

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
- Explain what is meant by first order phase transition.
 - Depict quinhydrone electrode and indicate the electrode process occurring in it.
 - If we measure L_z of a particle whose state function is an eigenfunction of \hat{L}^2 with eigenvalue $12\hbar^2$, what are the possible outcomes of the measurements?
 - Set up the Schrödinger equation for helium atom and identify the factor which prevents a direct solution of this equation.
 - Is the lowering of chemical potential of solvent in a dilute solution is an enthalpy effect or an entropy effect? — Explain.
 - 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} .
 - Calculate the mean ionic activity of a 0.0350 m Na_3PO_4 solution for which the mean activity coefficient is 0.685.
 - 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
- 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
 - Derive a relationship between depression of freezing point and osmotic pressure of a dilute solution stating all the assumptions and approximations. 5
 - 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, $\langle r \rangle = \int_0^\infty r^3 [R_{nl}]^2 dr$.

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:



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

- (a) (i) For the hydrogen atom ground state, find $\langle V \rangle$.

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

- (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 $\Delta G_f^\circ (H^+, \text{aq}) = 0$ 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.

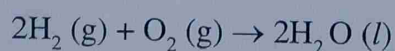
(I) An azeotrope in a binary system

(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:



- (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) Methylisobutylketone 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