

**U.G. 4th Semester Examination - 2020**

**CHEMISTRY**

[HONOURS]

Course Code : CEMH-CC-T-8

Physical Chemistry

Full Marks : 40

Time : 2½ Hours

*The figures in the right-hand margin indicate marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any **five** questions: 2×5=10
- Define linear operators. Is SQRT a linear operator?
  - What do you mean by an ideal solution and an ideal dilute solution?
  - Write down the basics of Hartree-Fock SCF method.
  - Ammonium chloride decomposes on heating to give ammonia and hydrogen chloride gas. How many components and phases are present if the salt is heated in an otherwise empty container?
  - Explain Konowaloff's rule.

- What do you mean by azeotropes? Give an example.
- Write down the advantages of using other reference electrodes compared to SHE.
- Calculate the ionic strength of a solution containing 0.01 m BaCl<sub>2</sub>.

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

- Derive Clausius – Clapeyron equation in the integrated form for a liquid -vapour equilibrium. Clearly mention the assumptions involved. Discuss the difference between triple point and the freezing point. 3+2
- “Four phases of sulphur cannot exist simultaneously at equilibrium.” Justify or criticize. Deduce thermodynamically the van't Hoff equation for the osmotic pressure of a dilute binary solution, mentioning the assumptions involved. 2+3
- Draw the plots of radial distribution function against electron-nuclear distance for 1s and 2s hydrogenic orbitals. Show that in case of a hydrogen atom the probability of finding the 1s electron within the first Bohr orbit,  $a_0$ , is about 0.32.

$$\text{Given } \psi(1s) = (1/\pi) \cdot (Z/a_0)^{3/2} \exp(-Zr/a_0)$$

2+3

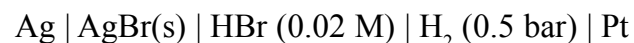
- d) Explain, with proper equation, the variation of molar polarization of a polar molecule with temperature. How can the dipole moment be determined from this? 3+2

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

- a) i) Calculate the most probable radius ( $r_{mp}$ ), at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom of atomic number Z.

$$\text{Given } \psi(1s) = (1/\pi) \cdot (Z/a_0)^{3/2} \exp(-Zr/a_0)$$

- ii) Determine the cell reaction and  $E_{cell}$  for the following cell at 25°C



$$\text{Given } E^0_{\text{Br}^-/\text{AgBr}/\text{Ag}} = 0.07 \text{ V}$$

- iii) What do you understand by bonding, antibonding and nonbonding molecular orbitals? 3+4+3
- b) i) Write down the expression for Debye – Huckel limiting law for strong electrolytes. Comment on the validity and limitations of the law.

- ii) Show that  $E_n$  of a hydrogen atom is  $n^2$  fold degenerate.

- iii) Explain the difference between the electrochemical cells with transference and electrochemical cells without transference. 4+4+2

- c) i) Draw a temperature – composition phase diagram for a binary system A -B having single eutectic, a single peritectic (corresponding to the incongruently melting compound AB) and no solid solutions. Label all the areas.

- ii) Draw, with explanation, the pH-metric titration curve for the titration of oxalic acid with NaOH.

- iii) What is the freezing point of a 0.01 molal solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , which is 78 % dissociated in water ( $K_f = 1.85$ )? 4+3+3

- d) i) What is Born – Oppenheimer approximation? How does the Born – Oppenheimer approximation simplify the quantum mechanical treatment of the covalent bond? Explain.

- ii) Using Debye – Huckel limiting law calculate the mean activity coefficient of 0.001 (M) aq. Solutions of  $K_3[Fe(CN)_6]$  and  $K_4[Fe(CN)_6]$ . Debye – Huckel constant is 0.51.
- iii) As supercooled water at  $-10^\circ C$  freezes spontaneously, its temperature rises to  $0^\circ C$ . What is the source of heat for the process?

4+4+2

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