M.Sc - I · Sem - II · Oct · 2016 ·

Chemistry - Paper - I

(Physical)

QP Code : 75731

(2½ Hours) [Total Marks : 60

N.B. : (1) All questions are **compulsory.**

(2) **Figures to the right indicate maximum marks.**

(3) Use of **Non-programmable scientific calculator is allowed.**

Useful constants :

c	$= 2.998 \times 10^{8}$ ms^{-1}	e	$= 1.602 \times 10^{-19}$ C
R	$= 8.314$ J K^{-1} mol^{-1}	k	$= 1.3811 \times 10^{-23}$ J K^{-1}
h	$= 6.625 \times 10^{-34}$ Js	1 J	$= 6.24 \times 10^{18}$ eV
m_e	$= 9.109 \times 10^{-31}$ kg	1 eV	$= 8.06 \times 10^{3}$ cm^{-1}
N_A	$= 6.023 \times 10^{23}$ mol^{-1}	1 amu	$= 1.66 \times 10^{-27}$ kg

Atomic Mass of C = 12, O = 16.

1. (a) Attempt any two of the following :

(i) Explain the terms : 4

(1) Linear operator

(2) Hermitian operator .

(ii) Formulate the Schrödinger wave equation for a particle in one dimensional box and obtain the normalised wave function for it. 4

(iii) Show that the functions : 4

$$\psi_1 = \left(\frac{1}{2\pi}\right)^{1/2}$$

$$\psi_2 = \left(\frac{1}{\pi}\right)^{2} \cos x$$

$$\psi_3 = \left(\frac{1}{\pi}\right)^{2} \sin x$$

in the interval $x = 0$ to $x = 2\pi$ are orthogonal to each other.

(iv) What is linear harmonic oscillator? Obtain an expression for linear harmonic oscillator from the following equation. 4

$$\frac{d^2\psi}{dy^2} + \left(\frac{\alpha}{\beta} - y^2\right)\psi = 0$$

(b) Attempt **any one** of the following :

(i) If $\hat{A} = 3x^2$ and $\hat{B} = \frac{d}{dx}$ then show that $\hat{A}$ and $\hat{B}$ do not commute. 4

(ii) A particle of mass 'm' is confined in one dimensional box of length 'a'. Calculate the probability of finding the particle at x where $0 \leq x \leq a/4$. 4

2. (a) Attempt **any two** of the following :

(i) Obtain the equations of separation of variables from the Schrödinger wave equation in terms of spherical coordinates. 4

(ii) Explain the need for approximate solution to two electron system. Show how the problem of two electron system can be reduced to problem of one electron system. 4

(iii) What are radial probability distribution curves? Qualitatively plot the radial probability distribution curves for 3s, 3p and 3d orbital's. 4

(iv) With respect to hydrogen like atom, answer the following : 4

(1) Write the Hamiltonian operator for it and identify the terms involved.

(2) Mathematically express the coordinates of the centre of mass and relative coordinates of the system.

(b) Attempt **any one** of the following :

(i) The internuclear distance between carbon and oxygen atom in carbon monoxide molecule, which acts as a rigid rotor, is 1.13×10^{-10} m. What is the rotational energy for $J = 3$? 4

(ii) A hydrogen like orbital is given below : 4

$$\psi = \frac{\sqrt{2}}{81\sqrt{\pi}} Z^{3/2} \cdot (6 - Zr)\, Zre^{-Zr/3} \cdot \cos\theta \text{ (in a.u.)}$$

Determine the quantum numbers n, l and m by inspection and identify the orbital.

3. (a) Attempt **any two** of the following :

(i) On the basis of the collision theory, derive an expression for the rate constant of a bimolecular gaseous reaction. 4

(ii) Define kinetic chain length and show that the rate of polymerization reaction is proportional to the square root of the initiator concentration. 4

(iii) Explain the variation of the rate of reaction with pressure and the three explosion limits in the reaction between H_2 and O_2. 4

(iv) For the thermal decomposition of acetaldehyde, show that 4

$$\frac{d}{dt}[CH_4] = k[CH_3CHO]^{3/2}$$

(b) Attempt **any one** of the following :

(i) On the top of a certain mountain, the atmospheric pressure is 530 mm Hg and the pure water boils at 360 K. A climber finds that it takes 300 minutes to boil an egg as against 3 minutes at 370 K. 4

(1) What is the ratio of the rate constant k_{370} / k_{360}?

(2) Calculate the energy of activation for the reaction that occurs when the egg is boiled assuming that the pre-exponential factor A remains constant.

(ii) Consider the following consecutive reaction : 4

$$R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3.$$

where k_1 and k_2 are the rate constants for a first order reaction. If $k_1 : k_2 = 1.0 : 0.15$ and $k_1 = 4.0 \times 10^{-2}$ min^{-1}, then calculate the time required for the concentration of R_2 to reach a maximum.

4. (a) Attempt **any two** of the following :

(i) Derive an expression for the kinetics of reactions in the solid state for spherical particles. 4

(ii) Derive an expression for the rate law of kinetics of reactions in solid state. 4

(iii) Discuss with mathematical expression the enzyme inhibition by competitive method. 4