

U.G. 4th SEMESTER SYLLABUS
DEPARTMENT OF CHEMISTRY
COTTON UNIVERSITY

PAPER : CHM 401C

INORGANIC CHEMISTRY- III
(Credits: 3+0+2=5)

Theory: 45 Lectures

Unit 1: Transitional and Inner Transitional Elements

(11 Lectures)

Transitional elements: Electronic configuration and general periodic trends, comparative study of first transition series elements. Trends in physical and chemical properties of second and third transition series in comparison to the first. Chemistry of Cr, Mn, Fe and Co in various oxidation states with special reference to the following compounds: peroxo compounds of chromium, potassium dichromate, potassium permanganate, potassium ferrocyanide, potassium ferricyanide, sodium nitroprusside and sodium cobaltinitrite.

Lanthanides and Actinides: Electronic configuration, oxidation states, colour spectral and magnetic properties, lanthanide contraction, separation of the lanthanides (ion exchange method only). Comparison of actinides with lanthanides, coordination compounds.

Unit 2: Chemistry of Coordination Compounds

(12 Lectures)

Coordination Compounds: Werner's theory, EAN rule, Structural and stereoisomers of complex compounds, Survey of different types of ligands, IUPAC nomenclature of coordination compounds, Structure and bonding (valence bond theory) of complexes containing the following as one of the ligands: CO, CN, CH₃COO⁻, C₂O₄²⁻, NH₃, en, acac. Coordination chemistry of Hg, metal carbonyls and nitrosyls.

Crystal field theory, factors affecting 10 Dq value, crystal field stabilization energy, Magnetic properties from crystal field theory, spectrochemical series, nephelauxetic effect, high spin and low spin complexes

Jahn-Teller distortion, structural and thermodynamic effects of orbital splitting, octahedral versus tetrahedral coordination in spinels. Adjusted crystal field (i.e., ligand field) theory, Molecular orbital theory of octahedral complexes (without and with π bonding).

Metal-metal bonding and quadrupole-bonding

Unit 3: General Principles of Metallurgy

(10 Lectures)

Chief modes of occurrence of metals based on standard electrode potentials, Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent, Electrolytic Reduction. Principle of extraction of Cu, Al and Fe. Hydrometallurgy with reference to cyanide process for silver and gold, Methods of purification of metals: Electrolytic process, van Arkel-de Boer process and Mond's process, Zone refining.

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Unit 4: Organometallic Compounds (12 Lectures)

Defination and classification, IUPAC nomenclature, 18 electron rule, electron count in complexes, Synthesis, structure and bonding of complexes with olefins, allyl and cyclopentadiene, Metal alkyls: Important structural features of methyl lithium (tetramer) and trialkyl Aluminium (dimer), Homogeneous catalysis by transition metal complexes (isomerisation, hydrogenation, hydroformylation and Ziegler-Natta polymerisation). Isolobal analogy in organometallic compounds. Synergic effect and use of IR data to explain extent of back bonding.

PRACTICAL: 60 HOURS

Unit 5: Inorganic Chemistry Lab (2 Credits)

A. Inorganic Preparation – Preparations of:

1. Chrome Alum / Potash Alum
2. Tetrammine Copper (II) Sulphate
3. Hexammine Nickel (II) Chloride
4. Acetylacetonate complexes of $\text{Cu}^{2+}/\text{Fe}^{3+}$
5. Cuprous Chloride, Cu_2Cl_2
6. Manganese (III) phosphate, $\text{MnPO}_4 \cdot \text{H}_2\text{O}$

(Students should recrystallise the prepared product and verify the presence/ absence of anions and cations, as are applicable, by qualitative analysis.)

B. Inorganic Quantitative Analysis:

Separation and Estimation of individual inorganic ions in two component system of

- (i) Fe and Ca (ii) Fe and Cu

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ORGANIC CHEMISTRY- III

(Credits: 4+1+0=5)

Theory: 75 Lectures

Unit 1: Nitrogen Containing Functional Groups (16 Lectures)

Preparation and important reactions of nitro compounds, nitriles and isonitriles.

Amines: Preparation and properties: Effect of substituent and solvent on basicity; Gabriel phthalimide synthesis, Carbylamine reaction, Mannich reaction, Hoffmann's exhaustive methylation, Hofmann-elimination reaction; Distinction between 1°, 2° and 3° amines with Hinsberg reagent and nitrous acid. Diazonium Salts: Preparation and their synthetic applications.

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Unit 2: Polynuclear Hydrocarbons

(8 Lectures)

Aromaticity of polynuclear hydrocarbons, structure elucidation of naphthalene; Preparation and properties of naphthalene, phenanthrene and anthracene.

Unit 3: Pericyclic Reactions

(12 Lectures)

Definition and examples of [2+2] and [4+2] cycloaddition reactions. The conservation of orbital symmetry. Woodward-Hoffman rules. Diels Alder reaction: regioselectivity and stereoselectivity in simple compounds. 1,3 Dipolar Cycloaddition. Sigmatropic rearrangements: 1,3 & 1,5 migration of hydrogen and alkyl group. Cope and Claisen rearrangements. Electrocyclic reactions- HOMO-LUMO approach.

Unit 4: Heterocyclic Compounds

(20 Lectures)

Classification and IUPAC nomenclature, Structure, aromaticity in 5-membered and 6-membered rings containing one heteroatom.

Synthesis: Furan, Pyrrole (Paal-Knorr synthesis, Knorr pyrrole synthesis, Hantzsch synthesis), Thiophene, Pyridine (Hantzsch synthesis), Indole (Fischer indole synthesis), Quinoline (Skraup synthesis, Knorr quinoline synthesis) and isoquinoline (Bischler-Napieralski reaction, Pomeranz-Fritsch reaction).

Reactions and mechanism of electrophilic and nucleophilic substitution reactions of: Furan, thiophene, Pyrrole, Pyridine, Indole, Quinoline, Isoquinoline.

Unit 5: Alkaloids

(8 Lectures)

Natural occurrence, General structural features, Isolation and their physiological action, Hoffmann's exhaustive methylation, Emde's modification; Structure elucidation and synthesis of Nicotine and Atropine. Medicinal importance of Nicotine, Hygrine, Quinine, Morphine, Cocaine, and Reserpine.

Unit 6: Terpenes

(6 Lectures)

Occurrence, classification, isoprene rule; Elucidation of structure and synthesis of Citral. Commercial use of different terpenoids.

Unit 7: Steroids and Hormones

(5 Lectures)

Elementary introduction, classification, structure and functions of hormones, Neurotransmitters

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PHYSICAL CHEMISTRY- IV
(Credits: 3+1+1=5)

Theory: 60 Lectures

Unit 1: Molecular Reaction Dynamics

(20 Lectures)

Collision theory, activated complex theory, Eyring equation – thermodynamic formulation. Theory of unimolecular reactions (Lindemann theory) – dynamic molecular collisions – potential energy surfaces. Reactions in solution: Bronsted-Bjerrum equation, kinetic salt effect.

Photochemistry: laws of photochemical equivalence, quantum yield. Kinetics of H_2-Br_2 , H_2-Cl_2 reactions, dissociation of HI. Photo-stationary equilibrium, dimerisation of anthracene. Luminescence phenomenon: fluorescence, phosphorescence, Jablonski diagram, photosensitised reactions, quenching of fluorescence. Chemiluminescence and bioluminescence.

Photochemistry of air and air pollution.

Unit 2: Surface Chemistry and Catalysis

(15 Lectures)

Introduction to solid surfaces, adsorption at surfaces – physisorption and chemisorption. Adsorption isotherms – Freundlich, Langmuir and BET isotherms. Derivation of Langmuir and BET isotherms, limitation of Langmuir isotherm, Langmuir isotherm as a special case of BET isotherm. Determination of surface area using Langmuir and BET adsorption isotherms. Concept of surface excess, Gibbs isotherm relating surface excesses.

Catalytic activity at surface with examples. Heterogeneous catalysis: types of catalyst, specificity and selectivity, mechanisms of catalysed reactions at solid surfaces. Zeolites and their use as catalysts in cracking of petroleum.

Homogeneous catalysis: gas-phase homogeneous catalysis with examples, acid-base catalysis – specific and generalised acid-base catalysis, enzyme catalysis and the Michaelis-Menten mechanism. Effect of pH and temperature on enzyme catalysis.

Unit 3: Colloids

(10 Lectures)

Definition of colloids, sols and lyophilic colloids; preparation and purification of colloids; structure, surface and stability of colloids. Surface-active agents (surfactants) and their cleansing action, micelle formation, critical micellar concentration (CMC). Electrical double layer and electrokinetic phenomena.

Unit 4: Introduction to Quantum Mechanics

(15 Lectures)

The postulates of quantum mechanics. Schrödinger wave equation – its time dependent and time independent forms, its application to a free particle in three dimension. Physical observables, their corresponding quantum mechanical operators and the commutation rules.

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Schrödinger equation for the 'particle-in-a-box' problem (rigorous treatment), concept of boundary conditions, quantisation of energy levels, the zero-point energy and the Heisenberg uncertainty principle. The wave functions and their Born interpretation, probability distribution functions, nodal properties, extension to two and three dimensional boxes, separation of variables, concept of degeneracy.

PRACTICAL: 30 HOURS

Unit 5: Physical Chemistry Lab (1 Credit)

- (1) To obtain the Freundlich adsorption isotherm for adsorption of oxalic acid on activated charcoal.
- (2) Preparation of ferric hydroxide colloid and determination of its precipitating value with NaCl/ KCl and Na₂SO₄/ K₂SO₄.
- (3) To determine the rate constant of hydrolysis of methyl acetate catalysed by a strong acid at room temperature.
- (4) Study the distribution of ammonia between water and chloroform by acid-base titrations using methyl orange indicator.
