

Ex/SC/CHEM/PG/CORE/TH/XI-P/2025

M. Sc. CHEMISTRY EXAMINATION, 2025

(3rd Semester)

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

Answer *any two* questions :

1. (a) Write down the essential features of quantum mechanical variation theorem.
- (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.
- (c) Consider a trial function (ϕ) consisting of n variational parameters $\{a_i\}, i = 1, \dots, n$ such for a set of that known functions $\{f_i\}, i = 1, \dots, n, \phi = \sum_{i=1}^n a_i f_i$. Show that the optimization of variational parameters requires the solutions of secular equations. 2+4+4

CHEM-1034

[Turn Over]

(2)

2. (a) Using Rayleigh-Schrödinger time-independent perturbation theory for non-degenerate system, establish an expression for first order wave function correction for its n^{th} state.
- (b) An electrical field of strength F is applied on H atom along the z -axis as a perturbation.
- (i) Show the effect of 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? 5+5
3. (a) Derive the expression of the transition rate ($w_{i \rightarrow f}$) for the dipole induced transition from i^{th} discrete level to f^{th} level due to electromagnetic radiation of frequency ν .
- Derive the relation between Einstein's A and B coefficients. 6+4

UNIT—P – 3112

Answer *any two* questions :

4. (a) How can you determine equilibrium exchange current density, transfer co-efficient and stoichiometric number experimentally using high and low field approximations of Butler-Volmer equation?
- (b) Draw the nature of sinusoidal signals when the two signals are either 'in-phase' or 'out-of-phase'. (4+4)+2

(3)

5. (a) The electrochemical potential is a measure of the total work from bulk to infinity- Justify.
- (b) Discuss the importance of Randles-Sevcik equation to determine the adsorption of the analytes on the electrode surface. 5+5
6. (a) Discuss, in brief, the principle of electrical impedance spectroscopy.
- (b) Show that the Nernst equation describes a special case when the electrochemical process is at equilibrium. 7+3

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