

(2½ Hours)

[Total Marks : 60

- N.B. : (1) All questions are compulsory.
(2) Figures to the right indicate full marks.
(3) Uses of non-programmable scientific calculator is allowed.

Useful constants

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

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

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$H = 1 \text{ amu}$$

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

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

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

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

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

$$I = 127 \text{ amu}$$

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

- (a) For a particle of mass 'm' moving in a cubical box of side 'a', write the expression for energy of the particle. With the help of suitable examples, explain degenerate and non-degenerate energy levels. 4
- (b) State the postulates of quantum mechanics. 4
- (c) Obtain Schrödinger wave equation as the eigen value equation of the Hamiltonian operator. 4
- (d) Using the classical expression for $V = \frac{1}{2}kx^2$ (potential energy) 4

and $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$ (oscillation frequency) and the definitions

$$\alpha = \frac{8\pi^2 mE}{h^2} \text{ and } \beta = \frac{4\pi^2 m\nu}{h}$$

Write the Schrodinger equation and obtain its asymptotic solution.

(B) Attempt any one of the following :

- (a) Which of the following are eigen function of the operator $\frac{d^2}{dx^2}$. 4

Find the eigen values of the same.

(i) $\cos \frac{x}{4}$

(ii) $\sin 4x$

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- (b) Find the degree of degeneracy of energy levels (i) $\frac{17h^2}{8ma^2}$ (ii) $\frac{19h^2}{8ma^2}$ for a particle in cubical box.

2. (A) Attempt any two of the following :

- (a) Discuss the angular probability distribution for p-orbitals.
 (b) Obtain the solution for the following "Azimuthal wave equation -

$$\text{constant} + \frac{1}{F} \frac{d^2F}{d\phi^2} = 0$$

- (c) Explain the term 'spherical harmonics' and discuss its physical representation.
 (d) For a two electron system write the Hamiltonian operator. Identify the kinetic energy and potential energy operator terms in it. Also explain why is it called an 'independent electron model'.

(B) Attempt any one of the following :

- (a) The radial wave function for 2s orbital of hydrogen atom is given

by $R_{20} = N \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}}$, N is a constant. Determine the number of

node in 2s wave function. Write down the expression for radial distribution function of a 2s electron. Also find the distance of the node from the nucleus.

- (b) The internuclear distance in HI molecule is 163 pm. Calculate the energy of the first rotational level.

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

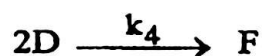
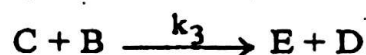
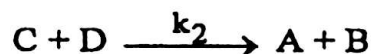
- (a) Explain the term -
 (i) Collision frequency factor (ii) Steric factor.
 (b) Hydrogen reacts with bromine to give hydrogen bromide according to the reaction $H_2 + Br_2 \xrightarrow{h\nu} 2HBr$ Using chain reaction mechanism, obtain the rate law equation for the same.
 (c) Describe the effect of pressure and temperature on the rate of an explosion reaction with the help of a suitable example.
 (d) Explain Rice-Ramsperger-Kassel-Marcus theory.

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(B) Attempt any one of the following :

(a) In the following reaction scheme, write the rate equation for the removal of species A, B, C, and D in the differential form. 4



(b) In a bimolecular reaction, the energy of activation is 180 kJ mol^{-1} at 550K . Calculate the specific reaction rate at 550K . The number of molecules colliding per cc per sec are 6×10^{31} . 4

4. (A) Attempt any two of the following :

(a) Derive Hammett equation of linear free energy relationship for reactions in solutions. 4

(b) Discuss the kinetics of diffusion - controlled reactions in solutions. 4

(c) Derive an expression for contracting volume rate law for reactions in solid state. 4

(d) Discuss the kinetics of reactions in the solid state deriving first order rate law. 4

(B) Attempt any one of the following :

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

(b) Explain with the help of suitable example how certain metal ion can enhance activity of certain enzyme. 4

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5. Attempt any four of the following :

- (A) The general solution for wave function of a particle in one dimensional box is 3
 $\psi = A \sin kx + B \cos kx$
Determine the values of A, B and k.
- (B) State and prove any one theorem of Hermitian operator. 3
- (C) Explain in general the significance of radial probability distribution curves. 3
- (D) With the help of a suitable diagram, give the relationship between cartesian and spherical coordinates. 3
- (E) Give the limitations of collision theory. 3
- (F) Explain the principle of microscopic reversibility. 3
- (G) Starting with Michaelis - Menten equation show that the rate and order of an enzyme catalysed reaction depends upon the concentration of the substrate. 3
- (H) Discuss the various factors affecting reactions in solids. 3
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