U.G. 4th Semester Examination - 2020

CHEMISTRY

[HONOURS]

Course Code : CEMH-CC-T-8

Physical Chemistry

Full Marks : 40 Time : $2\frac{1}{2}$ 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

   a) Define linear operators. Is SQRT a linear operator?

   b) What do you mean by and ideal solution and an ideal dilute solution?

   c) Write down the basics of Hartree-Fock SCF method.

   d) 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?

   e) Explain Konowaloff's rule.

   f) What do you mean by azeotropes? Give an example.

   g) Write down the advantages of using other reference electrodes compared to SHE.

   h) Calculate the ionic strength of a solution containing 0.01 m $BaCl_2$.

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

   a) Derive Clausius – Clayperon 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

   b) "Four phases of sulphur cannot exist simultaneously at equilibrium." Jusfify or criticize. Deduce thermodynamically the van't Hoff equation for the osmotic pressure of a dilute binary solution, mentioning the assumptions involved. 2+3

   c) 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.

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

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.

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

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

Ag | AgBr(s) | HBr (0.02 M) | H_2 (0.5 bar) | Pt

Given $E^0_{Br^-/AgBr/Ag} = 0.07$ 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 $K_3[Fe(CN)_6]$, 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°C freezes spontaneously, its temperature rises to 0°C. What is the source of heat for the process?

4+4+2

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