Explain the role of dispersive interaction on anomalous salt effect for the salt induced change in non-electrolyte solubility in water medium. 2+3+2

d) Describe the basic experimental procedure adopted by Halliwell and Nyburg to determine ΔH of the proton and hence absolute ΔH value for other positive and negative ions. Describe briefly the main considerations proposed by Bjerrum to calculate the fraction of ion-pair formation. Show theoretically that the steady state diffusional flux is proportional to the concentration gradient. 3+2+2

M. Sc. Chemistry Examination, 2023

(1st Semester, CBCS)

Paper: IV

[Physical Chemistry]

Time : Two Hours Full Marks : 40

(20 marks for each Unit)

Use a separate answer script for each Unit.

UNIT – 1041

1. Derive a relation between fugacity (f) with *observed pressure* (P) of a gas in terms of its *compressibility factor* (Z). 5

2. Derive a relation between *mole fraction scale activity coefficient* of solvent (γ_1) with that of solute (γ_2) of a binary solution. How will you determine γ_2 with the help of determination of γ_1 of same solution? 5

3. Answer *any one* question:

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

   ii) A barman attempts to prepare 100 mL of some drink by mixing 30 mL ethanol with 70 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 & 18.0 mL mol^{-1} respectively. *Mass densities* of ethanol and water are 0.785 and 1.0 g mL^{-1}. 5

iii) Calculate the *mole fraction scale activity coefficients* of Na^+ ion, SO_4^{2-} ion and Na_2SO_4 in 1×10^{-3} M Na_2SO_4 (aq) solution at 25°C. Given: 'A' of water at 25°C is 0.51 $M^{-1/2}$. 3

b) i) 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

ii) The *linearized Boltzmann-Poisson* equation, considering ionic atmosphere theory of *Debye-Huckel*, for dilute ionic solution is,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right)=\left(\frac{1}{\varepsilon k_B T}\sum_i n_i(0)Z_i^2e^2\right)\phi(r);$$

(symbols have their usual meanings).

Find the expression of $\phi(r)$. 5

UNIT – P-1042

4. Answer Question No. (a) and any ***two*** from the rest:

a) Deduce Einstein's relation of absolute mobility with diffusion coefficient and hence find the Nernst-Einstein relation between equivalent conductivity and diffusion. Why is the Nernst-Einstein relation valid only for very dilute solution? (3+2)+1

OR

Why is the spherical symmetry of ion-atmosphere lost during the drift motion, but not for the diffusive motion of ion? Describe the procedure to estimate the relaxation and electrophoretic components of drift velocity. 2+(3+1)

b) Explain briefly the method of calculating heat of ion-solvation (ΔH) according to Eley and Evan's ion-dipole model stating significance of different proposed terms appeared for this method. Does the magnitude of ΔH differ between positive and negative ions containing identical radii and charge values? What kind of experimental procedure is necessary to answer this question? 4+1+2

c) Is always solvation number equal to coordination number? Explain the compressibility method for the experimental determination of ion's solvation number stating the basic demerits of this method.