Q.P. Code : 24433

(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

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

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

(a) Write the Schrodinger wave equation for a particle in one dimensional box and obtain an energy expression for the same. Why is the value for quantum number n = 0 not permitted? **4**

(b) Formulate the Schrodinger wave equation for a particle of mass 'm' and wavelength 'λ' having motion in three dimensions. **4**

(c) What is the condition for orthogonality of wave functions? Show that two normalised wave functions ψ_1 and ψ_2 are orthogonal to each other. **4**

(d) Show that the probability of finding a free particle in limitless space at all points is the same. **4**

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

(a) The Hermite polynomials are derived from the 'generating function'. **4**

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

Calculate the polynomial for n = 1 and n = 2. **4**

(b) For a particle of mass 'm' moving in a cubical box of side 'a', calculate the degeneracy of the level corresponding to the energy

(i) $E = \frac{18h^2}{8ma^2}$ (ii) $E = \frac{21h^2}{8ma^2}$

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

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

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

(b) Explain why a two electron system can also be called "an independent electron model". 4

(c) On the basis of angular probability distribution curves, explain the shapes of s-orbital. 4

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

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

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

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

(a) Calculate the values for the first three rotational energy levels of a rigid rotor, whose moment of inertia is 1.457×10^{-46} kgm^2. 4

(b) Calculate the most probable distance of an electron from the nucleus in ground state of hydrogen atom. The normalised ground state function is $\psi_{1s}=\frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-\frac{r}{a_0}}$ 4

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

(a) What is collision number? Explain why the observed rate of bimolecular polymerisation of ethylene is much lower than predicted by collision theory. 4

(b) Explain the kinetics of free radical chain polymerisation. 4

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

(d) Give a brief account of Rice-Ramsperger - Kassel theory. 4

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

(a) A bottle of milk stored at 30°C sours in 36 hours, stored in a refrigerator at 5°C sours after one week. Assuming the rate constant to be inversely related to the souring time, estimate the activation energy of a chemical reaction involved in souring process. 4

(b) The molecular diameters of O_2 and H_2 gases are 3.39×10^{-10}m and 2.47×10^{-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 one dm^3 flask at 300 K. 4

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

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

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

(c) Derive an expression to show the effect of dielectric constant on the rate of reaction between ions in solution. 4

(d) Derive Hammett equation to show the effect of substituents on the reaction rates. 4

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

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

(b) Derive the Michaelis - Menten equation of enzyme catalysed reaction. 4

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

(A) With the help of suitable example, explain the terms eigen function and eigen value. 3

(B) "Eigen values of Hermitian operator are real". Prove. 3

(C) Write the expression for potential energy of hydrogen like system. Why is it characterised by spherically symmetric potential energy? 3

(D) Name the four quantum numbers required to specify the state of an electron in an atom. Give their allowed values and significance in general. 3

(E) Explain consecutive reactions with suitable examples. 3

(F) Explain free radical mechanism of polymerisation of ethylene. 3

(G) Explain how Lineweaver - Burk plot is used for analysing the rate data of enzyme catalysed reactions. 3

(H) Write a note on factors affecting reactions in solids. 3
