B.Sc

2024

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) Show that $\left[\widehat{L_x}, \widehat{L_y}\right] = i\hbar\widehat{L_z}$.

(b) "2s and 2p orbitals of Hydrogen atom have same energy."— Justify or Criticize.

(c) Write down the Schrödinger equation for 'He' atom clearly mentioning the terms involved.

(d) For which molecular phenomenon, does the simple harmonic oscillator serve as a model?

(e) Determine the bond order of He_2^+.

(f) In valence bond treatment of H_2, choose the correct option :

(i) $H_{22} = H_{11}$ (ii) $H_{12} = H_{21}$

(iii) $S_{22} = S_{11}$ (iv) All of (i), (ii) and (iii).

(g) Which thermodynamic state function of the system is directly related to the maximum value of probability?

(h) Calculate the thermodynamic probability for a distribution in which three identical but distinguishable particles are evenly distributed across three energy levels.

(i) State the principle of equal a priori probabilities in statistical thermodynamics.

(j) Identify Canonical and Grand Canonical Ensemble from (i) and (ii).

Feature	(i)	(ii)
Constant	T, V, μ	T, V, N
Fluctuating Parameter	E, N	E

(k) For what order of polynomials does the Simpson's $\frac{1}{3}$rd rule furnish an exact value of the integral?

(l) "Convergence of Newton-Raphson method depends on a good guess value of the root."— Explain.

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2. The wave function for the state of lowest energy of a one-dimensional harmonic oscillator is $\psi = Ae^{-Bx^2}$, where A is a normalization constant and $B = \frac{1}{2\hbar}(\mu K)^{1/2}$. The potential energy for the oscillator, $V(x) = \frac{1}{2}Kx^2$.

(a) Write the Schrödinger equation for the system.

(b) Show that the total energy E of the lowest state is $\frac{1}{2}h\nu$, where $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$ and $\hbar = \frac{h}{2\pi}$. 2+3

3. For a one-dimensional harmonic oscillator; $\langle x\rangle = 0, \langle p\rangle = 0, \langle x^2\rangle = \frac{h}{(\mu k)^{1/2}}\left(v+\frac{1}{2}\right)$ and $\langle p^2\rangle = h(\mu k)^{1/2}\left(v+\frac{1}{2}\right)$, the terms with their usual significance.

(a) Compute Δx and Δp.

(b) Show that the results obey the uncertainty principle. 3+2

4. The wave function for 1s orbital for a hydrogen atom is $\Psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$, where a_0 = Bohr radius.

Depict graphically the plots of (i) Ψ against r, (ii) $4\pi r^2\Psi^2$ against r and explain the graphs. 1+1+3

5. Using the method of separation of variables, break up the Schrödinger equation for a rigid rotator into ordinary angular equations. Discuss the nature and characteristics of the ϕ part of the solution. 3+2

6. For a particle in an infinitely deep one-dimensional potential box of length L, apply the trial wave function

$$\psi = Nx\left(L^2 - x^2\right),\ L \text{ is the length of the 1D-box}$$

to calculate the energy. Which wave function does this wave function approximate to? 3+2

7. Consider the simplest molecular orbital treatment of H_2^+, show that the molecular orbital corresponding to energy E_+ is,

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(1S_A + 1S_B)$$

and that corresponding to energy E_- is,

$$\psi_- = \frac{1}{\sqrt{2(1-S)}}(1S_A - 1S_B),$$

where terms have their usual meaning. 5

8. Derive the Boltzmann distribution equation

$$\frac{N_i}{N} = \frac{e^{-\beta\varepsilon i}}{q}$$

where, $\beta = \frac{1}{kT}$ and q is the partition function and other terms with their usual significance. 5

9. (a) Explain the principle of adiabatic demagnetization using a suitable labelled diagram.

(b) Calculate the weight of the configuration in which 16 objects are distributed in the arrangement 0, 1, 2, 3, 8, 0, 0, 0, 0, 2. 3+2

10. (a) What is the physical significance of the partition function? Explain your answer mentioning the values of the partition function for the cases $\lim_{T\to 0}$ and $\lim_{T\to\infty}$.

(b) Derive a relation connecting the entropy of a system with its partition function. 3+2

11. (a) Draw a curve showing the variation of entropy when a solid (at temperature T) is heated to form vapour (at temperature T', $T' >$ boiling point). Write an expression to find the absolute entropy of the substance in the vapour phase at temperature T'.

(b) ΔG for a reaction as a function of temperature (T) for low value of T (T approaching zero Kelvin) is given by $\Delta G = a + bT + cT^2$.

Show that $\underset{\lim T\to 0}{\Delta G} = \underset{\lim T\to 0}{\Delta H} = a.$ 3+2

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12. (a) The concentration of a reactant A is monitored over time during a reaction. The following data is recorded :

Time $t(s)$	0	10	20	30	40	50
Concentration $[A]$(mol/L)	1	0.82	0.68	0.55	0.45	0.37

Use *forward*, *backward* and *central* difference formulas to numerically estimate the reaction rate at $t = 20$s.

(b) Estimate the value of 'γ' and 'c' by performing least squares fit of the equation $PV^{\gamma} = c$ to the given data :

P(atm)	1.13	2.70	5.34	7.86	13.29
V(L)	0.82	0.49	0.33	0.25	0.16

2½+2½

13. Consider the chemical reaction described by the equation,

$$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$$

at a certain temperature T. If 100 mol of NOCl(g) is introduced into a reaction vessel, the pressures at equilibrium obey the equation,

$$\frac{p_{NO}^2 \cdot p_{Cl_2}}{p_{NOCl}^2} = 2.18, \text{ where } k_p = 2.18$$

Solve the equation to obtain p_{Cl_2} at equilibrium using Newton-Raphson method up to four significant figures. Consider the initial guess of p_{Cl_2} as 0.25. 5