B.Sc. 4th Semester Honours Examination, 2022 (CBCS)

Subject: Chemistry

Paper: CC-8

(Physical Chemistry-III Theory)

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.

A. Answer *any five* questions from the following: **2 × 5 = 10**

1. Find the mean ionic activity coefficient for a 0.01 M aqueous solution of $Ca_3(PO_4)_2$.
2. For the reaction, $CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$, find the value of $\Delta G°$ (in kJ mol^{-1}). Given: 1 F = 96485 C mol^{-1}; electrode potential values of $Cu^{2+}(aq)/Cu(s)$ = + 0.34 V and $Zn^{2+}(aq)/Zn(s)$ = −0.76 V,
3. A dilute solution prepared by dissolving a non-volatile solute in one litre water shows a depression in freezing point of 0.186 K. This solute neither dissociates nor associates in water. What is the boiling point of the solution in K? (Given: For pure water, boiling point = 373.15 K; cryoscopic constant = 1.86 K kg mol^{-1}; ebullioscopic constant = 0.51 K kg mol^{-1}.)
4. The emf (E) of the cell: (Pt) $\vert$ $H_2(g)$ $\vert$ HCl (aq) $\vert$ AgCl(s) $\vert$ Ag(s); is at 0.265V at 25℃ and at 0.260V at 35^0C. Calculate $\Delta_r H$ of the cell reaction at 25^0C.
5. Calculate the number of components and the number of degrees of freedom for the following equilibrium: an iceberg floating in a lake (consider lake, iceberg and atmosphere as one system).
6. For an ideal solution which of the following thermodynamic parameters will be zero? ΔV_{mix}, ΔG_{mix}, ΔH_{mix} and ΔS_{mix}.
7. What is overlap integral? When does the value of an overlap integral become zero? What are the names given to the overlapping functions?
8. Maximum value of $\boldsymbol{L_z}$ is less than $|\boldsymbol{L}|$. What does it imply?

B. Answer *any two* questions from the following: **5 × 2 = 10**

1. a) A point mass rotates in a circle with l = 2. Calculate the magnitudes of its angular momentum and the components along the z-axis.

b) Show that Hamiltonian operator $\hat{H}$ and angular momentum operators $\widehat{L^2}$ or its component $\widehat{L_z}$ commute. **2 + (2+1) = 5**

2. a) A pair of completely miscible liquids A and B cannot show azeotropism if they obey Raoult's law throughout the entire range of mole fraction. - Justify or criticize.

   b) Mention two azeotropic solutions having maximum and minimum boiling points.

   3 + 2 = 5

3. a) What do you mean by van't Hoff factor (*i*)? How can it be used for calculating the degree of association (β) of a solute in solution?

   b) 7.52 g of phenol is dissolved in 100 g of solvent with K_f = 14. If depression of freezing point is 7 K, calculate the percent of phenol that dimerizes. [Given: Molecular weight of phenol = 94 g mol^{-1}]

   3 + 2 = 5

4. a) In a potentiometric titration, the data points near the equivalence point are important while in a conductometric titration the same are not true. - Explain why?

   b) Set up a cell without transference for the cell process $CuSO_4$ (c_1) → $CuSO_4$ (c_2); $c_2 < c_1$. Write down the cell reactions at the electrodes. **2 + 3 = 5**

C. Answer *any two* questions from the following: **10 × 2 = 20**

1. a) The wavefunction for the electron in the ground state of hydrogen atom is $\Psi_{1s} = e^{\frac{-r}{a}}(\pi a_0^3)^{-\frac{1}{2}}$, where a_0 is the radius of the Bohr orbit. What is the probability of finding the electron somewhere inside a small sphere of radius 1.0 x 10^{-12} m centred at the nucleus?

   b) Construct sp hybrid orbitals by combining one 2s and one 2p atomic orbitals using LCAO method.

   c) What is the orbital angular momentum of an electron in the (i) 1s (ii) 2s (iii) 2p (iv) 3d states. Show the angular and radial nodes in each case. **3 + 3 + 4 = 10**

2. a) Suppose that a one-component system exhibits a gas phase, a liquid phase and three solid modifications. How many one-, two-, three- and four-phase equilibria are possible for the system. Give plausible explanation in favour of your answer.

b) What do you mean by isothermal critical point for a three-component system? Draw with proper description a suitable triangular plot to show the binodal curve and the plait point for acetic acid -chloroform -water ternary system.

c) Brisk effervescence is observed when a soda water bottle is opened. State the physical law to which this observation is related.

d) For ice, the graphical plot of pressure versus melting point has negative slope. Why?

4 + 4 +(1 + 1) = 10

3. a) 100 g of a 1:1 (by weight) mixture of water and phenol is taken at 40^0C. It shows two layers: (i) phenol (9.2%) in water and (ii) water (35%) in phenol. Find the amount of two layers by weight.

b) Write down the criteria for 1st order phase transition. Describe them with suitable diagram for vaporization of water at its boiling point.

c) Write down the Clausius-Clapeyron equation for liquid-vapour equilibrium. The boiling point of ethanol at 1 atm pressure is 78.3^0C with ΔH_{vap} = 39 kJ mol^{-1}. At what pressure would it boil at 25^0C? Mention the assumption(s), if any, used in your calculation.

2 + 4 + 4 = 10

4. a) Standard reduction potentials of the two electrodes at 25^0C are given, $E^0_{Cl-|Hg_2Cl_2(s)|Hg(l)} = 0.2676\,V$ and for quinhydrone electrode $E^0_{H^+|QH_2,Q|Pt} = 0.6994\,V$. Mean ionic activity coefficient $\gamma_\pm$ for HCl at 0.1 m solution is 0.796. Using above data find out E of the following cell at m_{HCl} = 0.1.

Pt(*s*)| Hg(*l*)|Hg_2Cl_2(*s*)|HCl (aq, *a*), Q, QH_2|Pt(*s*)

b) Write down the Debye-Hückel limiting law for any electrolyte clearly mentioning the significance of all the terms therein. Compare the values of mean activity coefficients for uni-bivalent and bi-bivalent type electrolytes having the same ionic strength in aqueous solution at the same temperature.

c) Write down the advantages of potentiometric titrations compared to different indicator based titrimetric methods.

4 + 3 + 3 = 10