

West Bengal State University
B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2012
Part - II

CHEMISTRY — HONOURS

Paper - IV A

Duration : 2 Hours

[Maximum Marks

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

The figures in the margin indicate full marks.

Answer any *three* questions taking *one* question from each Unit.

UNIT - I

1. a) Determine whether the following functions are acceptable or not as a wave function over the indicated intervals :

i) $\psi = \sin^{-1} x (-1, 1)$ ii) $\psi = e^{-x} (0, \infty)$ iii) $\psi = e^{-x^2} (-\infty, \infty)$

- b) Find the average distance [$\langle r \rangle$] of the electron from the nucleus of 1s state

a H-atom. [Given, $\psi_{1s} = \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} e^{-\frac{r}{a_0}}$]

- c) Calculate the de Broglie wavelength for an electron ($m_e = 9.1 \times 10^{-31}$ kg) having kinetic energy as 13.6 eV. (Given electronic charge = 1.6×10^{-19} coulomb).

- d) Find the value of the commutator $\left[\hat{x}, \hat{p}_x \right]$.

- e) What is photoelectric effect ? Draw a plot of kinetic energy for the ejected photoelectrons versus frequency of the incident radiation in a photoelectric experiment with three different metals. What inference regarding physical quantities may be drawn from the plot ?

2. a) The wave function for the state of lowest energy of a one-dimensional harmonic oscillator is $\psi = Ae^{-Bx^2}$, where A is normalisation constant and $B = \frac{1}{2h}(\mu k)^{\frac{1}{2}}$.

The potential energy of the oscillator $= \frac{1}{2}kx^2$. Write the Schrödinger equation

for the system and hence show that the total energy, E of the lowest state is

$$\frac{1}{2}h\gamma, \text{ where, } \gamma = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \text{ and } h = \frac{h}{2\pi}. \quad 4$$

- b) If ψ_1 and ψ_2 are two eigenfunctions of a quantum mechanical operation with same eigenvalue a , prove that any linear combination $c_1\psi_1 + c_2\psi_2$ is also an eigenfunction with the same eigenvalue. 2

- c) An operator (A) is defined as : $A = x \frac{d}{dx}$. Find A^2 . 2

- d) State Heisenberg uncertainty principle.

What is the uncertainty in the position of a bullet of 4 gm that is known to have a speed between 380.0001 ms^{-1} and 380.0000 ms^{-1} ? 1 + 2

- e) Show that the function $\psi = A \sin \frac{n\pi x}{L}$ is an eigenfunction of the energy operator for a particle in a one-dimensional box and hence find its energy. Calculate the average momentum of the particle in this state. 3 + 2

UNIT - II

3. a) Show that $\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i$. 2

- b) Starting from the Van't Hoff equation for a solid-vapour equilibrium, arrive at the Clausius-Clapeyron equation. 4

- c) Calculate the ionic strength of a solution obtained by mixing aqueous solutions of 50 ml of 0.02(M) AlCl_3 , 25 ml of 0.04 (M) K_2SO_4 and 50 ml of 0.02(M) urea at 25°C . 4

- d) For the cell $\text{Zn}|\text{ZnCl}_2 (m = 0.1)|\text{AgCl}|\text{Ag}$, write down the cell reaction and find out E_{cell}° , E_{cell} and ΔG at 25°C . [Given $E_{\text{Zn}|\text{Zn}^{++}}^\circ = 0.776 \text{ V}$ and

$$E_{\text{Cl}^-, \text{AgCl}|\text{Ag}}^\circ = 0.222 \text{ V}] \quad 4$$

- e) When N_2 and H_2 in the ratio 1 : 3 are allowed to react at 100 atm and $200^\circ C$, it was found that the conversion to NH_3 was 25% of original volume. Calculate K_p for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.
4. a) State Debye-Huckel limiting law. Show graphically the nature of variation of $\log \gamma_{\pm}$ vs square-root of ionic strength for 1-1 (e.g. NaCl, KCl etc.), 2-1 and (1-2) type electrolyte in aqueous solution. In which solution is the law applicable better?
- b) The *emf* of the concentration cell with transference is $pt; H_2 (1 \text{ atm}), HCl(a_{\pm} = 0.009048) \parallel HCl(a_{\pm} = 0.01751), H_2 (1 \text{ atm}); pt$ is 0.02802 V at $25^\circ C$. The *emf* of the corresponding cell without transference is 0.01696 V. Calculate the liquid junction potential and the transference number of H^+ ion.
- c) Discuss the physicochemical principle involved in the determination of pH of an aqueous solution by using a quinhydrone electrode.
- d) The standard reduction potentials for $Fe^{3+}, Fe^{2+}; pt$ and Sn^{4+}, Sn^{2+}, pt at $25^\circ C$ are respectively 0.77 V and 0.15 V. Set up the cell, write down the cell reaction and calculate the equilibrium constant of the reaction occurring in the cell.

UNIT - III

5. a) Define the terms 'ionic mobility' and 'transference number' of an ion.
- In a moving boundary experiment with a 0.011 (N) HCl solution, a current of 11.5 milliamps moved the boundary through a distance of 7.5 cms in 12 minutes. The radius of the tube is 5 mm. Calculate transport no. of H^+ .
- b) Explain the concentration dependence of equivalent conductance of a strong electrolyte. Draw and explain qualitatively the equivalent conductance versus square root of concentration plot for a weak electrolyte.
- c) Define work of cohesion in a liquid (A or B) and work of adhesion between two immiscible liquids (A and B). How do they determine spreading of 'A' on 'B'?
- d) Consider two liquids A and B, such that A has half the surface tension and twice the density of B. If liquid A rises to a height of 2.0 cm in a capillary, what will be the height to which liquid B will rise in the same capillary?

6. a) How does the viscous property of a liquid arise ? 2
- b) What is laminar flow of a liquid ? How one can characterize a liquid flow as turbulent or laminar ? 3
- c) The surface tension of a liquid increases as the temperature is lowered. Explain. 2
- d) The resistance of a cell with 0.02 (N) KCl at 18°C is 17.6 ohms and filled with 0.1 (N) CH₃COOH is 92 ohms. The specific conductance of 0.02 (N) KCl at 18°C is 0.0024 ohm⁻¹ cm⁻¹. Calculate the degree of dissociation of 0.1 (N) CH₃COOH at 18°C. 4
- [Given $\lambda_{H^+}^{\circ} = 315 \text{ ohm}^{-1}\text{cm}^2$ and $\lambda_{CH_3COO^-}^{\circ} = 35 \text{ ohm}^{-1}\text{cm}^2$]
- e) Depict with explanation the nature of conductometric titration curve of oxalic acid versus NaOH. 3
- f) The conductance of 0.1 (N) aqueous solution of KCl is measured in two conductivity cells with different cell constant values and the values of specific conductance and equivalent conductance are calculated. State with reasons whether the values will be same or different. 2