9. What is the ideal efficiency of a fuel cell? Show with example that ideal efficiency can be even greater than one. Show that the summation of the transmission co-efficients for the forward and backward reactions is equal to the ratio of total number of electron transferred and stoichiometric number for Generalised Butler Volmer reaction scheme. 5

M. Sc. Chemistry Examination, 2023

(3rd Semester, CBCS)

Paper: XI-P

[Physical Chemistry special]

Time : Two Hours Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

UNIT - P - 3111

1. (a) Write down the essential features of quantum mechanical Variation theorem. 2

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

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

   Show that the optimization of variational parameters requires the solutions of secular equations. 4

2. (a) Using Rayleigh Schrodinger time-independent perturbation theory for non-degenerate system, establish an expression for first order wave function correction for its n^{th} state. 5

   (b) An electrical field of strength F is applied on H atom along the z-axis as a perturbation. 5

   (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?

3. (a) Define transition probability. Consider a molecule exposed to an oscillating electric fiend, $E = 2E_0 Cos(\omega t)$, show that the probability of transition from a stationary state $|n\rangle$ to another state $|k\rangle$ increases linearly with time. 1+4

   (b) Derive the relation between Einstein's *A* and *B* coefficients. 5

UNIT - P - 3112

Answer any 4 questions :

4. Define concentration over-potential and derive an equation relating concentration over-potential and limiting current density of an electrochemical redox reaction. 5

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

6. Compare order of a chemical reaction and that of an electrochemical reaction. How does the order help in determining the mechanism of hydrogen evolution reaction? 5

7. Define equilibrium exchange current density. Derive Nernst equation of an electrochemical reaction from kinetic consideration. 5

8. (a) Calculate the change in Gibb's energy of activation of the cathodic process at an electrode, when potential difference changes from 0.5V to 0.75V at 25^0C. Use symmetry factor = 0.7 and number of electron transfer=2. $2\frac{1}{2}$

   (b) The equilibrium exchange current density of an electrode, $Pt/H_2(g)/H^+(aq)$ is 0.79 mA cm^{-2} at 298 K. Calculate the current obtained from the Pt foil of area 10 cm^2, when the over potential is 7 mV. $2\frac{1}{2}$