(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

$c = 2.998 \times 10^{8}\ ms^{-1}$	$e = 1.602 \times 10^{-19}C$
$R = 8.314\ JK^{-1}\ mol^{-1}$	$k = 1.3811 \times 10^{-23}\ JK^{-1}$
$h = 6.626 \times 10^{-34}Js$	$1J = 6.24 \times 10^{18}eV$
$m_e = 9.110 \times 10^{-31}kg$	$1eV = 8.06 \times 10^{3}cm^{-1}$
$N_A = 6.023 \times 10^{23}mol^{-1}$	$1\ amu = 1.66 \times 10^{-27}kg$
$H = 1\ amu$	$I = 127\ amu$

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 Schrodinger 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) and $\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ (oscillation frequency) and the definitions $\alpha = \frac{8\pi^2 mE}{h^2}$ and $\beta = \frac{4\pi^2 m\upsilon}{h}$. **4**

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. 4

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

(a) Discuss the angular probability distribution for p-orbitals. 4

(b) Obtain the solution for the following "Azimuthal wave equation - 4

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

(c) Explain the term 'spherical harmonics' and discuss its physical representation. 4

(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'. 4

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

(a) The radial wave function for 2s orbital of hydrogen atom is given by $R_{20} = N\left(2 - \frac{r}{a_o}\right)e^{-\frac{r}{2a_0}}$, 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. 4

(b) The internuclear distance in HI molecule is 163 pm. Calculate the energy of the first rotational level. 4

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

(a) Explain the term - 4

(i) Collision frequency factor (ii) Steric factor.

(b) Hydrogen reacts with bromine to give hydrogen bromide according to the reaction $H_2 + Br_2 \xrightarrow{h\upsilon} 2HBr$ Using chain reaction mechanism, obtain the rate law equation for the same. 4

(c) Describe the effect of pressure and temperature on the rate of an explosion reaction with the help of a suitable example. 4

(d) Explain Rice-Ramsperger-Kassel-Marcus theory. 4

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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

$$A + B \xrightarrow{k_1} C + D$$

$$C + D \xrightarrow{k_2} A + B$$

$$C + B \xrightarrow{k_3} E + D$$

$$2D \xrightarrow{k_4} F$$

(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

5. Attempt any four of the following :

(A) The general solution for wave function of a particle in one dimentional box is $\psi = A\sin kx + B\cos kx$ Determine the values of A, B and k. 3

(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
