

Department of Chemistry

Syllabus

Semester-V

UNIT- I: **14L**

A] Coordination Compounds:

Important terms namely molecular or addition compounds, double salts, complex salts, complex ion, ligand, coordination number, central metal ion, etc. Werner's theory of coordination and its experimental verification on the basis of conductance data and formation of AgCl precipitate in case of cobaltammines. Sidgwick's electronic interpretation and its drawbacks, effective atomic number. IUPAC rules for nomenclature of coordination compounds. Structural isomerism- ionization, linkage and coordination in complexes. Geometrical isomerism in octahedral complexes of the type Ma_4b_2 , Ma_3b_3 , $Ma_2b_2c_2$, Ma_4bc , $M(AA)_2b_2$. Square planar complexes of the type Ma_2b_2 and Ma_2bc . Optical isomerism in octahedral complexes of type $Ma_2b_2c_2$, $Mabcdef$, $M(AA)_3$, $M(AA)_2b_2$ and tetrahedral complexes of the type $Mabcd$ and $M(AA)_2$. Optical isomerism in square planar complexes. Valence bond theory as applied to structure and bonding in complexes of 3d-series elements (Only 4 and 6 coordinates complexes). Inner and outer orbital complexes. Magnetic properties of complexes of 3d series elements. Limitations of VB theory. [11]

B] Chelates:

Definition, classification and applications of chelates in analytical chemistry. Stability of chelate with special reference to chelate effect. [3]

UNIT- II: **14L**

A] Crystal Field Theory (CFT):

Postulates of CFT, Crystal field splitting in octahedral, distorted octahedral, square planar tetrahedral complexes, concept of CFSE, high spin and low spin complexes on the basis of Δ_0 and pairing energy, distribution of electrons in t_{2g} and e_g orbitals in high spin and low spin octahedral complexes. Factor affecting magnitude of crystal field splitting in octahedral complexes. [8]

B] Electronic Spectra of Transition Metal Complexes:

Introduction to spectra, selection rules for d-d transitions, spectroscopic terms-determination of ground term symbols for d^1 to d^{10} , spectra of d^1 and d^9 octahedral complexes, Orgel diagram for d^1 and d^9 states, electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ion. Spectrochemical series. [6]

UNIT- III:

14L

A] Heterocyclic compounds: Nomenclature,

Pyrrrole: Synthesis from acetylene, succinimide and furan, Basicity, Electrophilic substitution reactions (orientation) – nitration, sulphonation, acetylation and halogenation, Molecular orbital structure. [4]

Pyridine: Synthesis from acetylene and pentamethylene diamine hydrochloride, Basicity, Electrophilic substitution reactions (orientation) – nitration, sulphonation, Nucleophilic substitution reactions (orientation) - with NaNH_2 , $\text{C}_6\text{H}_5\text{Li}$ and KOH . [3]

B] Organometallic compounds:

Grignard reagents: Methyl magnesium bromide- Synthesis from methyl bromide (only reaction) Synthetic applications: Electrophilic substitution reactions formation of alkanes, alkenes, higher alkynes and other organometallic compounds, Nucleophilic substitution reactions- Reaction with aldehydes and ketones, ethylene oxide, acetyl chloride, methyl cyanide and CO_2 . [4]

Methyl lithium: Synthesis and reaction with water, formaldehyde, acetaldehyde, acetone, ethylene oxide and CO_2 . [3]

UNIT- IV:

14L

A] Dyes: Classification on the basis of structure and mode of application, Preparation and uses of Methyl orange, Crystal violet, Phenolphthalein, Alizarin and Indigo. [5]

B] Drugs: Analgesic and antipyretics: Synthesis and uses of phenylbutazone. Sulpha drugs: Synthesis and uses of sulphanilamide and sulphadiazine. Antimalarials: Synthesis of chloroquine from 4,7-dichloroquinoline and its uses. [5]

C] Pesticides: Insecticides: Synthesis and uses of malathion. Herbicides: Synthesis and uses of 2,4-dichloro phenoxy acetic acid (2,4-D). Fungicides: Synthesis and uses of thiram (tetramethyl thiuram disulphide). [4]

UNIT- V: Photochemistry **14L**

(i) Photochemical and thermal reactions. (ii) Lambert's law – Statement and derivation. Beer's law - Statement and derivation. Reasons for deviation from Beer's law. (iii) Laws of photochemistry. (iv) Quantum yield of photochemical reaction. Reasons for high and low quantum yield. Experimental determination of quantum yield. Photosensitized reaction. (v) Kinetics of photochemical decomposition of HI. (vi) Fluorescence and Phosphorescence. Selection rule for electronic transition. Internal conversion and inter-system crossing. Explanation of fluorescence and phosphorescence on the basis of Jablonski diagram. (vii) Chemiluminescence and Bioluminescence with examples. (viii) Numericals. [14]

UNIT- VI: Molecular Spectroscopy **14L**

(i) Electromagnetic radiation, characteristics of electromagnetic radiation in terms of wavelength, wave number, frequency and energy of photon. Spectrum of electromagnetic radiation. (ii) Types of spectra - Emission and absorption spectra, atomic and molecular spectra, line and band spectra (iii) Translational, vibrational, rotational and electronic motion. The degree of freedom in each motion. (iv) Energy level diagram of a molecule indicating electronic, vibrational and rotational transitions. (v) Condition for pure rotational spectrum (i.e. microwave active molecules), selection rule for rotational transition. Derivation of expression for moment of inertia of a diatomic rigid rotor. Isotope effect. Applications of microwave spectroscopy for the determination of moment of inertia and bonding. (vi) Condition for exhibiting vibrational spectra (i.e. IR active molecule), selection 17 18 rule for vibrational transition. Vibrational energy levels

of a simple harmonic oscillator. Zero point energy, position of a spectral line. Determination of force constant of a covalent bond. (v) Raman effect - Raman's spectrum of a molecule. Condition for exhibiting Raman spectrum (i.e. Raman active molecule), selection rule for rotational transitions. Pure rotational spectrum of diatomic molecule, vibrational Raman spectrum of a diatomic molecule. (vii) Numericals. **[14]**