approximation, show that the potential (ψ) extends upto infinity.

ii) Using the equation of the field, show that $\kappa^{-1} = \left(\frac{\epsilon \epsilon_o \, kT}{2C_o z^2 e_0^2} \right)^{1/2}$ is the effective thickness of Gouy chapman's diffuse double layer. 3+3

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

a) i) Derive an expression of the capacitance of an extrinsic semiconductor immersed in an electrolyte solution, as a function of potential.

ii) Show that the capacitance-potential profile is asymmetric for extrinsic semiconductor and symmetric for intrinsic semiconductor. $4\frac{1}{2}+2\frac{1}{2}$

b) i) How and why do the electron bands of a p-type semiconductor immersed in an electrolyte bend ? What is space charge region ?

ii) Distinguish between photovoltaic and photogalvanic cells stating their mechanisms of action. 4+3

Ex/P-XIII/P/2019

M. Sc. Chemistry Examination, 2019

(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 ***any two*** questions.

1. a) Many electron wave functions written in Slater determinantal form satisfies the antisymmetry requirement. Justify using a 3-electron system. 3

b) Derive the analytical form of the square of the total spin angular momentum operator ($\hat{S}^2$) using a Slater determinantal function of a ($n_\alpha + n_\beta$) electron system (n_α and n_β are the number of α and β spin electrons). 6

c) Find the number of possible spin multiplets of a 6 electron system using Branching rule. $1\frac{1}{2}$

d) Show that for an atom with two non-interacting electrons, the two electron wave function is the product of eigen functions of two single electrons. 2

2. a) What are Slater Condon rules ? Derive an expression for the energy expectation value of the wave function $\psi = \frac{1}{\sqrt{2}}\left(|\bar{f}_1 f_2 f_3| - |f_1 \bar{f}_2 f_3|\right)$ using Slater-Condon rules. 6

   b) Show with detailed derivation that the separation between the energy levels of excited singlet and triplet states of H_2 molecule is twice the exchange integral. $6\frac{1}{2}$

3. a) Show that transition moment from the singlet ground state to an excited singlet state of H_2 depends on the bond length. $3\frac{1}{2}$

   b) Using Huckel Molecular Orbital (HMO) theory, derive general expression of energy level and wave function of a cyclic conjugated polyene having N-carbon atoms (N may be odd or even) 5

   c) Using HMO theory, calculate the energy levels for cyclo-propenyle radical and butadiene. 2+2

UNIT - P - 4132

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

   a) Distinguish between inner and outer potential difference of a metal solution interface. How can the Volta Potential difference between a metal and a solution be measured ? 2+4

   b) i) How does the contact adsorption influence the capacity of the interface ? Derive the necessary relation and explain.

      ii) How is the extent of contact adsorption on the surface of an electrode determined from electro-capillary measurements ? 3+3

   c) i) Show that the parallel plate condenser model can explain the electro-capillary curve which is perfect parabolic in nature.

      ii) Give salient features of the Stern model of double layer and explain the total capacity at an electrode solution interface at high and low concentrations separately. 3+3

   d) i) The potential gradient $(d\psi/dx)$ at a distance x from an electrode is given by Gouy-Chapman model as $\frac{d\psi}{dx} = -\left(\frac{8kTCo}{\epsilon\epsilon_o}\right)^{1/2} \sinh\frac{ze_o\psi_x}{2kT}$, using low field