c) i) What is an electrocapillary curve ? What information can be derived from an analysis of the electrocapillary curves ? 3

ii) Justify why usually the larger ions and often anions are specifically adsorbed on the metal surface from aqueous solution. 3

d) i) Derive langmuir adsorption equation for a reaction of the type :

$$H_3O^+(soln.) + e(M) \rightleftharpoons M - H + H_2O .$$ 3

ii) Distinguish Langmuir, Frumkin and Temkin types of adsorption of ions at an electrode-solution interface. 3

5. Answer ***any one*** question :

a) Explain with necessary diagrams the mechanism of action of photovoltaic, photosynthetic and photocatalytic cells using both n and p-type semiconductors. $2\frac{1}{2}+2\frac{1}{2}+2$

b) i) How and why do the electron bands bend for n and p-type of semiconductors immersed in an electrolyte ? What is flat-band potential ? 4

ii) Explain the mechanism of action of a photogalvanic cell.

Ex/M.Sc/CHEM/4/XIII/P-4131/2018

M. Sc. Chemistry Examination, 2018

(4th Semester)

Physical Chemistry Special

Paper - XIII-P

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - P - 4131

Answer question ***no.1 and any one*** from question no. 2 and 3

1. a) How many independent spin wave functions do you expect for a 5-electron system ? 1

b) For a many electron system, the spin-adaptation depends on the nature of the two-electron permutation operator ($\hat{P}^{\alpha\beta}$) that leads to an interchange of α and β spin–Justify. $3\frac{1}{2}$

c) Construct spin eigenfunctions for $S = \frac{1}{2}$ and $M_s = \pm\frac{1}{2}$ for a 3-electron system using spin projection operator. 4

d) Find out the expression of the energy expectation value of a 5-electron wave function having two closed shell and one open shell in terms of one and two electron integrals using Slater-Condon rules. 4

2. a) Show how one can construct Hartree quuation in the independent particle model under the Central Field Approximation for n-electron system. 5

   b) Write down the expression of the Hartree-Fock operator for 2N electron closed shell atomic system. 2

   c) What are the steps involved in performing Hartree-Fock Self-Consistent-Field calculations for a molecule under Born-Oppenheimer approximation ? 4

   d) State Koopmans' theorem. What is its drawback ? $1\frac{1}{2}$

3. a) Show that a single configuration description of H_2 in MO theory is not sufficient to produce the correct dissociation behavior of the ground-state molecule from both energy and wave function consideration. 6

   b) Apply Hückel Molecular Orbital theory to find out delocalization energy of cyclobutadiene. 3

   c) Show how quantum mechanical Virial theorem can be employed to prove that H-atom is most stable under Coulombic force. $3\frac{1}{2}$

UNIT - P - 4132

4. Answer ***any three*** questions :

   a) Write down the thermodynamic relation of the polarizable interface relating interfacial tension (V), potential (V) and chemical potential (μ), describing the meaning of the different terms. Using the above mentioned thermodynamic relation, prove that

   $$\left(\frac{\partial\gamma}{\partial \ln a_{\pm}}\right)_{V-} = -2RT\Gamma_{+}$$

   for uni-univalent electrolyte, where the terms bear usual significance. 1+5

   b) i) Prove that the potential gradient $(-d\psi/dx)$ at a distance x from an electrode is given by

   $$\frac{d\psi_x}{dx} = -\left[\frac{8kTC_O}{\epsilon\epsilon_o}\right]^{1/2} \mathrm{Sinh}\left(\frac{Ze_o\psi_x}{2kT}\right)$$

   according to Gouy-Chapman model of double layer.

   ii) Also show that the potential (ψ) extends theoretically up to infinity, using low field approximation. 4+2