JYOTI NIVAS COLLEGE AUTONOMOUS
SYLLABUS FOR 2018 BATCH AND THEREAFTER

Programme: B.Sc **Semester: V**

CHEMISTRY PAPER VI
PHYSICAL CHEMISTRY

Course Code: 18VCH6 **No. of Hours: 45**

COURSE OBJECTIVES:

By the end of the course students should be able to understand and explain

- Basic theories of conductance, the use of conductivity and potentiometry measurements as analytical tools, reference electrodes and their applications
- The fundamentals of Rotational, Vibrational, Raman and Electronic Spectroscopy as applicable to diatomic molecules and solve related numericals
- The concept of chemical potential and apply it to determine the changes in thermodynamic quantities (e.g. entropy, enthalpy, internal energy, Gibbs free energy) for open systems.
- Concepts in quantum mechanics such that the behaviour of the physical universe can be understood from a fundamental point of view. It provides a basis for further study of quantum mechanics.
- The fundamental laws of Photochemistry and the applications of Beer Lambert law, Concept of Quantum Efficiency
- And master the use of a potentiometer and conductivity meter in quantitative analysis, carry out an experiment to study the kinetics of a first and a second order reaction (The laboratory component).

LEARNING OUTCOMES:

On completion of the course, the student should be able to:

- Discuss the use of different spectroscopic techniques to understand the structure of molecules
- Discuss and appreciate the use of electrochemical techniques in analysis
- Use the Gibbs-Duhem equation to relate activity coefficients in a mixture
- Apply principles of quantum mechanics to calculate observables on known wave functions
- Use a potentiometer and conductivity meter to perform acid base and redox titrations

UNIT I **16 HRS**

Chapter 1:1 ELECTROCHEMISTRY

Review: Specific conductance, equivalent conductance and molar conductance and their determination. Variation of conductance with concentration, weak and strong electrolytes.

Transport number: Concept of ionic mobility, ionic conductance and transport number and relationship between them. Factors influencing transport number. Abnormal transport numbers. Problems Kohlrausch's law and its applications: determination of : (i) solubility of a sparingly soluble salt (ii) degree of dissociation and dissociation constant of a weak

electrolyte (iii) ionic product of water (iv) molar conductance at infinite dilution of a weak electrolyte. Problems.

Conductometric titrations: acid base and precipitation titrations.

Arrhenius theory and its limitations. Theory of strong electrolytes Debye-Huckel-Onsagar theory (qualitative treatment). Verification of DHO equation.

Review: Electrolytic and Galvanic cells, convention of representing cells, reversible and irreversible cells. Standard Hydrogen Electrode.

Single electrode potential , standard electrode potential , determination of E° of Zinc and Copper electrodes.

Types of electrodes - cation reversible, anion reversible and redox electrode.

Electrodes –calomel and quinhydrone. Determination of pH using quinhydrone, calomel and SHE. Problems.

EMF of cells, Weston-Cadmium cell, Nernst equation - thermodynamic deduction, equilibrium constant and free energy of a cell reaction. Problems.

Concentration cells: emf of concentration cells, determination of solubility of sparingly soluble salts. Redox potentials. Problems.

Potentiometric titrations: redox, acid base and precipitation.

UNIT II **03 HRS**

Chapter 2:1 THERMODYNAMICS OF OPEN SYSTEMS

Maxwell's relations. Definition of partial molar properties and chemical potential. Derivation of Gibbs-Duhem equation. Variation of chemical potential with temperature and pressure.

Chapter 2:2 QUANTUM MECHANICS **04 HRS**

Concept of operators, properties – addition, subtraction and commutative property. Types of operators: commutator, linear, Laplacian and Hamiltonian. Conditions for acceptable wave function. Normalization and orthogonality of wave functions (for particle in a one-dimension box), problems.

Chapter 2:3 PHOTOCHEMISTRY **06 HRS**

Introduction: Differences between thermal and photochemical processes. Photostationary state. Molecular spin – singlet and triplet states. Laws of photochemistry – (i) Grotthus-Draper Law (ii) Stark-Einstein Law (iii) Beer-Lambert's Law – derivation and its limitations.

Qualitative description of photophysical process: (i) non radiative – vibrational relaxation, internal conversion, intersystem crossing. (ii) Radiative – fluorescence and phosphorescence differences. Jablonski diagram.

Photochemical Reactions: Decomposition (ammonia and acetone), Combination (hydrogen and halogen), Isomerisation (maleic acid to fumaric acid), Dimerisation (anthracene) and Cleavage reaction (cyclopentadienone).

Quantum yield: definition and experimental determination**.** Problems. Deviations from Stark-Einstein Law.

Photosensitisation – dissociation of H_2 molecule using mercury vapour.

UNIT III **16 HRS**

Chapter 3:1 SPECTROSCOPY

Introduction: Electromagnetic radiation, regions of the spectrum, statement of Born-Oppenheimer approximation.

Rotational Spectroscopy: Diatomic molecules. Expression for rotational energy. Energy levels of a rigid rotor (semi-classical principles), selection rule. Isotope effect.

Vibrational Spectroscopy: Energy levels of simple harmonic oscillator, selection rule, pure vibrational spectrum, intensity of spectral lines. Force constant: Determination and qualitative relation with bond energy. Problems. Anharmonicity. Rotational vibrational spectroscopy. PQR branches (qualitative treatment only).

Modes of vibration for polyatomic molecules, identification of IR active modes - water and carbon dioxide.

Raman Spectra: Concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules. Origin of Stokes and anti-Stokes lines. Selection rules. Rule of mutual exclusion. Advantages of Raman spectroscopy over IR spectroscopy.

Electronic Spectra: Franck-Condon principle.

REFERENCES:

1. 1. P.W. Atkins and Julio de Paula, Physical Chemistry, 7th Edition, 2002, Oxford Univ. Press.
2. B. R. Puri, L. R. Sharma and M. S. Pathania, Principles of Physical Chemistry, 1997, S. L. N. Chand & Co.
3. Colin, N. Banwell and Elaine N. Mc Cash, Fundamentals of Molecular Spectroscopy, 4th Edition, 2005, McGraw Hill.
4. Essentials of Physical Chemistry, B.S. Bahl ,Arun Bahl and G.D.Tuli,2008, S. Chand & Co.
5. Quantum Chemistry, R K. Prasad, 4th revised edition, 2006.

CHEMISTRY PRACTICAL

V SEMESTER - PAPER VI (PHYSICAL)

DURATION: 3 HRS / WEEK **NO. OF UNITS: 15**

1. Determination of pKa of a weak acid by pH metric method.

2. Verification of Beer-Lambert's law by Colorimetric method.

3. Kinetics of the oxidation of KI by $K_2S_2O_8$ by titrimetric method

4. Determination of the equivalent conductivity of 0.1N NaCl and verification of DHO theory

5. Determination of the dissociation constant of monochloroacetic acid by conductivity method

6. Conductometric titration of HCl with NaOH

7. Determination of standard redox potential of an electrode

8. Redox titration of $K_2Cr_2O_7$ with ferrous ammonium sulphate by potentiometry

9. Preparation of a buffer solution and determination of its pH by potentiometry

10. Determination of the solubility of a sparingly soluble salt (AgCl) by conductivity method

11. Determination of transition temperature of a salt hydrate by thermometric method.

Test, repetition and demonstration experiments.

REFERENCES

1. Finlay's Practical Physical Chemistry revised by Levitt, 1988, Longman's London.
2. Shoemaker and Garland, Experiments in Physical Chemistry, 1990, McGraw Hill International.
3. J B Yadav Advanced Practical Physical Chemistry, 30th edition.