

UNIVERSITY OF MUMBAI



Syllabus for the M.Sc. Part - I Program: M.Sc.CHEMISTRY

Course :

(Credit Based Semester and Grading System with
effect from the academic year 2012–2013)

M .Sc.
CHEMISTRY Syllabus
Restructured for Credit Based and Grading System
To be implemented from the Academic year 2012-2013

SEMESTER I

Course Code –(Physical Chemistry) PSCH 101

Total Lectures 60 L]

Unit - I

Topic - Thermodynamics-I

[15L]

- [5L]
- 1.1 State function and exact differentials. Maxwell equations, Maxwell thermodynamic square, Joule Thomson experiment, Joule Thomson coefficient, inversion temperature, Joule Thomson coefficient in terms of van der Waals constants, Temperature dependence of enthalpy and entropy, Gibbs energy of reaction
- 1.2 Third law of Thermodynamics, Entropy change for a phase transition, absolute entropies, determination of absolute entropies in terms of heat capacity data, standard molar entropies and their dependence on molecular mass and molecular structure. Residual entropy.

[10]

Unit-II

Topic - Thermodynamics-II

[15L]

- 2.1 Fugacity of real gases, Determination of fugacity of real gases using graphical method and from equation of state. Equilibrium constant for real gases in terms of fugacity. Gibbs energy of mixing, entropy and enthalpy of mixing.
- [4 L]
- 2.2 **Real solutions:** Chemical potential in non ideal solutions excess functions of non ideal solutions calculation of partial molar volume and partial molar enthalpy, Gibbs Duhem Margules equation.
- [6 L]
- 2.3 Applications of thermodynamic functions to life processes Entropy and free energy changes of a biochemical reaction, Free energy changes involved in reactions that synthesize and utilize ATP.

[5L]

Unit-III

Topic - Applied Thermodynamics

[15L]

- 3.1 Two component system**
(Solid –Gas System) I-Hydrate formation **II**- Amino compound formation [2L]
(Solid – Liquid System) I – Formation of a compound with congruent melting point
II- Formation of a compound with incongruent melting point [2L]
- 3.2 Three component system**
Recapitulation: Graphical representation of three component system; system of three liquids: having partial miscibility.
Type-I Formation of one pair of partially miscible liquids
Type-II Formation of two pairs of partially miscible liquids
Type-III Formation of three pairs of partially miscible liquids [2L]
- 3.3 Ternary system of two solid compounds and one liquid**
- 1. Double salt formation –**
 - (a) Double salt not decomposed by water
 $\text{H}_2\text{O} - \text{AgNO}_3 - \text{NH}_4\text{NO}_3$
 - (b) Double salt decomposed by water
 $\text{H}_2\text{O} - \text{AgNO}_3 - \text{KNO}_3$ [2L]
 - 2. One salt forming a hydrate –**
 - (a) Hydrate not dehydrated by second salt
 $\text{H}_2\text{O} - \text{Na}_2\text{SO}_4 - \text{NaCl}$
 (Hydrate $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ is formed)
 - (b) Hydrate dehydrated by second salt.
 $\text{H}_2\text{O} - \text{Na}_2\text{SO}_4 - \text{NaCl}$
 (Na_2SO_4 is dehydrated by addition of NaCl) [2L]
 - 3. Double salt forming hydrate –**
 - (a) Hydrated double salt not decomposed by water (Alums stable in presence of water)
 - (b) Hydrated double salt decomposed by water [1L]
- 3.4 Thermodynamics of surfaces,** Pressure difference across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, BET isotherm (derivations expected). [4L]

Unit - IV

Topic - Electrochemistry

- [15L]
- 4.1** Debye-Huckel theory of activity coefficient, Debye-Huckel limiting law and its extension to higher concentration (derivation expected). [3L]
- 4.2.** Electrolytic conductance and ionic interaction, relaxation effect,. Debye-Huckel-Onsager equation (derivation expected). Validity of this equation for aqueous and non-aqueous solution, deviations from Onsager equation, Debye -Falkenhagen effect (dispersion of conductance at high frequencies), Wien effect. [4L]
- 4. 3** Batteries: Alkaline fuel cells, Phosphoric acid fuel cells, High temperature fuel cells, General development of a fuel cell based technology [3L]
- 4. 4** Bioelectrochemistry: Introduction, cells and membranes, membrane potentials, theory of membrane potentials, interfacial electron transfer in biological systems, adsorption

of proteins onto metals from solution, electron transfer from modified metals to dissolved protein in solution, enzymes as electrodes, electrochemical enzyme-catalysed oxidation of styrene.

5L]

Course Code —(Inorganic Chemistry) PSCH 102

[Total Lectures 60 L]

Unit - I

Topic - Inorganic Reaction Mechanisms

[15L]

- (i) Rate of reactions, factors affecting the rate of reactions, techniques for determination of rate of reaction.
- (ii) Ligand substitution reactions of (a) octahedral complexes without breaking of metal-ligand bond, (b) square planar complexes – trans-effect, its theories and applications. Mechanism and factors affecting these substitution reactions and (c) Tetrahedral complexes.
- (iii) Redox reactions: electron and atom transfer reactions, inner and outer sphere mechanisms, Marcus theory, complimentary and non-complimentary reactions.
- (iv) Isomerization and racemization reactions.

Unit – II

Topic - Organometallic Chemistry

[15 L]

- (i) Organometallic compounds of transition metals: Preparation and properties of the following organometallic compounds: (a) Alkyl and Aryl derivatives, (b) Carbenes and Carbynes, (c) Alkene complexes, (d) Alkyne complexes, (e) Allyl complexes, (f) Cyclopentadiene complexes and (g) Arene complexes (sandwich and half sandwich complexes).
- (ii) Structure and bonding in Zeise's salt, bis(triphenylphosphine) diphenylacetylene platinum(0), diallyl nickel, ferrocene and dibenzene chromium(0).
- (iii) Sixteen electron rule and electron counting with examples.

Unit – III

Materials Chemistry and Nanomaterials

[15 L]

- (i) Solid State Chemistry
 - (a) Electronic structure of solids and band theory, Fermi level, K Space and Brillouin Zones.
 - (b) Structures of Compounds of the type : AB [nickel arsenide (NiAs)], AB₂ [fluorite(CaF₂) and antiferite structures, rutile (TiO₂) structure and layer structure [cadmium chloride and iodide (CdCl₂, CdI₂)].
 - (c) Methods of preparation for inorganic solids: Ceramic method, precursor method, sol-gel method, microwave synthesis (discussion on principles, examples, merits and demerits are expected).

- (ii) Nanomaterials
 - (a) Preparative methods
 - Chemical methods : solvolthermal, microwave, coprecipitation, Langmuir Blodgett (L-B) method Biological methods : synthesis using microorganisms
 - (b) Applications in the field of semiconductors and solar cells.

Unit - IV

Spectral and Magnetic Methods

[15 L]

- (i) Interpretation of electronic spectra for octahedral (Ni(II) and Cr(III)) and square planar complexes for d^8 ions [Ni(II), Pd(II), Pt(II)], IR and Raman spectroscopy with reference to metal- nitrogen, metal-oxygen and metal-sulfur bonds.
- (ii) Spectroscopic methods viz., Job's method, mole-ratio and slope-ratio methods for determination of stepwise formation constants of metal complexes.
- (iii) Application of ESR and magnetic susceptibility studies of metal complexes: interpretation of ESR spectra of Cu(II) complexes (octahedral, square planar and tetragonal complexes) and susceptibility results for the same.

Course Code —(Organic Chemistry) PSCH 103 [
Total Lectures 60 L]

Theory and practical

[From the academic year 2011-2012]

Semester – I

60L

Unit-I

1. Molecular Orbital Theory for organic chemistry **8L**

1.1. LCAO and MOs: π -MOs of ethylene, higher polyenes, and benzene and their energies. Effect of conjugation on stability and reactivity of polyenes.

1.2. FMOs: Use of FMOs in ethylene dimerization to cyclobutane, Diels-Alder reaction, reaction of allyl cation with allyl anion, reactivity of carbonyl group. Significance of HOMO-LUMO gap in absorption spectra and chemical reactions. FMOs of hard and soft acids and bases, nucleophiles and electrophiles.

1.3. Aromaticity **7L**

1.3.1. Structural, thermochemical, and magnetic criteria for aromaticity, including NMR characteristics of aromatic systems. Delocalization and aromaticity.

1.3.2. Application of HMO theory to monocyclic conjugated systems. Frost-Muslin diagrams. Huckel's $(4n+2)$ and $4n$ rules.

1.3.3. Aromatic and antiaromatic compounds upto 18 carbon atoms. Aromaticity of benzenoid systems, heterocycles, metallocenes, azulenes, annulenes and tropylium cations. Homoaromatic compounds.

Unit-II

2. Physical Organic Chemistry **12L**

2.1 Thermodynamic and kinetic requirements of a reaction: Transition state theory, Hammond's postulate, Principle of microscopic reversibility, Kinetics vs thermodynamic control.

2.2. Acids and bases: Factors affecting acidity & basicity. Acid & base catalysis - specific & general catalysis

2.3 Determining mechanism of a reaction: Product analysis, Kinetic studies, Stereochemical outcome, Detection and trapping of intermediates, Crossover experiments, Kinetic isotope effect –primary kinetic & secondary kinetic isotope effect.

2.4. Elimination Reactions

3L

2.4.1. Types of elimination reactions. E_1 , E_2 and E_{1cB} mechanisms.

2.4.2. Pyrolytic elimination: Chugaev reaction, Cope reaction and Pyrolysis of acetates.

Unit-III

3. Stereochemistry

15L

3.1 Symmetry operations: Rotation, reflection, inversion, rotation- reflection.

Identification of the different axes and planes of symmetry.

3.2 Molecules with tri and tetracoordinate chiral centres: Compounds with carbon, silicon, nitrogen, phosphorous and sulfur chiral centres and their relative configurational stabilities.

3.3. Molecules with two or more chiral centres: Configurational nomenclature
Constitutionally unsymmetrical molecules: Erythro-threo and syn-anti systems.
Constitutionally symmetrical molecules with odd and even number of chiral centres: enantiomeric and meso forms, concept of stereogenic, chirotopic and pseudoasymmetric centres.

3.4 Axial and planar chirality: Principles of axial and planar chirality. Stereochemical features and configurational descriptors (R, S) for the following classes of compounds: allenes, alkylidene cycloalkanes, spiranes, biaryls (including BINOLs and BINAPs), ansa compounds and cyclophanes.

3.5 Prochirality: Homotopic, heterotopic and diastereotopic ligands and faces. Identification using substitution and symmetry criteria. Nomenclature of stereoheterotopic ligands and faces. Symbols for stereoheterotopic ligands in molecules with one or more prochiral centres, pro-pseudoasymmetric centre, chiral and prochiral centre; prochiral axis and prochiral plane. Symbols for enantiotopic and diastereotopic faces.

Unit-IV

4. Oxidation

8 L

General mechanism, selectivity, and important applications of the following:

4.1 Dehydrogenation of C-C bonds including aromatization of six membered rings using metal (Pt, Pd, Ni) and organic reagents (chloranil, DDQ).

4.2 Dehydrogenation/oxidation of alcohols to aldehydes and ketones: chromium reagents such as $K_2Cr_2O_7/H_2SO_4$ (Jones reagent), CrO_3 -pyridine (Collin's reagent), PCC (Corey's reagent) and PDC, hypervalent iodine reagents (IBX, Dess-Martin periodinane). DMSO based reagents (Swern oxidation) and Oppenauer oxidation.

4.3 Oxidation involving C-C bonds cleavage: Glycols using HIO_4 ; cycloalkanones using CrO_3 ; carbon-carbon double bond using ozone, $KMnO_4$, CrO_3 , $NaIO_4$ and OsO_4 ; aromatic rings using RuO_4 and $NaIO_4$.

4.4 Oxidation involving replacement of hydrogen by oxygen: oxidation of CH_2 to CO by SeO_2 , Oxidation of aryl methanes by CrO_2Cl_2 (Etard oxidation).

4.5 Oxidation of aldehydes and ketones: with H_2O_2 (Dakin reaction), with peracid (Baeyer-Villiger oxidation).

4.6.Reduction

7L

General mechanism, selectivity, and important applications of the following reducing reagents:

4.6.1 Reduction of CO to CH_2 in aldehydes and ketones -Clemmensen reduction, Wolff-Kishner reduction and Huang-Minlon modification. Ra-Ni desulfurization of thioketal

4.6.2 Metal hydride reduction: Boron reagents ($NaBH_4$, $NaCNBH_3$, $Na(OAc)_3BH$), aluminium reagents ($LiAlH_4$, DIBALH, Red Al, L and K selectrides).

NH_2NH_2 (diimide reduction) and other non-metal based agents including organic reducing agents (Hantzsch dihydropyridine).

4.6.3. Dissolving metal reductions: using Zn, Li, Na, and Mg under neutral and acidic conditions, Li/Na-liquid NH_3 mediated reduction (Birch reduction) of aromatic compounds and acetylenes

Course Code —(Analytical Chemistry) PSCH 104

[Total Lectures 60 L]

M.Sc.

Draft Syllabus for

[From the Academic year 2012-13]

[Apart from Unit-II numerical problems are expected on Unit-IV, Unit -V and Unit VII and VIII]

Semester –I

[60L]

Unit –I

1.1 Introduction to Analytical Chemistry: Classification of analytical methods, an overview of analytical methods, types of instrumental methods, instruments for analysis, data domains, electrical and non electrical domains, detectors, transducers and sensors, selection of an analytical method, accuracy, precision, selectivity, sensitivity, detection limit and dynamic range, classification of techniques: calibration curve, standard addition and internal standard methods. **[7L]**

1.2 Quality in analytical chemistry: quality systems in chemical laboratories, cost and benefits of a quality system, types of quality standards for laboratories, total quality management, quality audits and quality reviews, responsibility of laboratory staff for quality. **[8L]**

Unit-II

Chemometrics: The following topics are to be covered in the form of numerical problems only.

A] Concentration of a solution based on volume and mass units.

B] Calculations of ppm, ppb and dilution of the solutions, concept of mmol

C] Stoichiometry of chemical reactions, concept of kgmol, limiting reactant, theoretical and practical yield.

D] Solubility and solubility equilibria, effect of presence of common ion.

E] Calculations of pH of acids, bases and acidic and basic buffers.

F] Concept of formation constants, stability and instability constants, step wise formation constants. **[15L]**

Unit –III

3.1 Introduction to separation methods in analytical chemistry:

precipitation, filtration, distillation, extraction and chromatography, modes of separation in chromatography: adsorption, partition, ion exchange, size exclusion and electrochromatography. [2L]

3.2 Solvent extraction: Recapitulation, factors affecting the solvent extraction

of inorganic species, separation of metal ions as chelates, concept of $[pH]_{1/2}$ and its significance, ion association, solvation with suitable examples, Craig's counter current extraction: principles, apparatus and applications, use of crown ethers in solvent extraction. [8L]

3.3 Solid phase extraction: principle, process and applications. [2L]

3.4 HPTLC: conversion of TLC to quantitative measurements, densitometric detectors, fluorimetric detectors, [3L]

Unit-IV

4.1 General classification of chromatographic methods: column efficiency, plate and rate theories, resolution, selectivity and separation capability, Van Deemter equation, [quantitative treatment and mathematical derivations not expected.] [3L]

4.2 Gas chromatography: instrumentation, sample introduction systems, packed and capillary columns, detectors: selectivity, limit of detection, operative principles of coulometric, thermionic and NP detectors, temperature programming, applications in various fields. [6L]

4.3 HPLC: column efficiency in LC, mobile phase reservoirs, solvent treatment systems pumping systems, sample introduction systems, types of columns, detectors: EC and diode array detectors, fluorimetric detectors. [6L]

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SEMESTER II

Course Code – –(Physical Chemistry) PSCH 201

[Total Lectures 60]

Unit - I

Topic - Quantum Chemistry – I

- [15L]**
- 1.1 Recapitulation: Black body radiation, photoelectric effect, wave particle duality, Heisenberg's uncertainty principle, [15L]
- 1.2 Particle waves and Schrödinger wave equation, wave functions, properties of wave functions, Normalization of wave functions, orthogonality of wave functions.
- 1.3 Operators and their algebra, linear and hermitian operators, operators for the dynamic variables of a system such as, position, linear momentum, angular momentum, total energy, eigen functions, eigen values and eigen value equation, Schrödinger wave equation as the eigen value equation of the Hamiltonian operator, average value and the expectation value of a dynamic variable of the system, Postulates of Quantum Mechanics Time independent Schrödinger wave equation. [6 L]
- 1.4 Application of quantum mechanics to the following systems: [2L]
- A] Free particle, wave function and energy of a free particle. [2L]
- B] Particle in a one, two and three dimensional box, separation of variables, Expression for the wave function of the system, expression for the energy of the system, concept of quantization, introduction of quantum number, degeneracy of the energy levels. [5L]
- C] Harmonic oscillator, approximate solution of the equation, Hermite polynomials, expression for wave function, expression for energy, use of the recursion formula, [2L]

Unit-II

Topic - Quantum Chemistry-II

- [15L]**
- 2.1 Rigid rotor, spherical coordinates Schrödinger wave equation in spherical coordinates, separation of the variables, the phi equation, wavefunction, quantum number, the theta equation, wave function, quantization of rotational energy, spherical harmonics. [4L]
- 2.2 Hydrogen atom, the two particle problem, separation of the energy as translational and potential, separation of variables, the R the theta* and the phi equations, solution of the reequation, introduction of the four quantum numbers and their interdependence on the

- basis of the solutions of the three equations, total wave function, expression for the energy, probability density function, distances and energies in atomic units, radial and angular plots., points of maximum probability, expressions for the total wave function for 1s,2s, 2p and 3d orbitals of hydrogen [9L]
- 2.3 Application of the Schrödinger equation to two electron system, limitations of the equation, need for the approximate solutions, methods of obtaining the approximate solution of the Schrödinger wave equation. [2L]
 * *Derivation not expected*

Unit - III

Topic - Chemical Kinetics and Molecular Reaction Dynamics-I

- [15L]**
- 3.1 **Composite Reactions:** [10L]
 Recapitulation of rate laws, Differential rate equations, Consecutive reactions, Steady state Approximation, rate determining steps, Microscopic Reversibility and Detailed Balance
Chain reactions-chain initiation processes.
Some inorganic mechanisms: formation and decomposition of phosgene, decomposition of ozone, Reaction between Hydrogen and Bromine and some general examples
Organic Decompositions: Decomposition of ethane, decomposition of acetaldehyde
Gas phase combustion: Reaction between hydrogen and oxygen, Semenov – Hinshelwood and Thompson mechanism, Explosion limits and factors affecting explosion limits.
Polymerization reactions: Kinetics of stepwise polymerization, Calculation of degree of polymerization for stepwise reaction. Kinetics of free radical chain polymerization, Kinetic chain length and estimation of average no .of monomer units in the polymer produced by chain polymerization.
- 3.2 **Reaction in Gas Phase** [5L]
 Collision Theory of Reaction Rates for Bimolecular Reactions: Collision number, collision frequency factor, Steric factor, Reaction cross section, Macroscopic rate constant, line-of-centers model. Unimolecular Reactions: Lindeman-Hinshelwood theory, Rice-Ramsperger-Kassel (RRK) theory, Rice-Ramsperger-Kassel-Marcus(RRKM) theory

Unit – IV

Topic - Chemical Kinetics and Molecular Reaction Dynamics-II

- [15L]**
- 4.1 **Elementary Reactions in Solution** [5L]
Solvent Effects on reaction rates, Reactions between ions- influence of solvent Dielectric constant, influence of ionic strength, Linear free energy relationships

(LFER), Effect of substituent on reaction rates (Hammett relationships)

4.2 Enzyme Catalysis

[5L]

Enzyme action, **Kinetics of reactions catalyzed by enzymes** -Michaelis-Menten analysis, Lineweaver-Burk and Eadie Analyses.

Inhibition of Enzyme action: Competitive, Noncompetitive and Uncompetitive Inhibition. Effect of pH, Enzyme activation by metal ions, Regulatory enzymes.

4.3 Kinetics of reactions in the Solid State

[5L]

Factors affecting reactions in solids

Rate laws for reactions in solid: The parabolic rate law, The first order rate law, the contracting sphere rate law, Contracting area rate law, some examples of kinetic studies.

M.Sc

Course Code – –(Inorganic Chemistry) PSCH 202 [Total Lectures 60]

Unit I

Topic - Chemical Bonding and Magnetism

[15L]

- (i) Hybridisation: Derivation of wave functions for the following orbital hybridisation types: sp (BeH_2); sp^2 (BF_3); sp^3 (CH_4) considering only sigma bonding.
- (ii) Molecular Orbital Theory (LCAO-MO approach) for (a) Electron deficient species (B_2H_6), and (b) Electron rich species (triiodide ion, I_3^-).
- (iii) Hydrogen bonding – concept, types, properties, methods of detection and importance. van der Waal's forces, ion-dipole, dipole-dipole, London forces.
- (iv) **Theory of magnetism, diamagnetism, paramagnetism, ferromagnetism and antiferromagnetism, Curie and Curie-Weiss laws, Faraday's method of determination of magnetic susceptibility.**

Unit - II

Topic - Molecular Symmetry and Group theory

[15 L]

- (i) Concepts of Groups, Sub-groups, Classes of Symmetry operations, Group Multiplication Tables. Abelian and non-Abelian point groups.
- (ii) Symmetry criterion of optical activity, symmetry restrictions on dipole moment. A systematic procedure for symmetry classification of molecules.
- (iii) Representation of Groups: Matrix representation of symmetry operations, reducible and irreducible representations. The Great Orthogonality Theorem. Construction of character tables for point groups C_{2v} , C_{3v} and D_{2h} , structure of character tables, determination of symmetry species for translations and rotations; Mulliken's notations for irreducible representations, reduction of reducible representations using reduction formula, group-subgroup relationships, descent and ascent in symmetry, correlation diagrams showing relationship between different groups.
- (iv) Symmetry adapted linear combinations, symmetry aspects of MO theory, sigma- and pi-bonding in AB_4 (**tetrahedral**) **molecule.**

Unit - III

Topic - Environmental Chemistry

[15 L]

- (i) Water pollution: Heavy metal pollutants like mercury, lead, cadmium, arsenic, **copper** and chromium, with respect to their sources, distribution, speciation, toxic effects, control and treatment.
- (ii) Radiation pollution: Sources and biological implication of radioactive pollutants. Effects of radioactivity on cell proliferation and cancer.
- (iii) Sources of energy at present and for the future: Fossil fuels, coal, oil, oil shales and natural gas. Nuclear fission and fusion, Solar energy, Use of solar energy **in water**

heating, Production of electricity using solar **energy**, **Power** from indirect solar energy- Hydro power, Wind power, Biomass energy, Production of **ethanol and methane** from biomass, Geothermal **energy and Tidal** power.

Unit - IV

Topic - Bioinorganic Chemistry

[15 L]

- i) Biological oxygen carriers: hemoglobin, hemerythrin and hemocyanin. Hill equation, Bohr effect and their implications.
- (ii) Reactions of dioxygen in biological system with examples of peroxidase, monooxygenase, superoxide dismutase and oxidase reactions.
- (iii) Nitrogen fixation-nitrogenase, Hydrogenases.
- (iv) Metal ion transport and storage: Ionophores, transferrin and Ferritin.
- (v) Metal ions in medicines, cis-platin and related compounds.

Unit I

I. Chemistry of enolates

15L

I.1 Enolates: Structure and stability of enolates. Generation of enolates using nucleophilic and non-nucleophilic bases. Kinetic and thermodynamic control in regiochemistry of enolates, Reactions of enolates ions.

I.2 Alkylation and acylation of enolate ions

I.3 Halogenations of carbonyl compounds: Acid catalysed and base catalysed reactions e.g. Haloform reaction, α -bromination of carboxylic acids- Hell-Volhard-Zelinsky reaction (HVZ).

I.4 Condensation reactions involving Ester enolate ions: Claisen condensation, Dieckmann cyclization. Enolate of active-methylene compound - Mannich reaction.

I.5 Conjugate addition to α , β -unsaturated carbonyl compounds: Michael addition, Robinson annulation.

Unit II

II. Rearrangements

15L

Mechanisms of the following reactions with examples

2.1. Concerted rearrangements: Cope (including Oxy-Cope), Claisen, Curtius, Lossen, olefin metathesis, Wolff.

2.2 Cationic rearrangements: Demjanov, Pummerer, Schmidt, Dienone-phenol.

2.3 Anionic rearrangements: Brook, Favorski, Neber, Von Richter, Sommelet-Hauser, Wittig

Unit-III

3. Nucleophilic Substitution Reactions

8L

3.1 Aliphatic nucleophilic substitution at sp^3 carbon: S_N^1 , S_N^2 , S_N^i reactions. NGP reactions - participation by aryl rings, π and σ bonds. Ion pair in S_N^1 reactions. Stereochemistry of all the above reactions. Factors affecting these reactions: substrate, nucleophilicity, solvent, steric effect, hard-soft interaction, leaving group. Ambident nucleophiles. $S_{NC}A$ and S_N' reactions.

3.2 Aliphatic nucleophilic substitution reactions at sp^2 (vinylic) carbon.

3.3 Aromatic nucleophilic substitution reaction: S_{NAr} , S_N1 , Benzyne mechanisms. ipso, cine and tele substitutions, vicarious substitution.

3.4 Ester hydrolysis: All mechanisms of acid and base catalyzed hydrolysis.

3.5 UV and IR spectroscopy

7L

3.5.1 Ultraviolet spectroscopy: Factors affecting the position and intensity of UV bands – effect of conjugation, steric factor, pH, solvent polarity. Calculation of absorption maxima by Woodward-Fieser Rules (using Woodward-Fieser tables for values for substituents) for the following classes of organic compounds: conjugated polyenes (cyclic and acyclic), enones and substituted benzene derivatives.

3.5.2 Infrared spectroscopy: Fundamental, overtone and combination bands, vibrational coupling, important group frequencies for the common functional groups.

Unit-IV. NMR spectroscopy and Mass spectrometry

15L

4.1 Proton magnetic resonance spectroscopy: Chemical shift, Factors affecting chemical shift, Chemical and magnetic equivalence, Spin-spin coupling, Coupling constant J, Factors affecting J, Karplus equation, First order spectra, Geminal, vicinal and long range coupling (allylic and aromatic)

4.2 Mass spectrometry: Molecular ion peak, base peak, isotopic abundance, metastable ions. Nitrogen rule, Determination of molecular formula of organic compounds based on isotopic abundance and HRMS Fragmentation pattern in various classes of organic compounds (including compounds containing hetero atoms), McLafferty rearrangement, Retro-Diels-Alder reaction, ortho effect.

4.3. Structure determination involving individual or combined use of the above spectral techniques.

Course Code – –(Analytical Chemistry)PSCH 204

[Total Lectures 60]

ANALYTICAL

Semester –II

[60L]

Unit-I

1.1 General introduction to spectroscopic methods: recapitulation of basic concepts, general instrumentation: sources, wavelength selectors, sample containers, radiation transducers, signal processors and read out system, fiber optics, types of optical instruments, Fourier transform optical instruments., [5L]

1.2 Molecular ultra violet and visible spectroscopy: factors affecting molecular absorption, types of transitions, pH, temperature, solvent, effect of substituents, Derivative and dual wavelength spectroscopy, applications including simultaneous determinations. [5L]

1.3 Infrared absorption spectroscopy: instrumentation, FTIR, advantages of FTIR, applications of IR, qualitative and quantitative analysis, advantages and limitations of quantitative IR methods. [5L]

Unit -II

2.1 X-ray spectroscopy: principles instrumentation and applications of X-ray fluorescence, absorption and diffraction spectroscopy. [7L]

2.3 Mass spectrometry: recapitulation, instrumentation, ion sources for molecular studies, electron impact, field ionization, field absorption, chemical ionization and fast atom bombardment sources. mass analyzers: quadrupole, time of flight and ion trap. applications, use of mass spectrometer as

a detector in chromatography.

[8L]

Unit –III

3.1 Ion selective potentiometry: solid state, precipitate, liquid –liquid, enzyme and gas sensing electrodes with applications, ion selective field effect

transistors, biocatalytic membrane electrodes, enzyme based biosensors. [8L]

3.2 Electrogravimetry: introduction, factors affecting the nature of the deposit, instrumentation and applications. [4L]

3.3 Coulometry: coulometry: at controlled potential and controlled current. [3L]

Unit-IV

4.1 Voltammetry

4.1.1 Polarography: Ilkovic equation, derivation starting with Cottrell equation,[5L]

effect of complex formation on the polarographic waves, organic polarography,

4.1.2 Introduction to modern voltammetric techniques:

a) Differential pulse polarography.

b) Cyclic voltammetry

c) Stripping voltammetry both anodic and cathodic. [6L]

4.2 Bi-amperometric Titrations: principle, instrumentation, titration curves and detection of endpoint, Karl Fischer method: principle, process and instrumentation .[4L]