2023

CHEMISTRY — HONOURS

Paper : CC-11

(Physical Chemistry - 4)

Full Marks : 50

The figures in the margin indicate full marks.

*Candidates are required to give their answers in their own words
as far as practicable.*

Answer *question no.* 1 and *any eight* questions from the rest.

1. Answer *any ten* questions :

    1×10

    (a) Find out the average amplitude of oscillation $<x>$ of a harmonic oscillator in its ground state

    $$\left(given\ \psi_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}}\right).$$

    (b) What approximation method do we choose to solve a many-electron problem and why is it necessary?

    (c) "The angular momentum operators $\widehat{L_x}$, $\widehat{L_y}$ and $\widehat{L_z}$ commute with each other."— Comment on the statement.

    (d) How do cannonical and grand cannonical ensembles differ? Which type of systems do they describe?

    (e) Name one paramagnetic salt that is generally used in the adiabatic demagnetization process.

    (f) How would you define partition function of a system in a phase space?

    (g) Why Trapezoidal rule is called so?

    (h) "Though Newton-Raphson method converges rapidly, it requires more computing time."— Comment of the statement.

    (i) Write down the potential energy $V(r)$ operator of a central force problem like Hydrogen atom.

    (j) Can Maxwell-Boltzmann statistics to be applied to a system of real gas?— Explain.

    (k) Why can not temperature below 1 Kelvin be obtained using liquid Helium?

    (l) Write the expression of the Hamiltonian operator of the Helium atom in atomic unit.

Please Turn Over

2. (a) Find out the normalising factor of the wave function (ψ_1) of a harmonic oscillator at $v = 1$ level. Also show that ψ_0 and ψ_1 of a harmonic oscillator are orthogonal.

[Given : $\psi_0(x) = \left(\dfrac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{\frac{-\alpha x^2}{2}}$; $\psi_1(x) = A.x.e^{\frac{-\alpha x^2}{2}}$, where A is the normalization constant.

Integration $\displaystyle\int_0^\alpha x^{2n} e^{-\alpha x^2} dx = \dfrac{(2n)!}{2^{2n+1} \cdot n!} \left(\dfrac{\pi}{\alpha^{2n+1}}\right)^{\frac{1}{2}}$, $\alpha > 0$ where n is a positive integer].

(b) Calculate the $\left\langle p_x^2 \right\rangle$ for harmonic oscillator in its ground state. 3+2

3. (a) Express the $\widehat{L^2}$ and $\widehat{L_y}$ in spherical polar coordinate and show whether they are simultaneously accurately measurable or not.

(b) Using the expression of $\widehat{L^2}$, find out the kinetic energy of a rigid rotator having the wave function

$$Y_1^1(\theta, \phi) = \left(\dfrac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{i\phi} .$$ 3+2

4. (a) Find out the probability density of finding the 1s electron of Hydrogen atom (with wave function

$\dfrac{1}{\sqrt{\pi}} \left(\dfrac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$) at the nucleus and at the first Bohr orbit a_0.

(b) Find out the probability of finding the 1s electron in the first Bohr orbit and at a distance of $1 \times 10^{-4} \, a_0$ from the nucleus. Comment on the result. 2+3

5. (a) Considering a trial wavefunction for the particle in a box (PIB) problem to be $\phi = x(L - x)$.

With appropriate boundary conditions, the Hamiltonian being $\hat{H} = -\dfrac{\hbar^2}{2m} \dfrac{\partial^2}{\partial x^2}$, the box being 1-D, find the expected ground state energy expression, where 'L' is the length of the 1-D box.

(b) What are the properties to be considered when we choose the trial wave function for a one-dimensional (PIB) box? 3+2

6. (a) State the Born-Oppenheimer approximation as used in LCAO method.

(b) State limitations of the LCAO-MO and V_B treatments of Hydrogen (3 each). 2+3

7. Show that the two maxima of $r^2 \psi_{2s}(r)$ against r occur at $\left(3 \pm \sqrt{5}\right)a_0$. Find the nodal point for the radial distribution for ψ_{2s} wavefunction.

    Given : $\psi_{2S} = \sqrt{\dfrac{1}{32\pi}} \cdot \left(\dfrac{1}{a_0}\right)^{\frac{3}{2}} \cdot \left(2 - \dfrac{r}{a_0}\right) e^{-\frac{r}{2a_0}}.$ 5

8. (a) Calculate the value of ln5! with and without Sterling's approximation. Comment on the result.

    (b) For a system having three energy levels 0, ϵ and 2ϵ, where $\epsilon = 4.267 \times 10^{-14}$ erg, find out the probability function $\left(\dfrac{1}{z}\right)$ at 300 K, 400 K and 800 K. Interpret the results. (where z = partition function)   2½+2½

9. (a) Calculate the thermodynamic probabilities of arranging 6 classical particles among three energy levels having configurations (6,0,0), (5,1,0), (4,1,1), (3,2,1), (2,2,2) and (4,2,0). Show clearly which configuration will be the most dominating configuration.

    (b) Could you guess the above answer without doing any calculation? Explain.   3+2

10. (a) For a system the available energy levels are 0, ϵ, 2ϵ and 3ϵ, where $\epsilon = 4.14 \times 10^{-21}$ erg and the degeneracy of the levels are 1,1,3,5 respectively. Find out the molecular partition function at 300 K.

    (b) At what altitude, the atmospheric pressure gets reduced to its $\dfrac{1}{4}$ th? [Assume average value of temp = 250 K and the average molar mass = 0.029 kg mol^{-1}]   3+2

11. (a) One mole of an ideal gas is allowed to expand at 300 K from 1 lit to 5 lit. Find out the magnitude of the Boltzmann constant k.

    (b) In an experiment, the ratios of the number of molecules in the excited levels with respect to the ground level are given below :

$\epsilon_i - \epsilon_0$	$5 \cdot 52 \times 10^{-21}$ J	$1 \cdot 104 \times 10^{-20}$ J	$1 \cdot 104 \times 10^{-19}$ J
$n_i - n_0$	$0 \cdot 368$	$0 \cdot 135$	$2 \cdot 06 \times 10^{-9}$

    Calculate the temperature of the system applying Boltzmann distribution law.   2½+2½

12. (a) Evaluate $I = \displaystyle\int_0^1 \dfrac{1}{1+x} dx$ correct to three decimal places, using $h = 0.5$ using both Trapezoidal and Simpson rules.

    (b) Comment on the accuracy of these two rules. (Given the exact value of the integral = 0.693147)   3+2

Please Turn Over

13. Determine the constants 'a' and 'b' by the method of least squares such that $y = a.e^{bx}$ fits the following sets of data : 　　　　　　　　　　　　　　　　　　　　　　　　　5

x	2	4	6	8	10
y	4·077	11·084	30·128	81·897	222·62