

## 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  $\Delta V_{\text{mix}}$  and  $\Delta H_{\text{mix}}$ .
  - Calculate the mean ionic activity of a 0.0350 m  $\text{Na}_3\text{PO}_4$  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-Margules 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

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

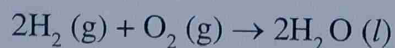
(I) An azeotrope in a binary system

(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  $\text{Ag}^+$  ion by KCl solution. Find the expression for emf of that cell.

4+3+3=10