

B.Sc II Year – Paper-II

120 hrs (30 weeks)

UNIT-I (Inorganic Chemistry – II)

30 hrs (1 h /w)

- | | |
|--|-----|
| 1. Chemistry of d-block elements | 9 h |
| 2. Chemistry of f-block elements | 8 h |
| 3. Theories of bonding in metals | 6 h |
| 4. Metal carbonyls and related compounds | 7 h |

UNIT-II (Organic Chemistry – II)

30 hrs (1 h /w)

- | | |
|-------------------------------------|------|
| 1. Halogen compounds | 4 h |
| 2. Hydroxy compounds | 6 h |
| 3. Carbonyl compounds | 10 h |
| 4. Carboxylic acids and derivatives | 5 h |
| 5. Active methylene compounds | 3 h |
| 6. Exercises in interconversions | 2 h |

UNIT-III (Physical Chemistry – II)

30 hrs (1 h /w)

- | | |
|---------------------|------|
| 1. Phase Rule | 5 h |
| 2. Dilute solutions | 8 h |
| 3. Electrochemistry | 17 h |

UNIT-IV (General Chemistry – II)

30 hrs (1 h /w)

- | | |
|------------------------------------|-----|
| 1. Molecular symmetry | 5 h |
| 2. Theory of quantitative analysis | 8 h |
| 3. Evaluation of analytical data | 4 h |
| 4. Introductory treatment to | |
| a. Pericyclic reactions | 5 h |
| b. Synthetic strategies | 4 h |
| c. Asymmetric synthesis | 4 h |

LABORATORY COURSE – II

90 hrs (3 h /w)

Practical Paper- II (Inorganic Chemistry)

Titrimetric analysis and Gravimetric analysis

UNIT – I (Inorganic Chemistry – II)

30 h (1h/w)

I. Chemistry of d-block elements: Characteristics of d-block elements with special reference to electronic configuration variable valence, magnetic properties, catalytic properties and ability to form complexes. Stability of various oxidation states and e.m.f. Comparative treatment of second and third transition series with their 3d analogues. Study of Ti, Cr and Cu traits in respect of electronic configuration and reactivity of different oxidation states.

9 h

II. Chemistry of f-block elements: Chemistry of lanthanides – electronic structure, oxidation states, lanthanide contraction, consequences of lanthanide contraction, magnetic properties, spectral properties and separation of lanthanides by ion exchange and solvent extraction methods. Chemistry of actinides – electronic configuration, oxidation states, actinide contraction, position of actinides in the periodic table, comparison with lanthanides in terms of magnetic properties, spectral properties and complex formation.

8 h

III. Theories of bonding in metals: Valence bond theory, Explanation of metallic properties and its limitations. Free electron theory, thermal and electrical conductivity of metals, limitations, Band theory, formation of bands. explanation of conductors, semiconductors and insulators.

6 h

IV. Metal carbonyls and related compounds – EAN rule, classification of metal carbonyls, structures and shapes of metal carbonyls of V, Cr, Mn, Fe, Co and Ni. Metal nitrosyls and metallocenes (only ferrocene).

7 h

UNIT-II

(ORGANIC CHEMISTRY – II)

30hrs (1 h / w)

1. Halogen compounds

4 h

Nomenclature and classification of alkyl (into primary, secondary, tertiary), aryl, aralkyl, allyl, vinyl, benzyl halides.

Chemical Reactivity, formation of RMgX

Nucleophilic aliphatic substitution reaction- classification into $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$.

Energy profile diagram of $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions. Stereochemistry of $\text{S}_{\text{N}}2$ (Walden Inversion) $\text{S}_{\text{N}}1$ (Racemisation). Explanation of both by taking the example of optically active alkyl halide – 2-bromobutane. Ease of hydrolysis – comparison of alkyl, benzyl, allyl, vinyl and aryl halides

2. Hydroxy compounds

6 h

Nomenclature and classification of hydroxy compounds.

Alcohols: Preparation with hydroboration reaction, Grignard synthesis of alcohols.

Phenols: Preparation i) from diazonium salt, ii) from aryl sulphonates, iii) from cumene.
Physical properties- Hydrogen bonding (intermolecular and intramolecular) Effect of hydrogen bonding on boiling point and solubility in water.

Chemical properties:

- acidic nature of phenols.
- formation of alkoxides/phenoxides and their reaction with RX.
- replacement of OH by X using PCl_5 , PCl_3 , PBr_3 , SOCl_2 and with HX/ZnCl_2 .
- esterification by acids (mechanism).
- dehydration of alcohols.
- oxidation of alcohols by CrO_3 , KMnO_4 .
- special reaction of phenols: Bromination, Kolb-Schmidt reaction, Riemer-Tiemann reaction, Fries rearrangement, azocoupling.

Identification of alcohols by oxidation with KMnO_4 , ceric ammonium nitrate. Lucas reagent and phenols by reaction with FeCl_3 .

Polyhydroxy compounds: Pinacol-Pinacolone rearrangement.

3. Carbonyl compounds

10 h

Nomenclature of aliphatic and aromatic carbonyl compounds, structure of the carbonyl group.

Synthesis of aldehydes from acid chlorides, synthesis of aldehydes and ketones using 1,3-dithianes, synthesis of ketones from nitriles and from carboxylic acids.

Physical properties: absence of hydrogen bonding, keto-enol tautomerism, reactivity of carbonyl group in aldehydes and ketones.

Nucleophilic addition reaction with a) NaHSO_3 , b) HCN ; c) RMgX , d) NH_2OH , e) PhNHNH_2 , f) 2,4-DNPH, g) Alcohols-formation of hemiacetal and acetal.

Halogenation using PCl_5 with mechanism.

Base catalysed reactions: a) Aldol, b) Cannizzaro reaction, c) Perkin reaction, d) Benzoin condensation, e) Haloform reaction, f) Knoevenagel reaction.

Oxidation of aldehydes- Baeyer-Villiger oxidation of ketones.

Reduction: Clemmensen reduction, Wolf-Kishner reduction, MPV reduction, reduction with LiAlH_4 and NaBH_4 .

Analysis of aldehydes and ketones with a) 2,4-DNT test, b) Tollen's test, c) Fehling test, d) Schiff test, e) Haloform test (with equation).

4. Carboxylic acids and derivatives

6 h.

Nomenclature, classification and structure of carboxylic acids.

Methods of preparation by a) hydrolysis of nitriles, amides and esters.

b) carbonation of Grignard reagents.

Special methods of preparation of aromatic acids by a) oxidation of side chain.

b) hydrolysis by benzotrichlorides.

c) Kolbe reaction.

Physical properties: Hydrogen bonding, dimeric association, acidity- strength of acids with examples of trimethyl acetic acid and trichloroacetic acid. Relative differences in the acidities of aromatic and aliphatic acids.

Chemical properties: Reactions involving H, OH and COOH groups- salt formation, anhydride formation, acid chloride formation, amide formation and esterification.

(mechanism) } Degradation of carboxylic acids by Huns-Diecker reaction, decarboxylation by Schmidt reaction } Arndt-Eistert synthesis, halogenation by Hell-Volhard- Zelinsky reaction. }

Derivatives of carboxylic acids: Reaction of acid chlorides, acid anhydrides, acid amides, esters (mechanism of the hydrolysis of esters by acids and bases).

5. Active methylene compounds

4 h

Acetoacetic esters: preparation by Claisen condensation. keto-enol tautomerism. Acid hydrolysis and ketonic hydrolysis. }

Preparation of a) monocarboxylic acids.

b) dicarboxylic acids.

Reaction with urea }

Malonic ester: preparation from acetic acid.

Synthetic applications: Preparation of

a) monocarboxylic acids (propionic acid and n-butyric acid) }

b) dicarboxylic acids (succinic acid and adipic acid).

c) α,β -unsaturated carboxylic acids (crotonic acid).

Reaction with urea }

6. Exercises in interconversion

2 h

Unit - III physical chemistry - II

30hrs (1h / w)

1. Phase rule

5 h

Concept of phase, components, degree of freedom. Derivation of Gibbs phase rule. Phase equilibrium of one component – water system. Phase equilibrium of two-component system, solid-liquid equilibrium. Simple eutectic diagram of Pb-Ag system, desilverisation of lead. Solid solutions- compound with congruent melting point- (Mg-Zn) system, compound with incongruent melting point – NaCl- water system. Freezing mixtures.

2. Dilute solutions

8 h

Colligative properties. Raoult's law. relative lowering of vapour pressure, its relation to molecular weight of non-volatile solute. Elevation of boiling point and depression of freezing point. Derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods of determination. Osmosis, osmotic pressure, experimental determination. Theory of dilute solutions. Determination of molecular weight of non-volatile solute from osmotic pressure. Abnormal Colligative properties. Van't Hoff factor, degree of dissociation and association.

3. Electrochemistry

17 h

Specific conductance, equivalent conductance, measurement of equivalent conductance. Variation of equivalent conductance with dilution. Migration of ions, Kohlrausch's law. Arrhenius theory of electrolyte dissociation and its limitations. Ostwald's dilution law. Debye-Huckel-Onsagar's equation for strong electrolytes (elementary treatment only). Definition of transport number, determination by Hittorf's method. Application of conductivity measurements-determination of dissociation constant (K_a) of an acid, determination of solubility product of sparingly soluble salt, conductometric titrations.

Types of reversible electrodes- the gas electrode, metal-metal ion, metal-insoluble salt and redox electrodes. Electrode reactions, Nernst equation, single electrode potential, standard Hydrogen electrode, reference electrodes, standard electrode potential, sign convention, electrochemical series and its significance. Reversible and irreversible cells, conventional representation of electrochemical cells. EMF of a cell and its measurements. Computation of cell EMF. Applications of EMF measurements, Calculation of thermodynamic quantities of cell reactions (ΔG , ΔH and K). Determination of pH using quinhydrone electrode. Solubility product of AgCl. Potentiometric titrations.

Unit IV (General chemistry-II)

30 hrs (1h/w)

1. Molecular symmetry

5h

Concept of symmetry in chemistry-symmetry operations, symmetry elements, Rotational axis of symmetry and types of rotational axes, Planes of symmetry and types of planes. Improper rotational axis of symmetry, Inversion centre. Identity element. The symmetry operations of a molecule form a group. Flow chart for the identification of molecular point group.

2. Theory of quantitative analysis

8 hrs

- Principles of volumetric analysis, Theories of acid-base, redox complexometric, iodometric and precipitation titrations, choice of indicators for the above titrations.
- Principles of gravimetric analysis: precipitation, coagulation, peptization coprecipitation, post precipitation, digestion, filtration and washing of precipitate, drying and ignition, precipitation from homogenous solutions, requirements of gravimetric analysis.

3. Evaluation of analytical data.

4 h

Theory of errors, idea of significant figures and its importance, accuracy – methods of expressing accuracy, error analysis and minimization of errors, precision – methods of expressing precision, standard deviation and confidence limit.

4. Introductory treatment to:

a) Pericyclic Reactions

5 h

Concerted reactions, Molecular orbitals, Symmetry properties HOMO, LUMO, Thermal and photochemical pericyclic reactions, Types of pericyclic reactions – electrocyclic, cycloaddition and sigmatropic reactions – one example each.

b) Synthetic strategies

4 h

Terminology – Disconnection (dix), Symbol (), synthon, synthetic equivalence (SE), Functional group interconversion (FGI), Linear, Convergent and Combinatorial, Target molecule (TM) Retrosynthesis of the following molecules

- acetophenone
- cyclohexene
- phenylethylbromide

c) Asymmetric (Chiral) synthesis

4 h

Definition, enantiomeric excess, diastereomeric excess, stereospecific reaction – definition – example – dehalogenation of 1,2-dibromides by I_2 , stereoselective reactions – definition – example – acid catalysed dehydration of 1-phenylpropanal

LABORATORY COURSE – II

90 hrs (3 h / w)

Practical Paper – II (Inorganic Chemistry)

I. Titrimetric analysis:

- ✓ 1) Determination of carbonate and bicarbonate in a mixture ✓
- ✓ 2) Determination of Fe(II) using $\text{K}_2\text{Cr}_2\text{O}_7$
- 3) Determination of Fe(II) using KMnO_4 with oxalic acid as primary standard. ✓
- ✓ 4) Determination of Cu(II) using $\text{Na}_2\text{S}_2\text{O}_3$ with $\text{K}_2\text{Cr}_2\text{O}_7$ as primary standard
- ✓ 5) Determination of Zinc using EDTA
- ✓ 6) Determination of hardness of water
- ✓ 7) Determination of Zinc by ferrocyanide

II. Gravimetric analysis (any three of the following)

- 1) Determination of barium as barium sulphate
- 2) Determination of sulphate as barium sulphate
- 3) Determination of lead as lead chromate
- 4) Determination of nickel as Ni-DMG complex
- 5) Determination of magnesium as magnesium pyrophosphate.