

2019

Part-II

Chemistry

(Honours)

Paper – IV

Full Marks - 45

Time - 2 Hours

The questions are of equal value for any group / half.

The figures in the right-hand margin indicate marks.

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

Illustrate the answers wherever necessary.

Group – A

Answer any **one** question :

15 × 1

1. (a) For weak electrolytes, the equivalent conductance, Δ increases with dilution indefinitely and hence no equivalent conductance at infinite dilution can be defined for such electrolytes. Comment on this statement.

3

P.T.O.

- (b) How does the de Broglie hypothesis lead to one important postulate made by Bohr in his theory of the hydrogen atom? 3
- (c) Find the simplest formula of a solid containing A and B atoms in a cubic arrangement in which A occupies corner and B the centre of faces of the unit cell. If the edge length is 5.0 \AA , estimate the density of the solid assuming the atomic weights of A and B to be 60 and 90, respectively. 3
- d) KCl or NH_4NO_3 is preferred to construct a salt bridge. Explain. 3
- e) When 2 grams of a non-volatile hydrocarbon containing 94.4% carbon is dissolved in 100 gm of benzene, the vapour pressure of benzene at 20°C is lowered from 74.66 mm of Hg to 74.01 mm of Hg. Calculate the molecular formula of the hydrocarbon. 3

2. (a) Show that the function,

$f(y) = (16y^4 - 48y^2 + 12)e^{-y^2/2}$ is an eigenfunction of the operator $B = -(d^2/dy^2) + y^2$, and calculate the eigenvalue. 3

- (b) Why is camphor more suitable than water as a solvent in the determination of molecular weights of organic substances by the depression of freezing point measurement? 3
- (c) Does the equilibrium constant of a reaction depend upon (i) the standard states chosen for the reactants and the products, and (ii) the stoichiometric representation of the reaction? Justify your answer. 3
- d) What will be the pH of a solution obtained by mixing 10 ml of 0.2 (N)KOH with 20 ml of 0.1 (N)CH₃COOH? Given $K_a(\text{for CH}_3\text{CO}_2\text{H})=2 \times 10^{-5}$. 3
- e) The resistance of a conductivity cell was found to be 700 ohms and 800 ohms when filled with 0.01(N) KCl and 0.01(N)AgNO₃ solutions respectively. The equivalent conductance of KCl is 150 ohm⁻¹cm². Find the equivalent conductance of AgNO₃. 3

Group – B

Answer any Two questions from the following : 10 × 2

3. (a) Show that for a particle confined in a three-dimensional box the degeneracy of the energy states increases with an increase in the symmetry of the system. 2½
- (b) The plot of $\ell \ln k_p$ versus $1/T$ will be linear if $\Delta c_p=0$. Justify / Criticize the statement. 2½

(c) Show that : $(\partial H/\partial n_i)_{s,p,n_j(j \neq i)} = (\partial U/\partial n_i)_{s,p,n_j(j \neq i)}$ 2½

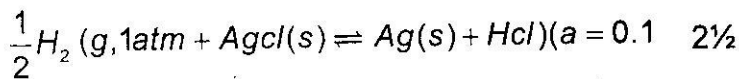
(d) Calculate the mean ionic activity coefficient of an aqueous solution of 0.001(M) $K_3[Fe(CN)_6]$ at 25°C. Given the Debye-Hückel constant for water at 25°C, $A = 0.509$. 2½

4. (a) From the expression for the chemical potential, μ_i , of the i^{th} component in an ideal gas mixture at constant temperature and pressure, obtain the relation $\Delta G^\circ = -RT \ln K_p$ for the equilibrium



(b) Consider a particle in a one-dimensional box with walls at $x = -a$ and $x = a$, where the state function is given by $\psi(x) = A(x^2 - a^2)$. Determine the expectation value of the particle's position and comment on your result. 2½

(c) Construct a reversible electrochemical cell in which the following overall reaction takes place :



(d) A substance, $A_x B_y$ is found to crystallize in a FCC lattice with A at each corner, and B at each face. What will be the formula for the compound? 2½

5. (a) Define ionic mobility, and mention its unit. State (without derivation) its relationship with the ion conductance. 2½
- (b) For AgI, the solubility product, $K_{sp} = 8.7 \times 10^{-17}$ at 25°C. What will be the potential of the Ag^+/Ag electrode in a saturated solution of AgI at 25°C? 2½
- (c) Show that the wavefunction $\psi(x,t) = e^{i(px-Et)/\hbar}$ is a solution of the one-dimensional time-dependent Schrödinger equation. 2½
- (d) For the reaction, $A_2(g) \rightleftharpoons 2A(g)$, the relation $K_p = K_c(RT)$ implies that the SI unit of K_p/K_c is joule mole⁻¹. Justify/Criticize the statement. 2½
6. (a) Which of the following quantities must be same for $CaCl_2(aq)$ and $NaCl(aq)$ at the same temperature? $\lambda_{Cl^-}^\circ$, $t_{Cl^-}^\circ$ and $u_{Cl^-}^\circ$. Give reasons. 2½
- (b) For the reaction $AB(g) \rightleftharpoons A(g) + B(g)$, $K_p = 8.0 \times 10^{-9}$ at 100°C. The forward reaction would be spontaneous under the following arbitrarily chosen partial pressures: $p_{AB(g)} = 0.1$ atm, $p_{A(g)} = p_{B(g)} = 2 \times 10^{-5}$ atm. Justify/Criticize the statement. 2½

- (c) A solution containing 0.011 kg of barium nitrate in 100 g of water boils to 100.46°C. Calculate the degree of ionization of the salt. Given that the K_b for 100 g of water is 5.2 K kg mole⁻¹. 2½
- d) A linear operator A is such that, $\hat{A}\phi = a\phi$. Find out the value of $e^{\hat{A}\phi}$ 2½

Group – C

Answer any five questions :

5 × 2

7. (a) For the solution of a solute in a non-polar solvent at a particular concentration $\Delta T_b/T_b$ is independent of the nature of the solvent. Justify.
- (b) Classify the following operators into linear and non-linear : (i) $\int dx$ (ii) $x^2(d^2/dx^2)$
- (c) The solubility product of PbI_2 in water at constant temperature always decreases in the presence of KI. Justify/Criticize the statement.
- (d) Amide ion in liquid ammonia has an abnormally high transport number. Why?

- (e) What will happen to the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ if neon gas is introduced into the system at constant temperature and pressure?
- (f) White tin ($S=7.29 \text{ g/cm}^3$) crystallizes in a tetragonal system with $a=b=582 \text{ pm}$ and $c=317.5 \text{ pm}$.
- g) Construct an electrochemical cell in which the following reaction takes place :
- $$2\text{Ag}(\text{s}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{AgCl}(\text{s}).$$
- h) The potential of an electrochemical cell is an intensive property. Justify/Criticize the statement.