(e) Deduce Einstein's relationship between absolute mobility and diffusion coefficient and find the significance of Fick's phenomenological coefficient "B". How one can experimentally verify the value of Avogadro number using Stokes-Einstein relationship between viscosity coefficient and diffusion constant? 2½+1+1½

(f) Why is the spherical symmetry of the ion-atmosphere destroyed during drift motion but not during diffusive migration of ions? Describe the method for estimating the relaxation components of drift velocity. 2+3

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M. SC. CHEMISTRY EXAMINATION, 2025

(1st Semester)

CHEMISTRY

PAPER : PG/CORE/TH/IV

(Physical Chemistry)

Time : *Two Hours* *Full Marks* : 40

20 marks for each unit

Use a separate Answer Script for each Unit.

UNIT—1041

Answer *any* **four** questions.

1. Derive a relation between fugacity (f) with observed pressure (P) of a non-ideal gas in terms of its compressibility factor (Z) and show that f = P for ideal gas. 5

2. Derive a relation between mole fraction scale activity coefficient of solvent (γ_1) with same of solute (γ_2) of a non-ideal binary solution. How will you determine the γ_2 with the help of determined value of γ_1 of same solution? 5

3. *(i)* Define partial molar volume. Does its value depend on composition of the solution? 2

(ii) Calculate the mole fraction scale activity coefficients of a Na^+ ion , PO_4^{3-} ion and Na_3PO_4 in 1×10^{-3} M Na_3PO_4 (*aq*) solution at 298 K. Given : A of water at 298 K is 0·51 $M^{-\frac{1}{2}}$. 3

4. A corrupt barman attempts to prepare 100 mL. of some drink by mixing 70 mL. ethanol with 30 mL water. Does he succeed? If not, what volumes should have been mixed in order to arrive at a mixture of the same strength but required volume? Given : Partial molar volumes of ethanol and water at this composition are 53·6 and 18·0 mL mol^{-1} respectively. Mass densities of ethanol and water are 0·785 and 1·0 g mL^{-1}. (All are at same temperature). 5

5. Show that partial molar volume of the solute in a binary solution is $V_{2,m}=\frac{1}{\rho}\left(M_2-V\frac{d\rho}{dm_2}\right)$; V is total volume of solution , ρ is its mass density, M_2 is molar mass of solute and m_2 is molality of solute in solution. 5

6. The linearized Boltzmann- Poisson equation, considering ionic atmosphere theory of Debye-Huckel, for dilute ionic solution is $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right)=\left(\frac{1}{\varepsilon k_BT}\sum_i n_i(0)Z_i^2e^2\right)\phi(r)$; (symbols have their usual meanings). Solve and find the general expression of $\phi(r)$. 5

UNIT—1042

7. Answer *any* **four** questions.

(a) Explain briefly a process for obtaining unambiguous relative heat of solvation values of positive and negative ions through clear-cut experiments and explain the utility of including the ion-quadrapole effect into the ion-dipole model for ion-solvent interactions. 3+2

(b) Does always solvation number is equal to coordination number? Explain the mobility method for the experimental determination of ion's solvation number. How does the dipole moment of a non-electrolyte influence its water solubility in the presence of ions? 1+2+2

(c) Briefly describe Bjerrum's major propositions for calculating the fraction of ion-pair formation and derive the analytical equation for determining the quantity of ion-pair formation. 2+3

(d) Determine the relationship between mean average ion displacements caused by random walking and the value of macroscopic diffusion constant in the presence of a steady chemical potential gradient. Find the relationship between time dependent concentration change and diffusion constant for non-steady state diffusion processes. 2½+2½