

**B.Sc. 4th Semester (Honours) Examination, 2023 (CBCS)**

**Subject : Chemistry**

**Course : CC-VIII**

**Time: 2 Hours**

**Full Marks: 40**

*The figures in the margin indicate full marks.*

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

1. Answer any five questions from the following:

2×5=10

- (a) What will be the value of mole fraction of the solute in 1.00 molal aqueous solution?
- (b) Find the molality of  $(\text{NH}_4)_2\text{SO}_4$  solution that has the same ionic strength as 1 mol  $\text{kg}^{-1}$  solution of KCl.
- (c) In a system of two components at equilibrium, what should be the maximum possible number of phases and maximum possible number of degrees of freedom?
- (d) The boiling point elevation constant for toluene is  $3.32 \text{ K kg mol}^{-1}$ . The normal boiling point of toluene is  $110.7^\circ\text{C}$ . Find the enthalpy of vaporisation of toluene.
- (e) Classify non-ideal solutions in the light of thermodynamic criteria.
- (f) For a particular cell reaction, the Nerust equation is expressed as  $E = E^0 - \frac{RT}{nF} \ln Q$ . Find the condition at which the equilibrium constant of the cell reaction ( $K_c$ ) will be equal to  $Q$ . What will be the Gibbs free energy change at that condition?
- (g) Write down the expression of mean activity coefficient ( $\gamma_{\pm}$ ) of ferric sulphate in solution.
- (h) Show that when  $x = r \cos \phi$  and  $y = r \sin \phi$  then  $dx dy = r dr d\phi$ .

2. Answer any two questions from the following:

5×2=10

- (a) (i) Arrange the following aqueous solutions according to increasing order of their vapour pressure at room temperature. Give plausible explanation in favour of your answer.
  - (I) 0.1 molal hexamine cobalt(III) chloride
  - (II) 0.1 molal barium chloride
  - (III) 0.1 molal glucose
  - (IV) 0.1 molal tris(ethylenediamine) copper (II) sulfate
- (ii) Write down the van't Hoff equation for osmotic pressure.

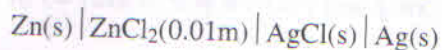
4+1

- (b) A solution of chloroform and ethanol at their mole-fractions of 0.01 and 0.99 respectively has a vapour pressure of 177.95 torr at 50°C, while pure ethanol has a vapour pressure of 172.76 torr. The solution is essentially ideally dilute. Find
- the partial pressure of the component gases in equilibrium with their solution at 50°C.
  - vapour pressure of pure chloroform at 50°C. Comment on the ideality / non-ideality of a 2% solution of chloroform in ethanol at 50°C. Given that the experimental vapour pressure of the solution is 183.38 torr. 2+1+2
- (c) (i) How does the phase diagram of water differ from that of carbon dioxide?
- (ii) Solid 'X' has melting point at 630°C and 'Y' has melting point at 348°C. X and Y exhibit a simple eutectic at 246°C with eutectic composition being 30% by weight of X. Draw and explain the cooling curve of the liquid having the eutectic composition. Also find the degrees of freedom at the eutectic point. 1+(2+2)
- (d) (i) Draw the potential energy curve for  $H_2^+$  molecular ion depicting the variation of energy of MOs with the internuclear distance. Give brief description for the nature of variation.
- (ii) Show that for the hydrogen molecular ion,  $H_{aa} = E_H + J + \frac{1}{R}$ . Give the meaning of each term in right-hand side of the equation,  $H_{aa} = \int 1s_a \hat{H} 1s_a d\tau$ . 3+2

3. Answer any two questions from the following:

10×2=20

- (i) Equal volumes of 0.01 m  $K_2SO_4$  and 0.02 m  $BaCl_2$  solutions are mixed. What will be the ionic strength of the resultant solution?
- (ii) The solubility of a sparingly soluble salt in water increases in presence of added electrolyte without common ion. — Explain.
- (iii) Mean ionic activity coefficient  $\gamma_{\pm}$  of  $ZnCl_2$  is 0.708 for 0.01 molal concentration at 25°C. Calculate equilibrium cell potential for the cell at 25°C.



The standard reduction potentials of  $AgCl(s) | Ag(s) | Cl^-$  and  $Zn^{2+} | Zn(s)$  electrodes at 25°C are 0.222 V and -0.762 V respectively.

3+3+4

- (b) (i) The e.m.f. of the cell



(Saturated solution)

is 0.965 V at 25°C. The temperature coefficient of cell e.m.f. is  $1.74 \times 10^{-4} \text{ VK}^{-1}$ ,

- What is the cell reaction?
- What are the values of  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  of the cell reaction?

(3)

- (ii)  $E^\circ$  is an intensive property. — Explain.
- (iii) Relative lowering of vapour pressure is an entropy effect. — Explain.
- (iv) "The Clausius-Clapeyron equation is a special case of the van't Hoff's equation for liquid-vapour equilibrium." — Justify or criticize. 4+2+2+2
- (c) (i) Show that  $[L_x, L_y] = i\hbar L_z$ .
- (ii) Show that  $Y_{1,0} = \cos\theta$  is an eigenfunction of both  $\hat{L}^2$  and  $\hat{L}_z$ . Give the corresponding eigenvalues, and also the magnitude and orientations of the angular momentum vector.
- (iii) Write down the form of the wave function that describes the situation where an electron spends 80% of its time in an orbital  $\psi_A$  on A and 20%  $\psi_B$  on B, in the molecule AB. 4+4+2
- (d) (i) Starting from the appropriate form of the Duhem-Margules equation, obtain Konowaloff's rule and use this to construct BP-composition curve to explain the distillation of binary liquid-pairs with minimum BP.
- (ii) What argument would you put forward to ascertain that azeotrope is a mixture but not a compound?
- (iii) Find out the number of components in the following chemical equilibrium: (3+3)+2+2
- $$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$