ii) Indicate the change of corrosion potential and corrosion current using Evans diagrams for both cathodic and anodic inhibitors and cathode and anode-affecting bacteria. 4

5. Answer ***any two*** questions : $2\frac{1}{2}\times2$

i) Calculate the change in activation energy of the cathodic process at an electrode, when potential difference changes from 0.5V to 0.75V at 25°C. Use $\beta = 0.7$ and n=2.

ii) The equilibrium exchange current density of an electrode, $Pt/H_2(g)/H^+(aq)$ is 0.79mA cm^{-2} at 298 K. Calculate the current obtained from the Pt-foil of area 10 cm^2, when the overpotential is 7 mV.

iii) Derive Nernst equation from kinetic consideration.

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M. Sc. Chemistry Examination, 2017

(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*** from the following questions

1. a) State and prove quantum mechanical variation theorem. How can it be extended to excited states ? 4+2

b) Consider a one dimensional Harmonic Oscillator whose trial wave function is represented by e^{-ax^2}. Apply variational method to determine the optimum value of the variational parameter, a. $6\frac{1}{2}$

2. a) Derive an expression of the first order wave function correction for the n^{th} non-degenerate state using Rayleigh-Schrödinger perturbation theory. Comment on the significance of such correction. $5+1\frac{1}{2}$

b) Show how degenerate perturbation theory can be applied to the first excited states of He (1s2s : 1s2p) atom to lift the degeneracy partially. Include only the first order perturbation energy correction. 6

or

Explain the concept of coordinate and momentum representation of eigenstates. Show how one representation can be converted into another. $1\frac{1}{2}+1\frac{1}{2}$

Explain Normal Zeeman Effect. Mention one application of it. 2+1

3. a) Find the eigenvalues and normalized eigenvectors of the following matrix, A.

$$A=\begin{pmatrix}2 & 2\\ 2 & -1\end{pmatrix}$$

i) Is A real and symmetric ? Is A hermitian ?

ii) Is the eigenvector matrix C orthogonal ? Is the eigenvector matrix C unitary ?

iii) Write down C^{-1} without doing any calculation.

iv) Verify that $C^{-1}AC$ equals the diagonal matrix of eigenvalues. $7\frac{1}{2}$

b) Consider a two-level system (level-a & b) perturbed by a time-dependent perturbation, $H'(t)$. Derive the general expressions governing the time-evolution of the two states. Obtain up to the second order expressions from it. 5

UNIT - P - 3112

Answer ***any two*** questions.

4. a) 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

ii) Derive the reciprocal relation : $1/i=1/i_F + 1/i_L$, where the terms bear usual significance. Show the condition of obtaining the activation controlled current from this relation. 4

b) i) How can you determine equilibrium exchange current density, transmission co-efficient and stoichiometric number experimentally using high and low field approximations of Generalized Butler Volmer equation ? 5

ii) Elucidate the mechanism of an electrochemical reaction : $Fe^{2+} + 2e \rightleftharpoons Fe$, given that $\vec{\alpha}=0.5,\ \overleftarrow{\alpha}=1.5, P_{Fe^{2+}}=1,\ P_{OH^-}=1$ and r = 1, where the terms bear usual significances. 5

c) i) Compare order of a chemical and electrochemical reaction. How does the order help in determining the mechanism of hydrogen evolution reaction ? Give two examples and derive their rate equations. 6