(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	$= 8.314 JK^{-1}mol^{-1}$	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	$= 6.022 \times 10^{23} mol^{-1}$	1amu	$= 1.66 \times 10^{-27} kg$

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

(i) Obtain the time independent Schrodinger wave equation for a particle in two dimensional box. **4**

(ii) What are the characteristics of a well behaved function? Indicate which of the following wave functions are acceptable. **4**

(i) $\psi = e^{-x^2}$ (ii) $\psi = \tan x$

(iii) What do you mean by degeneracy of energy levels? Determine the degree of degeneracy of the energy level $\frac{38h^2}{8ma^2}$ **4**

(iv) For Hermite's differential equation **4**

$$\frac{d^2F}{dy^2} - 2y\frac{dF}{dy} + \left(\frac{2\alpha}{\beta} - 1\right)F = 0$$

Obtain the recursion formula.

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

(i) Consider an electron moving in a one dimensional box of $3A^0$ width. Calculate the transition in energy when an electron jumps from second orbit to first orbit. Also calculate the wavelength of the emitted radiation. **4**

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(ii) The Hermite polynomials are derived from the generating functions. 4

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

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

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

(i) Explain the application of Schrodinger wave equation to two electron system. 4

(ii) Sketch qualitatively the probability density curve for Is, 2s and 3s orbitals. Also mention the number of nodes in each case. 4

(iii) Write the Schrodinger wave equation in terms of spherical coordinates. Why is it necessary to convert Schrodinger wave equation from cartesian coordinates to spherical coordinates? Give the limits of variation for x, y, z, r, θ, ϕ. 4

(iv) What are quantum numbers? Explain the significance of magnetic quantum number. 4

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

(i) The energy expression for an electron in a rigid rotator is given by the expression $E_M = \frac{M^2h^2}{8\pi^2 mr^2}$ where M is rotational quantum number. Calculate the first three energy levels using the above equation for the electron rotating in a circular orbit of radius $0.5A^0$. 4

(ii) Calculate the most probable distance of an electron from the nucleus in ground state. The function is 4

$$\Psi_{IS} = \frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$$

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

(i) Give a brief account of the Lindemann-Hinshelwoods theory of unimolecular reactions in gas phase. 4

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(ii) Show that the rate of polymerization reaction is proportional to the square root of its initial concentration of the monomer. 4

(iii) H_2 reacts with Br_2 to give HBr according to the reaction $H_2 + Br_2 \xrightarrow{205-302^0C} 2HBr$. Using the chain reaction mechanism, obtain the rate equation for the above thermal reaction. 4

(iv) Using the following reaction mechanism for the decomposition of acetaldehyde: 4

$$CH_3CHO \xrightarrow{k_1} \bullet CH_3 + \bullet CHO$$
$$\bullet CH_3 + CH_3CHO \xrightarrow{k_2} \bullet CH_4 + \bullet CH_2CHO$$
$$\bullet CH_2CHO \xrightarrow{k_3} \bullet CH_3 + CO$$
$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_4} CH_3CH_3$$

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

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

(i) Consider a bimolecular gaseous reaction between like molecules with collision diameter d = 200 pm ; mass M = 100 g mol^{-1} and a steric factor p = 1.00 . Calculate the Arrhenius pre-exponential factor A in $dm^3\ mol^{-1}s^{-1}$ at (1) 100°C and (2) 200°C if it is related to the other four parameters by the constant 3.893 x 10^{29} .What is the percentage increase of A between this range of temperature? 4

(ii) The following process follows the first order kinetics 4

$x \xrightarrow{22.5d} y \xrightarrow{33.0d} z$ where the times are the half lives of the reaction in days. At what stage of time will the concentration of y become maximum?

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

(i) Derive an expression to show the influence of ionic strength on rate of the reaction between ions in solution. 4

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(ii) Discuss the effect of substituent on reaction rates using Hammet relationship. 4

(iii) Derive Michaelis -Menten equation for reactions catalysed by enzymes. 4

(iv) Discuss the kinetics of enzyme inhibition by noncompetitive inhibition method. 4

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

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

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

5. Attempt any **four** of the following : 12

(a) Show that the eigen value of a Hermitian operator is real.

(b) Which of the following are eigen function of the operator d^2/dx^2 ?

(i) cos 4x (ii) $3x^3$

(c) Write the expression for radial wave function for 2p and 3d orbitals.

(d) Explain the statement 'There is an equal chance of finding 1s electron in any direction with respect to nucleus.'

(e) Explain the three explosion limits of a non-stationary chain reaction.

(f) Explain the terms:

(i) collision frequency factor

(ii) reaction cross section.

(g) Discuss the factors which affect the reactions in solid state.

(h) Predict the effect of increase in ionic strength on the rate constant for each of the following reactions :

(i) $H_2O_2 + 2Br^- + 2H^+ \rightarrow$ Products

(ii) $CH_2ICOOH + CNS^- \rightarrow$ Products

(iii) $S_2O_8^{2-} + 2I^- \rightarrow$ Products
