Semester – 3

BRANCH	Subject Title	Subject Code
B.Sc. (Chemistry– Major)	Reactions, Reagents and Mechanisms in Organic Chemistry	CHM1-131

Course Learning Outcomes (CLO)

By the end of this course students will acquire the knowledge of following aspects of chemistry:

- Various organic reactions, reagents and their mechanisms, which will be helpful in understanding organic synthesis.
- Application of the reactions in the various industries like pharmaceutical, polymer, pesticides, textile, dyes etc.
- Important key reaction used in further study and research work

Unit - 1

Substitution reactions

1.1 Aliphatic Nucleophilic Substitution: Introduction, the Syl, SN2 and SNi mechanisms, neighbouring group participation, effect of substrate, nucleophile, leaving group and reaction medium.

1.2 Aliphatic Electrophilic Substitution: Elementary treatment.

1.3 Aromatic Nucleophilic Substitution: the SNAT, SNl and Benzyne mechanisms, effect of substrate, nucleophile, leaving group and reaction medium.

1.4 Aromatic Electrophilic Substitution: Arenium ion mechanism, orientation/directive influence (electronic explanation only) and reactivity, diazonium coupling, Vilsmeir realion.

Unit - 2

Addition and Elimination Reactions

2.1 Addition Reactions: Introduction, reactions involving addition of nucleophile, electrophile, and free radicals, regio-selectivity and chemo-selectivity, orientation and reactivity, Markovnikov and Anti-Markovnikov's addition.

2.2 Elimination Reactions: Introduction, E1, E2 and EleB mechanisms, effect of substrate, attacking species, leaving group and reaction medium, orientation- Saytzeff and Hofmann rule.

Unit - 3

Reagents, Catalysts and Rearrangements. (Mechanisms and Applications)

3.1 Reagents and Catalysts: Preparation; properties and applications of important reagents and catalysts in organic synthesis with mechanistic details: Grignard reagent, N-bromo succinimide (NBS), diazomethane, anhydrous aluminium chloride (AIC), sodamide (NaNH), Ziegler- Natta catalyst.

3.2 Rearrangements (Reaction, Mechanism & Applications): Introduction, Types of Rearrangements, Rearrangement to Electron Deficient Carbon (Pinacol-pinacolone, benzilic acid & Wagner- Meerwein), Rearrangement to Electron Deficient Nitrogen (Hofmann-Lossen-Cuftius & Beckmann), Rearrangement to Electron Deficient Oxygen (Baeyer-Villiger & Dakin), Rearrangement to Electron-Rich Carbon (Wittig), Aromatic Rearrangements (Fries & Claisen).

Unit - 4

Oxidation & Reduction Reactions

4.1 Oxidation Reactions: Introduction, metal based and non-metal based oxidations, oxidation of alcohols to carbonyls (chromium, manganese, and silver based reagents), alkenes to epoxides (peroxides/peracids based, alkenes to diols (manganese and osmium based), alkenes to carbonyls with bond cleavage (manganese and lead based). Oppenauer oxidation

Oxidation of amino groups to nitro groups: oxidation by alkaline KmnO4, oxidation of aliphatic and aromatic amines by peracids, oxidation of primary and secondary amines to hydroxyl amine by hydrogen peroxide.

4.2 Reduction Reactions: Introduction, Reduction of carbon-carbon multiple bonds, carbonyl groups and nitro compounds: catalytic hydrogenation: heterogeneous (Palladium-carbon & Raney Nickel), homogeneous (Wilkinson's catalyst)

Hydride transfer reagents: Sodium borohydride and Lithium aluminium hydride, Metal based reductions: Birch reduction, Clemmensen Reduction.

Reduction of nitro compounds by catalytic hydrogenation and metals (with mechanism).

Unit - 5

Photochemical and Pericyclic reactions

5.1 Photochemical reactions: Introduction to photochemistry, electronic excitations, Jablonski diagram, Norrish type I and II reactions and cis- trans isomerization.

5.2 Pericyclic reactions: Introduction of pericyclic reaction and their classification (Electrocyclic, Sigmatropic rearrangement and cycloadditions), 2+2 and 4+2 cycloadd Claisen and Cope rearrangement.

Practical

Part-A
Qualitative Analysis

Separation of binary organic mixture (by solvent and chemical separation methods), systematic identification of separated organic compounds and preparation of their derivatives.

Part-B
Organic Reactions and Reagents:

Oxidation Reactions: Synthesis, monitoring of the reaction using TLC, purification of product and determination of melting point.

(i) Oxidation of benzaldehyde to benzoic acid by potassium permanganate.

(ii) Oxidation of cyclohexanone to adipic acid by nitric acid.

Reduction Reactions: Synthesis, monitoring of the reaction using TLC, purification of product and determination of melting point.

(i) Reduction of benzophenone to benzhydrol by sodium borohydride.

(ii) Reduction of acetophenone to ethyl benzene (Wolff- Kishner reduction).

Photochemical and Pericyclic reactions:

(i) (4+2) Cycloaddition reaction of anthracene and maleic anhydride (Diels-Alder reaction).

(ii) Photochemical synthesis of benzpinacol from benzophenone.

Rearrangement Reactions:

(i) Pinacol-pinacolone Rearrangement (benzopinacol benzpinacolone),

(ii) Benzil-benzilic acid Rearrangement

Part-C
Two Step Organic Preparations, purification of product and determination of melting point.
(i) Acetanilide-para-bromo acetanilide-para- bromo aniline,

(ii) Acetanilide-para-nitro acetanilide→→→ para- nitroaniline.

Semester -4

BRANCH	Subject Title	Subject Code
B.Sc. (Chemistry–MAJOR)	Transition Elements, Chemi-energetics, Phase Equilibria	CHM1-141

Course Learning Outcomes (CLO)

By the end of this course students will learn the following aspects of Chemistry:

- Introductory idea about Traditional Indian Chemistry
- Chemistry of d&f-block Elements, Basic Concepts of Coordination Chemistry.
- Stereochemistry of Transition Metal Complexes.
- Laws of Thermodynamics.
  - Concept of Phase Equilibrium with reference to Solid Solution, Liquid-Liquid Mixtures, Partially Miscible Liquids.
- Basic Concepts of Electrochemistry

Unit - 1

Knowledge Tradition of Indian Chemistry

1.1 Ancient Indian chemists and their works: Nagarjuna, Vagbhata, Govindacharya, Yashodhara, Ramchandra, Somadeva, etc.

1.2 Introductory idea about rasas
Main rasa: Maharus, Uparas, Common ras, Ratna, dhatu, poison, alkali, acid, salt, lauhabhasma.
1.3 Maharas: Abram, Vaikrant, Bhasik, Vimala, Shilajatu, Sasak, Chapala, Rasak.

1.4 Uparas: Gandhak, Garik, Kashis, Suvari, Lalak, Manah, Shila, Anjana, Kankushtha.
Common Rasa: Koyla, Gauripashan. Navasara, Varataka, Agnijar, Lajavarta, Giri Sindoor, Hingul, Murdad Shrangakam.

Chemistry of d- & f-block clements

1.1.1 . Chemistry of Transition elements: First, Second and Third Transition series
General group trends with special reference to- Electronic Configuration. Coordination Geometry, Colour, Variable Valency, Spectral, Magnetic and Catalytic Properties, Ability to form Complexes
1.2.1 Chemistry of Inner Transition elements: Lanthanides and Actinides General group trends with special reference to Electronic Configuration, Oxidation States, Colour, Spectral and Magnetic Properties. Lanthanide Contraction. Separation of Lanthanides (Ion-exchange method only).
1.3.1 Transuranic elements: General Introduction

Unit - 2

Coordination Chemistry

1. **Structures, Stereochemistry and Metal-Ligand Bonding in Transition Metal Complexes**
   Werner theory for complexes. Electronic interpretation by Sidwik.

2. **Valence Bond Theory (VBT)**- Postulates and applications for Tetrahedral, Square planar and Octahedral complexes. Limitations of VBT.

3 Crystal Field Theory (CFT) - Postulates and application: Crystal field splitting of d-orbitals. Crystal field stabilisation energy (CFSE) in Tetrahedral, Square planarland Octahedral complexes, CFSE of weak and strong fields. Factors affecting the crystal field parameters.
Measurement of 10 Dq (A) and factors affecting its magnitude, Comparison of octahedral and tetrahedral coordination. Tetragonal distortions from octahedral geometry, Jahn-Teller theorem. Square planar geometry Limitations of CFT.
Qualitative aspect of Ligand field and Molecular Orbital (MO) Theory,
Spectrochemical and Nephelauxetic series.
Coordination number, coordination geometries of metal ions, types of ligands.

2. **Isomerism in coordination compounds:**

1. **Structural isomerism**- Ionization, Linkage, Coordination-Ligand Isomerism
2. **Stereo isomerism** Geometrical isomerism: Square planar metal complexes of type-[MA2B2), [MA2BC], [M(AB)2], [MABCD]. Octahedral metal complexes of type- [MA4B2], [M(AA)2B2], [MA3B3].

Optical isomerism: Tetrahedral complexes of type- [MABCD]. Octahedral complexes of type- [M(AA),B2], [M(AA)3].

Unit - 3

Thermodynamics

1. First law of Thermodynamics

Concept of heat (Q), work (W), internal energy (U), Statement of first law, Enthalpy (H), Relation between heat capacities.

Calculations of Q. W. AU and AH under isothermal and adiabatic conditions for Reversible, Irreversible and Free (ideal and van der Waals) expansions of gases. Joule Thomson effect and its theory, Inversion temperature.

2. Second Law of Thermodynamics

Carnot cycle, Statement of the second law of thermodynamics.

Concept of Entropy, Calculation of entropy change for Reversible and irreversible processes, Concept of residual entropy.

Free Energy Functions: Gibbs and Helmholtz energy. Variation of entropy (S), Gibbs free energy (G), work function (A) with temperature (T). volume (V) & pressure (P). Free energy change and spontaneity, Gibbs- Helmholtz equation.

3. Third Law of Thermodynamics

Nernst heat theorem and its significance, Statement of third law, Calculation of absolute entropy of substance.

Unit - 4

Electrochemistry

1. Electrical Conduction: Conduction in metals and in electrolyte solutions. Specific, equivalent, and molar conductivity. Measurement of equivalent conductance. Effect of dilution on conductivity. Migration of ions. Kohlrausch law and its applications.

2. Weak and strong electrolytes: Theory of strong electrolytes, Debye- Huckel-Onsager (DHO) theory and equation.

3. Transport numbers: Determination of transport numbers by Hittorf method and Moving boundary method.

4. Electrode reactions: Nernst equation, Derivation of equation for singie electrode potential.

5. Electrodes: Reference electrodes, Standard hydrogen electrode, Quinhydrone electrode, Glass electrode, Calomel electrode.

6. Standard electrode potential, Electrochemical series and its applications.

7. Electrochemical cells: Nemst equation, calculation of e.m.f. of cell.

Unit - 5

Phase equilibrium

1. Concept of phases. Components and degrees of freedom. Thermodynamic derivation of Gibbs Phase Rule for reactive and nonreactive systems.

2. Clausius-Clapeyron equation and its applications to Solid-Liquid, Liquid-Vapour and Solid-Vapour equilibria.

3. Phase diagram for one component systems with applications-Water and Sulphur. Phase diagrams for systems of solid-liquid equilibria involving-Eutectic, Congruent and Incongruent melting points. Water and Sulfur system, Ag-Pb and Mg-Zn system, NaCl-H_2O system.

4. Binary solutions: Raoult's Law, Ideal and Non-ideal or Azeotropic mixtures, Immiscible liquids, Steam distillation

Practical

Part A
Preparation of Inorganic Complexes:

Tefraammine copper (II) sulphate

Copper (II)acetylacetonate complex

Iron (III) acetylacetonate

Tetraamiinecarbonatocobalt (III) nitrate

Potassium tri(oxalato) ferrate(III)

Nickel(II) dimethylglyoximate

Part B
Thermochemistry

(a) Determination of heat capacity of a calorimeter using following experiments-

(i) Change of enthalpy data of a known system (method of back calculation of heat capacity of calorimeter from known enthalpy of solution of sulphuric acid or enthalpy of neutralization)
(ii) Heat gained by cold water is equal to heat lost by hot water.

(b) Determination of enthalpy of following:
o Neutralization of hydrochloric acid with sodium hydroxide.
o lonization of ethanoic acid.

o Hydration of salt.

(c) Determination of enthalpy (endothermic and exothermic) of aqueous solution of salts (KNOs. NH4C1).

(d) Determination of basicity of a diprotic acid by the thermochemical method
Calculation of the enthalpy of neutralization of the first step in terms of the changes of temperatures observed in the graph of temperature versus time for different additions of a base.

(e) Study of the solubility of benzoic acid in water and determination ofenthalpy change (AH).

Part C
Phase Equilibria:

a) Determination of critical solution temperature (CST), composition of the phenol- water system at CST and to study the effect of impurities of sodium chloride and succinic acid on it.

b) Construction of the phase diagram using cooling curves or ignition tube method:
i. Simple eutectic and

ii. Congruently melting systems.

c) Distribution of acetic/ benzoic acid between water and cyclohexane

d) Study of the equilibrium of following reactions by the distribution method:

i. $I\ (aq) + I^-\ (aq) \rightarrow I^-\ (aq)$

ii. $Cu^{2+}(aq) + Nnh_3 \rightarrow Cu(NH_3)_n^{2+}$

Part D

Purification/ separation of compounds by Fractional distillation/ Steam distillation.

Presentation and analysis of UV spectra. Types of electronic transitions. Effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, Hyperchromic and hypochromic shifts. UV spectra of conjugated polyenes and enones.

Infra-red (IR) absorption spectroscopy-

Molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, Measurement of IR spectrum, finger print region, characteristic absorption of various functional groups and interpretation of IR spectra of simple organic compounds.

Practical

1 **Basic analytical exercises**

Calibration of different weights and glassapparatus (measuring cylinder. burette, pipette, volumetric flasks).

• Preparation of solutions of different molarity/normality by weighing and dilution.

2. Quantitative Analysis

Titrimetric Analysis

- Standardization of NaOH with Oxalic acid.

- Determination of carbonate and hydroxide present in mixture.

- Determinationof carbonate and bicarbonate present in a mixture.

- Determinationof free alkali present in different soaps/detergents.

3. Quantitative Analysis by Colorimetry

- Verification of Lambert-Beer Law

- Determination of concentration of coloured compounds (e.g.. CuSO KMnO4

4. Qualitative Analysis

-Systematic identification of organic compound by qualitative analysis.

- Chromatography:

Identification by determination of the Rvalues of the given organic/ inorganic compounds by paper/ thin layer chromatography.