M. Sc. Chemistry Examination, 2018

(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 the variation theorem and show how it can be extended to the m^{th} excited state. $3\frac{1}{2}$

   b) Using the trial function $e^{-\alpha r}$ for the ground-state H atom, find out the optimum value of α and the minimum energy. 4

   c) Consider a trial function ($\tilde{\phi}$) consisting of n variational parameters $\{a_i\}, i = 1, n$ such for a set of that known functions $\{f_i\}, i=1, n,$

   $$\tilde{\phi} = \sum_{i=1}^{n} a_i f_i .$$

   Show that the optimization of variational parameters requires the solutions of secular equations. 5

2. a) Apply time-independent Rayleigh - Schrödinger perturbation theory to find out the second order energy correction for the n^{th} nondegenerate state using intermediate normalization condition. For the ground state, such energy correction always stabilizes the state – Comment. 6

   b) An electric field of strength **F** is applied on H atom along the z-axis as a perturbation.

      i) Show the effect of first and second order perturbation on the energy of the ground state of H atom.

      ii) What happens to the first excited states of the H atom due to first order perturbation ? $6\frac{1}{2}$

3. a) A Hamiltonian matrix **(H)** of a system is given by

$$H = \begin{pmatrix} 2 & -2i \\ 2i & 2 \end{pmatrix}$$

   Find its eigenvalues and normalized eigenvectors by solving algebraic equations. Verify that the results of $\mathbf{C}^{\dagger}\mathbf{HC}$ transformation gives the eigenvalue matrix, where **C** represents the eigenvector matrix. $7\frac{1}{2}$

   b) Establish the relation between the Einstein's spontaneous emission coefficient and stimulated absorption coefficient. 5

   ii) Indicate the change of corrosion potential and corrosion current using Evans diagram for additional bacterial corrosion. Can you recognize the type of bacteria on that basis ? 3

   b) i) Prove that direct current cnnnot pass through a capacitor placed in series with a resistor. 3

      ii) How many times the peak current would change, when both the concentration of the electroactive species and scan rate of potential are trebled in reversible cyclic voltammetric experiment with a simple system ? 2

UNIT - P-3112

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

a) i) Show that the symmetry factor of simple Butler Volmer equation can be equated to a trigonometric function which is a proper fraction. 4

ii) For an electrode reaction of the type :

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

state and explain the condition under which electrons tunnel between the electode and the ions in a soludion. 4

iii) Distinguish between polarizable and non polarizable interface. 2

b) i) The reaction path of $I_3^- + 2e^- \rightleftharpoons 3I^-$ consists of the following steps :

I) $I_3^- \rightleftharpoons I_2 + I^-$

II) $I_2 \rightleftharpoons I + I$

III) $2(I + e^- \rightleftharpoons I^-)$

It is found experimentally that the transfer coefficients, $\vec{\alpha} = \frac{1}{2} = \overleftarrow{\alpha}$. Find out the rate determining step. Also find out anodic and cathodic reaction orders with respect to both I^- and I_3^-. 5

ii) How would you modify simple Butler Volmer equation on the basis of consideration of the existence of double layer at the electode solution interface ? How would you verify the result ? 5

c) i) 'Efficiency of an ideally operating fuel cell can be even greater than one' – Elucidate or justify. $2\frac{1}{2}$

ii) Explain why i_o of hydrogen evolution reaction increases with increase of work function for some metals but decreases for other metals. $2\frac{1}{2}$

iii) Electrochemical oxidation of Pb to Pb^{2+} provides current density of 50 and 250 $mAcm^{-2}$ at 200 and 400 mV of potential respectively at 25°C. Calculate the transmission co-efficient of the reaction. $2\frac{1}{2}$

iv) Estimate limiting current density at 27°C for an electrode immersed in a 0·2M aqueous Cu^{2+} unstirred solution in which the thickness of the diffusion layer is about 0·6 mm. Given $\lambda = 107$ S $cm^2\ mol^{-1}$. $2\frac{1}{2}$

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

a) i) "A corroding metal is analogous to a short-circuited energy producing cell" – explain. 2