

CHEM 221

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		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	10^{-2}	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
		8.205 74	10^{-2}	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
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	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	10^{-12}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	10^{-10}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^3)$
Magnetron				
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	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	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	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 51	10^{-8}	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c \epsilon_0^2$	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}	$\text{N m}^2 \text{kg}^{-2}$

*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 2.0×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3 \text{ N/m}^2$. Calculate the root mean square speed and temperature of the gas molecules if the ratio of most probable speed to the root 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 300 m/s to the number with a speed very close to 100 m/s (2 Marks)

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b (i) Van der Waals constant b of Ar is $3.22 \times 10^{-5} \text{ mol}^{-1}$. Calculate the molecular diameter of Ar. (1½ Marks)

(ii) The compression factor (compressibility factor) of 1 mole of a Van der Waals gas at 0°C and 100 atm atmospheric pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der Waals constant ' a '. (1½ Marks)

(iii) Gases NO and CH₄ obeying Van der Waals equation have T_c and P_c values given below.

	T_c K	P_c (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 V_c
- (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 gets heated while pumping air into a tire. (1 Marks)

(v) Hydrogen will dissociate into atoms at high enough temperature that is $\text{H}_2 = 2\text{H}$. Assuming ideal gas behavior of H_2 and H atom, what would be the density of hydrogen at 2000°C , if 35% dissociates into atoms? The pressure is 1 atm. (1½ Marks)

(vi) Two gases N₂ and C₂H₆ obeying Van der Waals equation have the following T_c and P_c

	T_c	P_c
N ₂	126K	34 atm
C ₂ H 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 V_c (2 Marks)
- (IV) Nearly ideal in behavior at 300K and 10atm pressure? give a reason (1½ Marks)
- (V) Calculate the temperature below which N₂ would be (1 Mark)

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c(i) Calculate the degree of hydrolysis of ammonium acetate, if the dissociation constant of ammonium hydroxide is 1.8×10^{-5} that for acetic acid is 1.8×10^{-5} and the ionic product of water is 1.0×10^{-14} (1½ Marks)

(ii) Calculate the pH of 0.15M solution of ammonium chloride if the dissociation constant for ammonium is 1.8×10^{-5} (1½ Marks)

QUESTION TWO (20 MARKS)

2(a) Calculate the solubility of $\text{Mg}(\text{OH})_2$ in

- (i) pure water (1 Mark)
- (ii) 0.01M NaOH (1 Mark)
- (iii) 0.01M $\text{Ba}(\text{OH})_2$, K_{sp} for $\text{Mg}(\text{OH})_2 = 1.2 \times 10^{-11}$ (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. $K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}$ and $K_{sp}(\text{AgSCN}) = 1.0 \times 10^{-12}$ (3 Marks)

(ii) Calculate the stability of $\text{Zn}(\text{OH})_2$ in 1M NH_3 at 298K. Given $K_{inst} = 6.1 \times 10^{-11}$ and $K_{sp} = 4.5 \times 10^{-17}$ (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 (2½ Marks)
- (ii) Raoult's law (2½ 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 2×10^{-2} kg of a substance in 0.1kg of water and ten times pure water. The loss in mass of the solution was 2.945×10^{-3} kg and that of pure water was 5.9×10^{-5} kg. Calculate the molar mass of the substance. (2½ Marks)

- (iv) A mixture of water and bromobenzene ($\text{C}_6\text{H}_5\text{Br}$) distills at 95°C and the distillate contains 1.6 times as much $\text{C}_6\text{H}_5\text{Br}$ as water by mass. At 95°C the vapor pressure of water and $\text{C}_6\text{H}_5\text{Br}$ are 640 mmHg and 120 mmHg respectively. Calculate the molecular weight of bromobenzene (1½ Marks)

QUESTION THREE (20 MARKS)

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

(ii) The lowering of freezing point of benzene was 2.33K when 4.12×10^{-4} kg of solute of unknown molar mass was dissolved in 9.31×10^{-3} kg of benzene. Calculate the molar mass of the solute molar depression constant for benzene is $5.1 \text{ k kg mol}^{-1}$ (1 Mark)

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

(iv) A solution containing 3.0×10^{-4} kg of benzoic acid ($M = 1.22 \times 10^{-1} \text{ kg mol}^{-1}$) in 2.0×10^{-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)

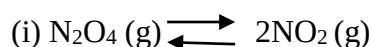
4(a) Explain the following in phase rule.

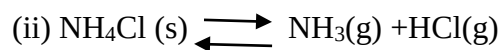
(i) component (2 Marks)

(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:





When

$$(I) P_{\text{NH}_3} \neq P_{\text{HCl}}$$

(1 Mark)

$$(II) P_{\text{NH}_3} = P_{\text{HCl}}$$

($1\frac{1}{2}$ 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 equilibria

($2\frac{1}{2}$ Marks)

PERIODIC TABLE OF THE ELEMENTS

IA		Metals										VIIA		0
1	1	Nonmetals										17	18	
1	1	Metalloids										17	18	
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