

**Time: 2.30 Hours****[Marks: 60]**

Please check whether you have got the right question paper.

N.B: 1. All questions are compulsory.

2. Figures to the right indicate full marks.

3. Use of non-programmable scientific calculator is allowed.

Useful constants

$$c = 2.998 \times 10^8 \text{ m.s}^{-1}$$

$$R = 8.314 \text{ J.K}^{-1} \text{ mol}^{-1} = 2.0 \text{ cal.mol}^{-1} \text{ .K}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$m_e = 9.110 \times 10^{-31} \text{ kg}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$k = 1.3811 \times 10^{-23} \text{ JK}^{-1}$$

$$1\text{J} = 6.24 \times 10^{18} \text{ eV}$$

$$1\text{eV} = 8.06 \times 10^3 \text{ cm}^{-1}$$

$$1\text{amu} = 1.66 \times 10^{-27} \text{ kg}$$

Atomic mass of N=14, O=16, H=1, C=12, Cl=35.5

**Q.1 A) Attempt any two of the following:**i) What are the conditions required for the wave function to be acceptable? A wave function is given as  $\psi = \cos x$  **04**

a) Is it acceptable?

b) Is it normalized? Explain

ii) Explain the expectation value of a dynamical quantity. **04**iii) Give the expression for energy of a particle in one dimensional box. Explain how it gives rise to the concept of quantization. Plot a graph of  $\psi^2$  against 'x' for n=1, 2 and 3 and state the number of nodes in each case. **04**iv) State the postulates of quantum mechanics. **04****B) Attempt any one of the following:**i) The Hermite polynomials are obtained from the following generating functions **04**

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

Calculate the value for the polynomial n=2 and n=3

ii) If  $\hat{A} = 7x^3$  and  $\hat{B} = d/dx$  are the two operators for the function  $f(x) = \sin x$ , then show that  $\hat{A}$  and  $\hat{B}$  do not commute with each other. **04**

**Q.2 A)** Attempt **any two** of the following:

- i) Explain the independent electron approximation as applied to two electron system. **04**
- ii) Give the physical significance of spherical harmonics. Write the expression for spherical harmonics for  $l=0$  and  $l=1$  **04**
- iii) What is radial wave function? Give its solution and sketch the radial wave function for 2s and 3d orbital. **04**
- iv) What are quantum numbers? Explain the significance of spin quantum number. **04**

**B)** Attempt **any one** of the following:

- i) Calculate the values of first two rotational energy levels of a rigid rotor whose moment of inertia is  $1.457 \times 10^{-46} \text{ m}^2$ . **04**
- ii) The radial wave function of 2s orbital of hydrogen atom is given by **04**

$$R_{20} = N \left[ 2 - \frac{r}{a_0} \right] e^{-r/2a_0}$$

where N is constant.

- a) Qualitatively sketch the radial distribution curve.
- b) Determine the distance of node from the nucleus in terms of  $a_0$

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

- (i) Write the reaction mechanism for decomposition of acetaldehyde and using steady state principle show that  $\frac{d[\text{CH}_4]}{dt} = k [\text{CH}_3\text{CHO}]^{3/2}$  **04**
- (ii) Explain the Rice-Ramsperger-Kassel-Marcus theory **04**
- (iii) Describe the kinetics of free radical chain polymerization **04**
- (iv) Give the mechanism of decomposition of ozone. **04**

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

- (i) In the following reaction scheme, write the rate equation for the removal of species A, B, C and D in the differential form. **04**



- (ii) The molecular diameters of  $O_2$  and  $H_2$  gases are  $2.59 \times 10^{-10} \text{ m}$  and  $1.67 \times 10^{-10} \text{ m}$  respectively. Calculate the number of collisions in  $\text{m}^{-3}\text{s}^{-1}$ , when 1.0 g of  $O_2$  and 0.1 g of  $H_2$  are mixed in one  $\text{dm}^3$  flask at 300K. **04**

**Q.4 (A)** Attempt any **two** of the following.

- (i) Describe the kinetics of enzyme inhibition by uncompetitive inhibition method. **04**

(ii) Derive mathematical expression for Lineweaver- Burk equation of enzyme catalysed 4 reaction.

- (iii) Derive Hammett equation. Explain how this equation is considered as a linear free energy relationship? **04**

(iv) Obtain the first order rate law for the reaction of a gas on the surface of solid particles. **04**

(B) Attempt any **one** of the following.

- (i) Deduce an expression for the contracting area rate law for reactions in solid particles. **04**

(ii) Give mathematical relation between rate constant and dielectric constant of medium in an elementary reaction in solution. **04**

Q.5) Attempt **any four** of the following:

12

- a) If  $\psi = e^{ix}$  and  $\phi = \sin x$  then show that the operator  $d^2/dx^2$  is Hermitian.  
 b) Normalise the following wave function and find the value of A

$$\psi = A \sin \left[ \frac{2\pi x}{L} \right] \quad \text{in the range } 0 < x < L$$

- c) Write the  $\phi$  equation,  $\theta$  equation and  $R$  equation from the three separate variables of Schrodinger equation in terms of spherical coordinates.  
 d) Transfer the Cartesian coordinates  $(x, y, z)$  to polar coordinates  $(r, \theta, \phi)$   
 (e) Explain consecutive reactions with examples.  
 (f) Give general characteristics of chain reactions.  
 (g) Discuss the factors affecting on kinetics of solid-state reactions.  
 (h) Write a note on effect of pH on inhibition of enzyme action.

-----X-----