

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  $[\widehat{L}_x, \widehat{L}_y] = i\hbar \widehat{L}_z$ .
- (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  $\text{He}_2^+$ .
- (f) In valence bond treatment of  $\text{H}_2$ , choose the correct option :
- (i)  $\text{H}_{22} = \text{H}_{11}$  (ii)  $\text{H}_{12} = \text{H}_{21}$
- (iii)  $\text{S}_{22} = \text{S}_{11}$  (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, $\mu$	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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(0527)

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;  $\langle x \rangle = 0$ ,  $\langle p \rangle = 0$ ,  $\langle x^2 \rangle = \frac{h}{(\mu k)^{1/2}}\left(\nu + \frac{1}{2}\right)$  and

$$\langle p^2 \rangle = h(\mu k)^{1/2}\left(\nu + \frac{1}{2}\right), \text{ the terms with their usual significance.}$$

(a) Compute  $\Delta x$  and  $\Delta p$ .

(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)  $\Psi$  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  $\phi$  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

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

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

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

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  $\lim_{T \rightarrow 0}$  and  $\lim_{T \rightarrow \infty}$ .  
 (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)  $\Delta G$  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  $\lim_{T \rightarrow 0} \Delta G = \lim_{T \rightarrow 0} \Delta H = a.$

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 $[A](\text{mol/L})$	1	0.82	0.68	0.55	0.45	0.37

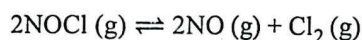
Use *forward*, *backward* and *central* difference formulas to numerically estimate the reaction rate at  $t = 20\text{s}$ .

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

$P(\text{atm})$	1.13	2.70	5.34	7.86	13.29
$V(\text{L})$	0.82	0.49	0.33	0.25	0.16

$2\frac{1}{2}+2\frac{1}{2}$

13. Consider the chemical reaction described by the equation,



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

$$\frac{p_{\text{NO}}^2 \cdot p_{\text{Cl}_2}}{p_{\text{NOCl}}^2} = 2.18, \text{ where } k_p = 2.18$$

Solve the equation to obtain  $p_{\text{Cl}_2}$  at equilibrium using Newton-Raphson method up to four significant figures. Consider the initial guess of  $p_{\text{Cl}_2}$  as 0.25.

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