

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: $2 \times 5 = 10$

- (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 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°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 (γ_{\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: $5 \times 2 = 10$

- (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 hexaamine 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

- (i) the partial pressure of the component gases in equilibrium with their solution at 50°C.
- (ii) 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

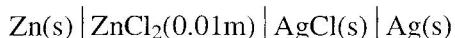
3. Answer *any two* questions from the following:

10×2=20

(a) (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?

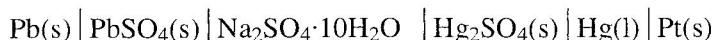
(ii) The solubility of a sparingly soluble salt in water increases in presence of added electrolyte without common ion. — Explain.

(iii) Mean ionic activity coefficient γ_{\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 $\text{AgCl(s)} | \text{Ag(s)} | \text{Cl}^-$ and $\text{Zn}^{2+} | \text{Zn(s)}$ 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 $1.74 \times 10^{-4} \text{ VK}^{-1}$,

(I) What is the cell reaction?

(II) What are the values of ΔG° , ΔS° and ΔH° of the cell reaction?

- (ii) E° 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 $[L_x, L_y] = i \hbar \hat{L}_z$.
- (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 ψ_A on A and 20% ψ_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
