M. Sc. Chemistry Examination, 2019

(1st Semester)

Physical Chemistry

Paper - IV

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - 1041

1. Answer ***any one*** question :

   a) Define *fugacity* (f) of a gas and derive its relation with *observed pressure* (P) in terms of *compressibility factor* (Z).

   b) Define *osmotic coefficient* of a solution (ϕ). How is it used to express chemical potential of solvent in a binary solution ? Derive a relation between mole fraction scale activity *coefficient* of solute , γ_2 and ϕ . 5

2. Answer ***any two*** questions :

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

   ii) A person attemprs 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 of 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}. 5

iii) Calculate the mole fraction scale *activity coefficients* of Zn^{2+} ion, Cl^- ion and $ZnCl_2$ in 1×10^{-3} M $ZnCl_2$ (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 *literalized Boltzmann-Poisson* equation, considering ionic atmosphere theory of *Debye-Huckel,* for dilute ionic solution is,

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

(symbols have their usual meanings).

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

4. Answer ***any one*** question :

a) i) Calculate the difference in the Born's values of Gibbs free energy of solvation of I^- ion, when the dielectric constant is changed from 40 to 80 at 25°C, given the radius of I^- ion is 220 pm. Given that electronic charge, e = 4·802 x 10^{-10} esu. $2\frac{1}{2}$

ii) Find out the radius of ion from the following data :

$\lambda^o (ClO_4^-) = 54$ mho cm^2 mol^{-1}, co efficient of viscosity of water = 0·893 cP at 20°C. $2\frac{1}{2}$

b) i) Derive an expression of 'Walden product' relating equivalent conductance and radius of moving ion. $2\frac{1}{2}$

ii) State the significance of 'Walden product' in the study of conductance of electrolyte solution. $2\frac{1}{2}$

c) i) Calculate *most probable radius* of the ionic atmosphere, considering *Debye-Huckel* theory, for a 0·1 M solution of 1:1 true electrolyte at 27°C. The relative permittivity of solvent is 40 at 27°C and charge of proton is $1{\cdot}62 \times 10^{-19}$ C. 4

ii) Derive *Robinson-Stokes* equation for concentrated ionic solution. 6

UNIT - 1042

3. Answer ***any two*** questions :

a) i) How do you obtain the enthalpy change for ion-solvent interaction following Born's model ? 4

ii) Distinguish between primary and secondary solvation of an ion in solution. 2

iii) Discuss the principle of determination of primary solvation number of an ion by any suitable method. 4

b) i) What are the conditions of ion-pair formation in Bjerrum's model ? Obtain an expression of critical distance for Bjerrum's ion pair formation and then derive ion-pair formation constant of an electrolyte in solution. 2+2+3

ii) Discuss qualitatively the role of relaxation and electrophoretic effects on the conductance of ions in solution. 3

c) i) Distinguish between conventional and absolute mobility. 2

ii) State Fick's first law of diffusion. Define diffusion co-efficient. Obtain its unit from the law. 2+1+1

iii) Prove that the diffusion co-efficient,

$$D_i = BRT\left(1 + \frac{d \ln f_i}{d \ln C_i}\right),$$

where the terms bear usual significance.

When does diffusion co-efficient become independent of concentration ? 3+1