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 $(NH_4)_2SO_4$ 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 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 ($\gamma_\pm$) of ferric sulphate in solution.

(h) S how that when $x = r\cos\phi$ and $y = r\sin\phi$ then $dxdy = r\,dr\,d\phi$.

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 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 $\gamma_\pm$ of $ZnCl_2$ is 0.708 for 0.01 molal concentration at 25°C. Calculate equilibrium cell potential for the cell at 25°C.

$$Zn(s)\,|\,ZnCl_2(0.01m)\,|\,AgCl(s)\,|\,Ag(s)$$

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

$$Pb(s)\,|\,PbSO_4(s)\,|\,Na_2SO_4\cdot 10H_2O\ (\text{Saturated solution})\ |\,Hg_2SO_4(s)\,|\,Hg(l)\,|\,Pt(s)$$

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

(I) What is the cell reaction?

(II) What are the values of $\Delta G°$, $\Delta S°$ and $\Delta H°$ 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 Hoffs 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:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (3+3)+2+2
