B.Sc. 4th Semester (Honours) Examination, 2019

Subject : Chemistry

Paper : CC-8

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) Explain what is meant by first order phase transition.

(b) Depict quinhydrone electrode and indicate the electrode process occurring in it.

(c) If we measure L_Z of a particle whose state function is an eigenfunction of $\widehat{L^2}$ with eigenvalue $12\hbar^2$, what are the possible outcomes of the measurements?

(d) Set up the Schrödinger equation for helium atom and identify the factor which prevents a direct solution of this equation.

(e) Is the lowering of chemical potential of solvent in a dilute solution is an enthalpy effect or an entropy effect? — Explain.

(f) One component of a binary liquid mixture exhibits negative deviation from Raoult's Law. — Comment on the signs (positive or negative) of ΔV_{mix} and ΔH_{mix}.

(g) Calculate the mean ionic activity of a 0.0350 m Na_3PO_4 solution for which the mean activity coefficient is 0.685.

(h) Evaluate the probability density at the nucleus for an electron with $n = 1$, $l = 0$ and $m = 0$.

$$\Psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

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

(a) Derive Duhem-Morgules equation starting from Gibbs-Duhem equation. Show that the vapour phase is richer in the component, the addition of which to the liquid mixture results in an increase of the total vapour pressure. 3+2=5

(b) Derive a relationship between depression of freezing point and osmotic pressure of a dilute solution stating all the assumptions and approximations. 5

(c) Draw and label the phase diagram of sulphur which exhibits the phenomenon of enantiotropy. 5

Please Turn Over

(d) (i) For a hydrogen like-atom in a stationary state with quantum numbers n, l, and m, prove that, $\langle r \rangle = \int_0^\alpha r^3 [R_{nl}]^2 dr$.

The terms have their usual significance.

(ii) A solution of NaCl of concentration m has an osmotic pressure of 2.0 atm at 25° C. Calculate ΔG for the process:

H_2O (solution, 25° C) = H_2O (pure, 25° C) 2+3=5

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

(a) (i) For the hydrogen atom ground state, find ⟨V⟩.

$$\Psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

(ii) For a given overall cell reaction at 298 K, $\Delta S_R^\circ = 16.5 \text{ J mol}^{-1}\text{K}^{-1}$ and $\Delta H_R^\circ = -270.0 \text{ K J mol}^{-1}$. Calculate E° and $\left(\frac{\partial E^\circ}{\partial T}\right)_P$. Assume that $n = 2$.

(iii) If you double all the coefficients in the overall chemical reaction in an electrochemical cell, the equilibrium constant changes. Does the emf change? Explain your answer.

(iv) Show that if $\Delta G^\circ_f (H^+, \text{aq}) = 0$ for all T, the potential of the standard hydrogen electrode is zero. 3+3+2+2=10

(b) (i) Depict an electrolyte concentration cell with transference and derive an expression for the emf of that cell.

(ii) Determine the number of degrees of freedom in each of the following systems stating briefly the considerations on which the results are based.

(I) An azeotrope in a binary system

(II) An eutectic mixture in a binary system 6+(2+2)=10

(c) (i) Prove that the operators $\hat{L}^2$ and $\hat{L}_z$ commute.

(ii) Devise a cell in which the following is the reaction:

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

(iii) Discuss how the thickness of the ion atmosphere changes as the temperature, dielectric constants and ionic strength of an electrolyte solution are increased. 4+2+4=10

(d) (i) Calculate the percent change in the vapour pressure per °C for benzene at around its normal boiling point of 80°C. Benzene obeys Trouton's rule.

(ii) Methylethylketone and water are partially miscible. At 30° C the two layers contain 21·9 and 89·9% by weight of ketone. What will be the weight of each layer when 50 g each of ketone and water are equilibrated at this temperature?

(iii) Represent the cell set up for the potentiometric titration of Ag^+ ion by KCl solution. Find the expression for emf of that cell. 4+3+3=10