

2025

## CHEMISTRY — HONOURS

Paper : DSCC-11

(Physical Chemistry - III)

Full Marks : 75

*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 nos. 1, 2, 3 and 4** (compulsory) and **any four** questions from the rest (**question nos. 5 to 10**).1. Answer **any ten** questions :

2×10

- (a) What do you mean by linear operator? Determine whether  $\frac{d^2}{dx^2}$  is linear or non-linear.
- (b) What do you mean by normalization of wave function? Why normalization is necessary?
- (c) Under what condition will the following equation be applicable in case of operator algebra :

$$(\hat{A} + \hat{B})^2 = \hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2$$

(d)

|                  | Microscopic body | Macroscopic body |
|------------------|------------------|------------------|
| mass (kg)        | $10^{-30}$       | 10               |
| velocity (km/hr) | 10               | 10               |

Using the de Broglie hypothesis, compare the wavelengths associated with the above macroscopic and microscopic bodies. Comment on the significance of the difference in their wavelengths.

- (e) Given a wave represented by  $\psi(x,t) = Ae^{i(kx-\omega t)}$ , write down the expression of its phase velocity and group velocity.
- (f) What do you mean by 'classically forbidden region'?
- (g) Consider the box potential  $V(x) = \begin{cases} 0 & (0 < x < L) \\ \alpha & (\text{elsewhere}) \end{cases}$ . An electron is moving in a box of size  
(i)  $L = 10^{-10}$  cm and (ii)  $L = 10$  cm. Discuss how quantum effects differ in these systems.
- (h) How does the probability of tunneling depend on the height and width of the potential barrier?
- (i) How will you distinguish a polar molecule from non-polar molecule using the temperature variation of molar polarization?

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- (j) During the coagulation of a given sol,  $\text{Al}(\text{NO}_3)_3$  was found to be far more effective than  $\text{NaNO}_3$ . Explain the reason for this difference in coagulating power.
- (k) How does a lyophilic colloid help in stabilizing a lyophobic colloid?
- (l) Give labelled diagram of adsorption isotherms, where (i) monolayer adsorption (ii) multilayer adsorption is taking place on non-porous solid surfaces.
2. (a) Write a short note on Black Body radiation covering the following points :
- Diagram for the distribution of the intensity of radiation emitted by a black body against wavelength at two different temperatures  $T_1$  and  $T_2$  where,  $T_1 > T_2$ .
  - Rayleigh Jean's Law clearly mentioning what is 'ultraviolet catastrophe'.
  - Expression for Planck's Distribution Law including the assumptions involved. Explanation of the distribution curve at a given temperature using Planck's law.  $(\frac{1}{2}+\frac{1}{2})+(1+1)+(1+1)$

**Or**

- (b) Write a short note on acceptable wave functions covering the following points :
- Physical significance of  $\psi^2$ . Conditions for acceptable wave function.
  - Orthonormal wave functions.
  - The functions  $\phi(\theta) = (2\pi)^{-1/2} e^{in\theta}$ , over range  $0 \leq \theta \leq 2\pi$  is orthonormal, where  $n$  is an integer.  $(1+1)+1+2$
3. (a) Write a short note on the system of a free particle based on the following points :
- Meaning free particle.
  - Schrödinger equation for a free particle and comparison with that of a particle bound in a one-dimensional box.
  - Comparison of their wave functions and energy values.  $1+2+2$

**Or**

- (b) Write a short note considering a particle in a finite potential well, such that

$$V(x) = \begin{cases} V_0, & x < -a \\ 0, & -a < x < a \\ V_0, & x > a \end{cases}$$

- Schrödinger equations of the particle in the above three regions.
  - Solutions of Schrödinger equations in the three regions, if  $0 < E < V_0$ .  $2+3$
4. (a) Write a short note on Langmuir Adsorption Isotherm covering the following points :
- Assumptions involved (*any two*).
  - Mathematical derivation for the expression of the adsorption isotherm.
  - Comparison of the experimental isotherm with the derived mathematical form.  $1+2+2$

Or

(b) Write a short note on micelles covering the following points :

(i) Amphiphilic nature of surfactants and structure of micelles.

(ii) Micellization equilibrium.

(iii) Thermodynamics of micellization process.

2+1½+1½

5. (a) Write the Gibb's adsorption isotherm explaining the terms involved. Give the diagram representing the variation of surface tension ( $\gamma$ ) versus concentration for a strong electrolyte and a weak electrolyte. Show how you can determine surface excess for these electrolytes using the Gibb's adsorption isotherm.

(b) An electron is confined in a molecule of length 2 nm. Calculate the minimum energy of electron and also calculate its first excitation energy. [Given :  $m_e = 9.11 \times 10^{-31}$  kg]

(c) If  $\psi_1$  and  $\psi_2$  are non-degenerate eigenfunctions of a hermitian operator ( $\hat{\alpha}$ ) and given

$$\hat{\alpha}|\psi_1\rangle = a_1|\psi_1\rangle$$

$$\hat{\alpha}|\psi_2\rangle = a_2|\psi_2\rangle$$

where  $a_1$  and  $a_2$  are eigenvalues of  $\psi_1$  and  $\psi_2$  respectively. Show that  $\langle\psi_1|\psi_2\rangle = 0$ .

(1½+1+1½)+(1½+1½)+3

6. (a) Use a properly labelled diagram to illustrate the 'Compton effect'. Determine the value of 'Compton wavelength'.

(b) Explain three major differences between micelles and reverse micelles based on molecular arrangement, solvent environment and solubilization behaviour.

(c) Compute the commutators  $[\hat{x}, \hat{p}_x]$  and  $[\hat{x}, \hat{p}_y]$ . Explain the physical significance of your result.

(2+2)+3+3

7. (a) Consider the wave function  $\psi_n(x) = A \sin\left(\frac{n\pi x}{a}\right)$ ,  $0 < x < a$  and  $n = 1, 2, 3 \dots$

(i) Examine whether  $\psi_1(x)$  function is an eigenfunction of the operator  $\hat{O}_1 = \frac{d^2}{dx^2}$  and  $\hat{O}_2 = x^2$ . In each case, justify or criticize your conclusion and determine the corresponding eigenvalue when applicable.

(ii) Demonstrate that the two wave functions  $\psi_1(x)$  and  $\psi_2(x)$  are mutually orthogonal.

(b) A surface-catalysed reaction is generally explained as taking place through five sequential steps. List these steps and briefly describe what happens in each stage of the process.

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(c) A particle of energy  $E$  is incident from the left on a rectangular potential barrier of height  $V_0$  ( $V_0 < E$ ) extending from  $x = 0$  to  $x = L$ . The space is divided into three regions : Region I ( $x < 0$ ,  $V(x) = 0$ ), Region II ( $0 < x < L$ ,  $V(x) = V_0$ ), and Region III ( $x > L$ ,  $V(x) = 0$ ). Draw a fully labelled diagram showing :

- (i) the potential-energy function  $V(x)$  in the three regions and the boundaries at  $x = 0$  and  $x = L$ .
- (ii) all possible wave components (incident, reflected, transmitted and the two inside the barrier) with appropriate exponential forms of the wave functions in each region.
- (iii) the directions of propagation using arrows. (2+2)+3+3

8. (a) For a particle in a 1D box of length ' $L$ ', determine the uncertainty in position,  $\Delta x$ .

(b) Consider the two Kets :

$$|\psi\rangle = \begin{pmatrix} -3i \\ 2-i \\ 6 \end{pmatrix}, |\phi\rangle = \begin{pmatrix} 3 \\ -i \\ 2+3i \end{pmatrix}$$

- (i) Find  $\langle\phi|\psi\rangle$ .
  - (ii) Evaluate the scalar product  $\langle\phi|\psi\rangle$ .
  - (iii) Examine why the products  $|\psi\rangle\langle\phi|$  makes no sense.
- (c) Write down the BET isotherm explaining the terms involved. How can you determine the surface area of a solid adsorbent using BET isotherm. 4+(1+1+1)+(1+2)

9. (a) Prove that, for any three operators  $\hat{A}, \hat{B}, \hat{C}$ ,

$$[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}].$$

Then evaluate  $[\hat{x}^n, \hat{p}_x]$ .

(b) Determine with proper explanation, whether the following are the acceptable wave functions :

- (i)  $\frac{1}{x}$  in the interval  $[-1, 1]$ .
  - (ii)  $e^{-x^2}$  in the interval  $[-\alpha, +\alpha]$ .
- (c) Decomposition of HI is a second-order reaction in absence of a catalyst. When the reaction is catalysed by a gold surface, it becomes first-order at low pressure and zero-order at high pressure. Explain. 4+3+3

10. (a) The wave function of a certain state of a system is the linear combination  $\psi = \sqrt{\frac{1}{4}}\phi_1 + \sqrt{\frac{3}{4}}\phi_2$ , where  $\phi_1$  and  $\phi_2$  are eigenfunctions of Hamiltonian operator with distinct eigenvalues  $E_1$  and  $E_2$  respectively. If  $\phi_1$  and  $\phi_2$  are orthonormal wave functions, find the expectation value for the energy of the system. Also find the probability of the energy of the system being (i)  $E_1$  and (ii)  $E_2$ .
- (b) Check whether  $-i\hbar\frac{\partial}{\partial x}$  is Hermitian or not.
- (c) The molar polarization of a substance is  $46 \text{ cm}^3 \text{ mol}^{-1}$  at  $25^\circ\text{C}$ . Calculate the dipole moment of the molecule if the distortion polarizability is  $1.808 \times 10^{-23} \text{ cm}^3$ . 4+3+3
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