

( 4 )

Ex./M.Sc/CH/II/U-1041/9/2018

4. Answer any **one** question :

- (a) (i) Estimate the transfer Gibbs energy of  $I^-$  (radius : 220 pm) from water ( $\epsilon = 78.54$ ) to ethanol ( $\epsilon = 24.30$ ) at 298 K by Born model [Given unit of charge,  $e = 4.802 \times 10^{-10}$  esu].  $2\frac{1}{2}$
- (ii) In ethyl alcohol, ion association becomes appreciable for KI but not in water – explain.  $2\frac{1}{2}$
- (b) How can you determine the viscosity B-coefficient experimentally? What does its value signify? How does it change on increasing temperature?  $2+3$

— X —

**M.Sc. CHEMISTRY EXAMINATION, 2018**

**(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) At concentration exceeding 0.25 molal, the volume of sodium chloride solution per 1000 gm of water at 25°C is given by  
 $V = 1002.9 + 16.40 m + 2.5 m^2 - 1.2 m^3$  ml  
Molar volume of water at 25°C is 18.069 ml/mole.  
What is the value of  $\bar{v}_2$  and  $\phi_v$ ? Compare the results for one molal solution. (The symbols have their usual meaning).  $5$
- (b) (i) Find the variation of fugacity of a gas with temperature at constant pressure.  $3$
- (ii) The temperature of one mole of an ideal gas is increased from 100 K to 300 K. Calculate change in entropy if the pressure remains constant.  $2$

(Turn over)

( 2 )

2. Answer any **two** of the following :

- (a) (i) When two components are mixed to form an ideal solution show that there is no interaction in solution, and there is neither evolution of heat nor absorption of heat in the system. 2+3
- (ii) State third law of thermodynamics and its limitations. 5
- (b) (i) For a binary liquid solution of two components in equilibrium with its vapour, deduce Duhem-Margules equation and show that if one component behaves ideally, the other component will also behave ideally. 5
- (ii) Deduce the relation of osmotic pressure for a dilute solution thermodynamically. 5
- (c) (i) Define activity of solvent in a solution. 2
- (ii) Calculate activity of 0.1 N HCl solution at 25°C. 3
- (iii) Find the ionic strength of a solution containing 0.008 m BaCl<sub>2</sub> and 0.005 m K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution. 3
- (iv) Calculate mean ionic molality of a 0.5m BaCl<sub>2</sub> solution. 2

( 3 )

**UNIT - 1042**

3. Answer any **two** questions :

- (a) (i) Derive an expression for work of ion-dipole interaction, when an ion interacts with a solvent dipole in vacuum. 4
- (ii) Derive the necessary relation to explain the effect of secondary solvation on addition of an electrolyte to the saturated solution of a non electrolyte. 6
- (b) (i) "Log  $\lambda - \log C$  profile [ $\lambda$  = equivalent conductance, C = concentration of electrolyte] in low dielectric medium passes through a minimum at moderately high concentrations". – Explain. 3
- (ii) How do you confirm the formation of triple ion in a given solvent-electrolyte pair? 3
- (iii) Prove  $\lambda_{\min} = 2 (\alpha \lambda_0)_{\min}$ , where the terms bear usual significance. 4
- (c) (i) What do you mean by absolute mobility? Derive a relation between absolute mobility and diffusion coefficient. 1+4
- (ii) Derive an expression of 'Walden product' with the radius of the ion and state its significance in the study of solvation by measurement of conductance of solution.  $2^{1/2} + 2^{1/2}$

(Turn over)