Chemistry M.Sc Sem II
Nov. 17

Q.P. Code : 09237

(2½ Hours) **[Total Marks : 60**

N.B. : (1) **All** questions are **compulsory.**
(2) **Figures to right indicate full 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 $= 6.24 \times 10^{18}$ e V
$m_e = 9.109 \times 10^{-31}$ kg	1 eV $= 8.06 \times 10^3$ cm^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1}	1 amu $= 1.66 \times 10^{-27}$ kg
	1 atm $= 1.013 \times 10^5$ Nm^{-2}

Atomic Mass of N = 14 amu
O = 16 amu
H = 1 amu

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

(i) What is an operator? Using the operator representation of the *x* component of the momentum of a particle, prove that 4

$$(x\hat{p}_x - \hat{p}_x x)\Psi = i\hbar\Psi$$

(ii) The particle in a one dimensional box of length L has the wave function : 4

$$\Psi_n = \sin\frac{n\pi x}{L}$$

Find the normalization factor. Determine the node of a particle in the states corresponding to n = 2 and n = 3. 4

(iii) Explain the following :
(p) Wave particle duality
(q) Heisenberg's uncertainty principle

(iv) For a particle of mass 'm' executing simple harmonic oscillation the potential energy is given as $V = \frac{1}{2}kx^2$ and the oscillation frequency as $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ where k is a force constant and 'x' is the displacement from the equilibrium position. Using the classical expressions of V, ν and the definition $\alpha = \frac{8\pi^2 mE}{h^2}$ and $\beta = \frac{4\pi^2 m\nu}{h}$, write the Schrodinger equation in simple form and find the asymptotic form of the solution. 4

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

(i) Calculate the spacing between the energy levels for : **4**

(p) an electron (of mass 10^{-30} kg) in one dimensional box of 1.04A° length.

(q) a ball (mass = 1 g) in a box of 10 cm length.

Comment on the energy gap in the two cases.

(ii) The Hermite polynomials are derived from the generating function : **4**

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n}\left(e^{-y^2}\right)$$

where 'n' is the vibrational quantum number and also the degree of polynomial. Calculate the polynomials for n = 2 and n = 3.

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

(i) Solve the following partial differential equation by separating the two variables to obtain ordinary differential equations containing one variable each. **4**

$$\frac{\partial^2\Psi}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial\Psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2} + \frac{8\pi^2 mr^2}{h^2}E\Psi = 0$$

(ii) What are atomic units? Write the value of the atomic units for the following physical quantities : **4**

(p) Angular momentum

(q) Energy of an electron in first orbit

(iii) What is radial wave function? Give its solution and sketch the radial wave function for 2p and 3d orbitals. **4**

(iv) Name the two particles in hydrogen atom. Obtain an expression which represents translational energy of hydrogen atom as a whole. **4**

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

(i) A hydrogen like orbital is given below : **4**

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

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

(ii) Calculate the energy of the third rotational energy level J = 2 in the molecule of NO having 110 pm inter-nuclear distance. **4**

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) Explain the kinetics of free radical polymerization. 4

(iii) Explain the mechanism of the decomposition of ozone. 4

(iv) For the thermal decomposition of acetaldehyde, 4

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

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

(i) The molecular diameters of O_2 and H_2 gases are 3.39×10^{-10} m and 2.42×10^{-10} m respectively. Calculate the number of collisions in $m^{-3}s^{-1}$ when 1.0g of O_2 and 0.1 g of H_2 are mixed in 1 dm^3 flask at 300 K. 4

(ii) For the consecutive first order reaction : 4

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$, the values of k_1 and k_2 are 45 s^{-1} and 15 s^{-1} respectively. If the reaction is carried out with pure A at a concentration of 1.0 mol dm^{-3}, how much time will be required for the concentration of B to reach a maximum?

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

(i) Derive the parabolic rate law for the reaction of a gas on the surface of solid particles. 4

(ii) Derive the rate law expression for the reaction of spherical particles. 4

(iii) Discuss the kinetics of inhibition of enzyme action by competitive inhibition method. 4

(iv) Derive mathematical expression of Michaelis - Menten equation of enzyme catalysed reaction. 4

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

(i) Discuss the effect of solvent polarity on rate of reactions in solutions. 4

(ii) Derive an expression to show the effects of ionic strength on the rate constant of the reaction. 4

5. (a) Attempt **any four** of the following : 12

(a) Give the applications of Schrodinger wave equation.

(b) If the eigen functions of an Hermitian operator have different eigen values, then prove that they are orthogonal.

(c) Sketch the radial distribution function for 2s, 3s and 3p orbitals.

(d) Write the expressions for theta equation, R-equation and phi equation of seperation of variables of Schrodinger wave equation.

(e) Explain the principle of microscopic reversibility.

(f) Explain the Rice - Ramsperger - Kassels (RRK) theory.

(g) Write a note on enzyme activation by metal ions.

(h) Discuss the various factors affecting reactions in solids.
