$ Marks)

(iv) A mixture of water and bromobenzene (C_6H_5Br) distills at 95°C and the distillate contains 1.6 times as much C_6H_5Br as water by mass. At 95°C the vapor pressure of water and C_6H_5Br are 640 mmHg and 120 mmHg respectively. Calculate the molecular weight of bromobenzene
($1\frac{1}{2}$ Marks)

QUESTION THREE (20 MARKS)

3a (i) What is Van't Hoff factor ($2\frac{1}{2}$ Marks)

(ii) When can the van't Hoff factor be integral (2 Marks)

b Comment on the following

(i) Colligative properties are intensive (1 Mark)

(ii) Lowering of vapour pressure of a liquid by a non- volatile solute is due to the attraction of solvent molecule through solution ($2\frac{1}{2}$ Marks)

(iii) The solid dissolved in the liquid solvent must be non- volatile for the case of colligative properties (2Marks)

c (i) A solution of $3.0x10^{-4}$kg of camphor($C_{10}H_{16}O$) in $2.53\ x10^{-2}$kg of chloroform boils at 334.3K. Boiling point of chloroform is 334.0K. Calculate $\Delta H_{vap,m}$ and K_b of chloroform. (2 Marks)

(ii) The lowering of freezing point of benzene was 2.33K when $4.12x10^{-4}$kg of solute of unkown molar mass was dissolved in $9.31\ x10^{-3}$kg of benzene. Calculate the molar mass of the solute molar depression constant for benzene is 5.1k $kgmol^{-1}$ (1 Mark)

(iii) x gm NaCl, y gm sucrose and z gm urea are mixed and dissolved in $0.5dm^3$ of water. Suppose that no chemical reaction sets in, what should be the osmotic pressure of the solution (Rmm for NaCl = 58.5$gmol^{-1}$, sucrose = 342$gmol^{-1}$, urea = 60$gmol^{-1}$) ($3\frac{1}{2}$ Marks)

(iv) A solution containing $3.0x10^{-4}$kg of benzoic acid (M =$1.22X10^{-1}$ $kgml^{-1}$) in $2.0x10^{-3}$kg of benzene freezes at 0.317°C below the freezing point of the solvent. Calculate

(I) The degree of association assuming that the acid exists as dimer in benzene ($1\frac{1}{2}$ Marks)

(II) The apparent molar mass of the acid exist as dimer in benzene (1 mark)

(III) The apparent molar mass of the acid, k_f for benzene is 5.1 (1 Mark)

QUESTION FOUR (20 MARKS)

4(a) Explain the following in phase rule.

(i) component (2 Marks)

(ii) degree of freedom (2 Marks)

(iii) phase (2 Marks)

(b) Write down the number of components, number of phases and evaluate the degree of freedom for the following equilibria:

(i) $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

(ii) $NH_4Cl\ (s) \rightleftharpoons NH_3(g) + HCl(g)$

When

(I) $P_{NH3} \neq P_{HCl}$ (1 Mark)

(II) $P_{NH3} = P_{HCl}$ ($1\frac{1}{2}$ Mark)

(iii) Reduction of Fe_2O_3 (s) by CO in the presence of

(I) Air ($2\frac{1}{2}$ Marks)
(II) Oxygen (1 Mark)

c. Discuss polymorphism ($5\frac{1}{2}$ Marks)

d. Classify two component solid- liquid equilibria based on the miscibility of the two components in the molten state and the nature of the solid phases that separate out during cooling, the solid-liquid equibria ($2\frac{1}{2}$ Marks)

PERIODIC TABLE OF THE ELEMENTS

Metals
Nonmetals
Metalloids

	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	VIIIB 9	VIIIB 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	0 18
1	1 H 1.008																1 H 1.008	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.9984	10 Ne 20.1797
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.085	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.9045	54 Xe 131.293
6	55 Cs 132.9055	56 Ba 137.327	57 La 138.9055 *	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.9666	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227) **	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

*Lanthanide Series

58 Ce 140.116	59 Pr 140.9076	60 Nd 144.242	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.500	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.054	71 Lu 174.9668

** Actinide Series

90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.