

**Core Course XIII : PHYSICAL CHEMISTRY II**

**UNIT 1: ELECTRICAL CONDUCTANCE :**

Electrical transport and conductance in metal and in electrolytic solution. - specific conductance and equivalent conductance. measurement of equivalent conductance. using Kohlraush's bridge. Arrhenius theory of electrolytic dissociation and its limitation. weak and strong electrolyte according to Arrhenius theory. Ostwald's dilution law - applications and limitation. variation of equivalent conductance with concentration - migration of ion- ionic mobility. Kohlrausch's law and its applications. The elementary treatment of the Debye - Huckel- Onsager equation for strong electrolytes. evidence for ionic atmosphere. The conductance at high fields (Wein effect) and high frequencies (Debye - Falkenhagen effect). Transport number & Hittorf's rule. determination by Hittorf's method and moving boundary method application of conductance measurements - determination of strong electrolytes and acids. Determination of  $K_a$  of acids. determination of solubility product of a sparingly soluble salt. common ion effect. conductometric titrations.

**UNIT 2: ELECTROCHEMICAL CELLS**

Electrolytic & galvanic cells - reversible and irreversible cells. conventional representation of electrochemical cells. Electromotive force of a cell and its measurement- computation of E.M.F- calculation of thermodynamic quantities of cell reactions ( $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  and  $K$ )- application of Gibbs Helmholtz equation. concentration and E.M.F- Nernst equation, Types of reversible electrodes - gas/metal ion - metal/metal ion; metal/insoluble salt/ anion and redox electrodes. electrode reactions - Nernst equation - derivation of cell. E.M.F and single electrode potential- standard hydrogen electrode - reference electrodes - standard electrode potentials - sign convention - electrochemical series and its significance. concentration cell with and without transport- liquid junction potential. application of EMF of concentration cells. Valency of ion- solubility product and activity co-efficient. Potentiometric titrations. Determination of pH using hydrogen and quinhydrone electrodes- determination of  $pK_a$  of acids by potentiometric method. Corrosion - general and electrochemical theory - passivity - prevention of corrosion.

**UNIT 3: PHOTO CHEMISTRY AND GROUP THEORY**

Consequences of light absorption - Jablonski diagram- radiative and non - radiative transitions. laws of photo chemistry - Lambert - Beer, Grothus - Draper and Stark - Einstein. quantum efficiency. photo chemical reactions - rate law - kinetics of

$H_2-Cl_2$ ,  $H_2-Br_2$  and  $H_2-I_2$  reactions. comparison between thermal and photochemical reactions. photo sensitization and quenching. Fluorescence, phosphorescence and chemiluminescence. Laser and uses of lasers - population inversion and optical pumping.

Group theory: symmetry elements and symmetry operation-group postulates and types of groups-Abelian and non Abelian- symmetry operation of  $H_2O$

molecule-illustration of group postulates using symmetry operations of  $H_2O$   
molecule-construction of multiplication table for the operation of  $H_2O$   
molecule-point group-definition –elements (symmetry operations) of the  
following point groups:  $C_n$  ( $C_2$ ,  $C_3$ )  
 $S_n$  ( $S_1$ ,  $S_2$ ) ,  $C_{1V}$  ( $C_{2V}$ ,  $C_{3V}$ ) and  $C_{2R}$  . group theory and optical activity

#### **UNIT 4: SPECTROSCOPY I**

Electromagnetic spectrum - The regions of various types of spectra.  
Microwave spectroscopy: Rotational spectra of diatomic molecules treated as rigid rotator, condition for a molecule to be active in microwave region, rotational constants (B), and selection rules for rotational transition. Frequency of spectral lines, calculation of inter - nuclear distance in diatomic molecules.

Infrared spectroscopy : Vibrations of diatomic molecules - harmonic and anharmonic oscillators, zero point energy, dissociation energy and force constant, condition for molecule to be active in the IR region, selection rules for vibrational transition, fundamental bands, overtones and hot bands, diatomic vibrating rotator - P,Q,R branches. Determination of force constant. UV visible spectroscopy : conditions - theory of electronic spectroscopy - types of electronic transitions - Franck - Condon principle – pre dissociation - applications.

#### **UNIT 5: SPECTROSCOPY II**

**Raman spectroscopy :** Rayleigh scattering and Raman scattering. Stokes and antistokes lines in Raman spectra, Raman frequency, quantum theory of Raman effect, condition for a molecule to be Raman active. comparison of Raman and IR spectra- structural determination from Raman and IR spectroscopy, rule of mutual exclusion.

**NMR spectroscopy :** Nuclear spin and conditions for a molecule to give rise to NMR spectrum- theory of NMR spectra, number of NMR signals, equivalent and non - equivalent protons, position of NMR signals, shielding, de-shielding, chemical shift,  $\delta$  and  $\tau$  scales. Peak area and number of protons. Splitting of NMR signals - spin - spin coupling.

#### **Books for Reference :**

1. Maron S.H. and Lando J.B., Fundamentals of Physical Chemistry, Macmillan.
2. Puri B.R., Sharma L.R., and Pathania B.K., Principles of Physical Chemistry, Vishal publishing company.
3. Glasstone S. and Lewis D. Elements of physical Chemistry, macmillan
4. Rajaram and Keeriacose, Thermodynamics for students of chemistry.
5. Khterpal S.C. Pradeeps, Physical Chemistry, Volume I & II, Pradeep publications Jalandhur, (2004).
6. Jain D.V.S and Jainhar S.P., Physical chemistry, Principles and problems, Tata Mc Graw Hill, New Delhi, (1988).