ii) Derive the reciprocal relation : $\frac{1}{i}=\frac{1}{i_F}+\frac{1}{i_L}$, Where the terms bear usual significance. Show the condition of obtaining the diffusion controlled current from this relation. 4

c) i) How does the transfer co-efficient help in determining the mechanism of the reaction ? Give two examples from hydrogen evolution reaction.

ii) Deduce the following polarographic wave equation :

$$E=E_{\frac{1}{2}}+\frac{0.0591}{n}\log\frac{i_d-i}{i}$$ at 25^0C, where the terms have their usual significance. 5

5. Answer ***any two*** questions : $2\times 2\frac{1}{2}$

a) Calculate the change in activation energy of the cathodic process at an electrode, when potential difference changes from 0.5V to 1.2V at 27^0c. Use $\beta = 0,7$ and n =2.

b) Estimate the limiting current density at 298K for an electrode immersed in a 0.1M aqueous Cu^{2+} unstirred solution in which the thickness of the diffusion layer in about 0.5mm. Given λ =107S $cm^2ol^{-1.}$

c) Distinguish reversible and irreversible reactions by a cyclic voltammetric experiment.

M. Sc. Chemistry Examination, 2019

(3rd Semester)

Physical Chemistry Special

Paper XI-P

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - P - 3111

Answer ***any two*** of the following questions

1. a) State and prove the quantum mechanical Variation theorem. 3

b) Evaluate the variational integral for the one dimensional harmonic oscillator using a trial function, $\phi(x) = e^{-cx^2}$ and hence find out the optimum valne of the variational parameter, c. 6

c) A trial function (ϕ) is expanded in two normalized basis function X_1 and X_2. In this basis, H_{11} = –13.6eV, H_{22} =–24.6eV, H_{12} =16.71 eV and S_{12} = 0.5. Using linear variation method, calculate the roots E_1 and E_2. $3\frac{1}{2}$

Or

Calculate the first order correction to the ground state energy of an anharmonic oscillator whose potential eneergy is $U(x)=\frac{1}{2}kx^2+\frac{1}{6}\gamma x^3=\frac{1}{24}\lambda x^4$. Assume the ground state wave function of the harmonic oscillator as

$$\phi(x)=\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}.e^{-\frac{\alpha x^2}{2}},\ \text{Where}\ \alpha=\sqrt{k\mu/\hbar^2}.$$

$$[\text{Given}: \int_0^\infty x^n e^{-qx}dx=\frac{n!}{q^{n+1}}; n>-1; q>0]$$

2. a) Using Rayleigh Schrödinger time-independent perturbation theory for non degenerate system, establish second order perturbation equation and hence find out the expression of the second order energy correction. 6

Or

Write down the time dependent Schördinger equation and express it to Heisenberg and Interation representation.

b) Show how degenerate perturbation theory can be applied to the first excited state of He (1s2s, 1s2p) atom to lift the degeneracy partially. Include only the first order perturbation energy correction. $6\frac{1}{2}$

Or

What is Stark effect ? Show that the first order correction to the ground state energy of hydrogen atom in the Stark effect is zero. Show that the energy gap of a perturbed state is equal in normal Zeeman effect. $1+2\frac{1}{2}+3$

3. a) Define transition probability. Consider a molecule exposed to an oscillating electric field, $E=2E_0\text{Cos}(\omega t)$, show that the probability of transition form a stationary state $|n\rangle$ to another state $|k\rangle$ increases linearly with time. $1+5\frac{1}{2}$

b) State the physical significance of Einstein's A and B coefficients. Derive the relation between them. 2+4

UNIT - P-3112

4. Answer ***any two*** questions :

a) i) How are the equilibrium exchange current density, transfer co-efficients and stoichiometric number determined for a multi-step electrode reaction ? 6

ii) Discuss the condition of tunneling of electrons for an electrode reaction of the type :

$$M(e)+H^+-OH_2\rightarrow M-H+H_2O \quad 4$$

b) i) When does the concentration overpotential arise ? Define it and derive an equation relating concentration overpotential and limiting current density of an electronation reaction. 1+1+4