# B.Sc. Part - III (Semester - V) 5S Chemistry

#### **Total Lectures: 84**

#### Marks: 80

#### 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 Ma4b2, Ma3b3, Ma2b2c2, Ma4bc, M(AA)2b2. Square planar complexes of the type Ma<sub>2</sub>b<sub>2</sub> and Ma<sub>2</sub>bc. Optical isomerism in octahedral complexes of type Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>, Mabcdef, M(AA)<sub>3</sub>, M(AA)<sub>2</sub>b<sub>2</sub> and tetrahedral complexes of the type Mabcd and M(AA)<sub>2</sub>. 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 Ä0 and pairing energy, distribution of electrons in t<sub>2g</sub> and e<sub>g</sub> orbitals in high spin and low spin octahedral complexes. Factor affecting magnitude of crystal field splitting in octahedral complexes.

**B]** Electronic Spectra of Transition Metal Complexes: Introduction to spectra, selection rules for d-d transitions, spectroscopic terms-determination of ground term symbols for d1 to d10, spectra of d1 and d9 octahedral complexes, Orgel diagram for d1 and d9 states, electronic spectrum of [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> complex ion. Spectrochemical series.

#### Unit III (14L)

**A] Heterocyclic compounds:** Nomenclature, Pyrrole: 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<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>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<sub>2</sub>. **[4]** 

Methyl lithium-Synthesis and reaction with water, formaldehyde, acetaldehyde, acetone, ethylene oxide and CO<sub>2</sub>. [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 intersystem crossing. Explanation of fluorescence and phosphorescence on the basis of Joblonski 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 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]

### Semester - V

### **5S Chemistry Practicals**

### **Total Laboratory sessions: 26**

# Exercise 1: Inorganic Preparations

1. Preparation of tetraamminecopper(II)sulphate.

- 2. Preparation of hexaamminenickel(II)chloride.
- 3. Preparation of potassiumtrioxalate aluminate (III).
- 4. Preparation of Prussian blue.
- 5. Preparation of chrome alum.
- 6. Preparation of sodium thiosulphate and dithionite.

(Comment on VB structure, magnetic properties and color of 1, 2 and 3 complexes)

### Exercise II: Physical Chemistry experiments

(Standard oxalic acid solution should be prepared by the students)

- 1. To determine strength of given HCl solution conductometrically.
- 2. To determine strength of given CH<sub>3</sub>COOH solution conductometrically.
- 3. To determine strength of given HCl solution potentiometrically.
- 4. To determine strength of HCl and CH<sub>3</sub>COOH in a given mixture conductometrically.
- 5. To determine redox potential of  $Fe^{+2}/Fe^{+3}$  system potentiometrically.
- 6. To determine molecular weight by Rast's method.
- 7. To determine specific rotation of optically active compound by Polarimeter.

### Marks: 50

**14 Laboratory sessions** 

12 Laboratory sessions

# B.Sc. Part - III (Semester - VI) 6S Chemistry

# Total Lectures: 84 80

## Unit I (14L)

# A] Kinetic Aspects of Metal Complexes :

# [6]

Thermodynamic and kinetic stability of the complexes, factors affecting stability of complexes. Brief idea about substitution reactions, SN<sup>1</sup>- dissociative and SN<sup>2</sup> - associative mechanism. Labile and inert complexes. Factors affecting lability of complexes namely arrangement of d-electrons (on the basis of VB theory), size of central metal ion, charge of central metal ion, geometry of complexes. Substitution reactions in square planar complexes mechanism.

# **B]** Analytical Chemistry:

# 1) Spectrophotometry and Colorimetry: -

# [4]

Concept of ëmax, Beer-Lambert's law (Only statement and final equation, no derivation). Calibration curve and its importance. Validity and limitations of Beer-Lambert's law. Verification of Beer's law. Block diagram of colorimeter and spectrophotometer with brief description of each component and its function. Difference between colorimetric and spectrophotometric technique for determination of concentration of metal ion (Example of determination of Cu (II).

# 2) Paper Chromatography: -

# [4]

Definition and classification of chromatographic techniques. Principle of differential migration. Principle and technique of paper chromatography -ascending, descending and circular, Rf value and factors affecting Rf value.

Marks:

### Unit II 14L

# A] Organometallic Chemistry:

Definition, nomenclature and classification of organometallic compounds. Metal carbonyls- definition and classification. Preparation, properties, structure and bonding in Ni(CO)<sub>4</sub>, Fe(CO)<sub>5</sub>, Cr(CO)<sub>6</sub>. Nature of M-C bond in metal carbonyls.

# **B] Inorganic Polymers:**

# [5]

Definition and classification. Silicones: preparation, properties structure and bonding and applications. Phosphonitrile halides polymers- preparation, properties, structure and bonding in cyclic polymers.

## C] Bio-inorganic Chemistry:

## [4]

Essential and trace elements in biological processes. Biological role of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions. Metalloporphyrins-Haemoglobin and Myoglobin and their role in oxygen transport.

### Unit III (14L)

# A] Electronic spectroscopy:

# [7]

Introduction, theory, instrumentation, types of electronic transitions, presentation of electronic spectrum, terms used- chromophore, auxochrome, bathochromic shift, hypsochromic shift, hyperchromic effect and hypochromic effect, Applications in the structure determination of dienes, á,â-unsaturated aldehydes and ketones, aromatic compounds.

### **B] Infrared spectroscopy:**

# [7]

Introduction, Types of molecular vibrations- stretching and bending, Calculation of vibrational modes, force constant, instrumentation, interpretation of IR, H-stretching, triple bond, double bond and Finger print regions, IR spectra of H<sub>2</sub>O, CO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CHO, CH<sub>3</sub>COOH and CH<sub>3</sub>CONH<sub>2</sub>.

### Unit IV (14L)

#### A] NMR spectroscopy:

Introduction, spin quantum number, instrumentation, Aspects of NMR - number of signals (equivalent and non-equivalent protons), positions of signals (chemical shift), intensities of signals, splitting of signals (spin-spin coupling), coupling constant, applications.

#### **B]** Mass spectroscopy:

Introduction, theory, instrumentation - (ion sources), Mass spectra of neopentane and methanol, molecular ion peak, base peak, metastable peak, Rules of fragmentation, applications.

### **Unit V - Elementary Quantum Mechanics (14L)**

(i) Limitations of classical mechanics. Plank's quantum theory (postulates only). Photoelectric effect - Experiments, observation and Einstein's explanation. Compton effect and its explanation. (ii) de Broglie hypothesis of matter waves. de Broglie's equation. Heisenberg's uncertainty principle. (iii) Classical wave equation, derivation of time independent Schrodinger's wave equation in one-dimension and its extension to a three-dimensional space. Well behaved wave function, physical significance of wave function (Born interpretation). (iv) Application of Schrodinger wave equation to a particle in one dimensional box and its extension to a three-dimensional box. Concept of atomic orbital. (v) Numericals. [14]

## Unit VI (14L)

#### A] Electrochemistry:

(i) Types of electrodes - Standard hydrogen electrode, Calomel electrode, Quinhydrone electrode and Glass electrode. Principle of Potentiometric titration. Study of acid-base, redox and precipitation titration. (ii) pH of a solution and pH scale. Determination of pH of a solution using hydrogen, quinhydrone and glass electrodes. Advantage and disadvantage of these electrodes. pH-metric titrations. Determination of pka of a weak acid by pH-metric measurement. (iii) Concentration cells - Types of concentration cells, concentration cell without transfer and determination of its emf. (iv) Numericals

[6]

[6]

#### **B]** Nuclear Chemistry:

(i) Shell model of a nucleus - Assumptions, evidences for existence of magic numbers, advantages and limitations. (ii) Liquid drop model of a nucleus - Assumptions, similarities between nucleus and liquid drop, advantages and limitations, explanation of nuclear fission reaction on the basis of liquid drop model. (iii) Nuclear force and its explanation on the basis of Meson theory. (iv) Characteristics of nuclear reaction, difference between nuclear and chemical reactions. Calculation of Q value of a nuclear reaction. (v) Characteristics of nuclear fission reaction as an alternative source of energy. (vi) Nuclear fusion reaction - Characteristic of a nuclear fusion reaction. Thermonuclear reactions as a source of energy of sun and other stars. Fusion reactions as a potential future source of energy. (vii) Applications of radio isotopes in industry, agriculture, medicines and bio-sciences with two examples each. (viii) Numericals.

#### **6S Chemistry Practical's**

#### **Total Laboratory sessions: 26**

### **Exercise I: Organic Chemistry Experiments**

1. Estimation of formaldehyde.

- 2. Estimation of glycine.
- 3. Estimation of ascorbic acid (vitamine C).
- 4. Estimation of phenol by bromination method.
- 5. Estimation of aniline by bromination method.
- 6. Estimation of urea by hypobromite method.
- 7. Estimation of unsaturation by bromination method.
- 8. Determination of iodine value of oil.
- 9. Determination of equivalent weight of an ester by saponification.
- 10. Separation of a mixture of methyl orange and methylene blue by thin layer chromatography (using benzene).

11. Separation of a mixture of 2,4-dinitro phenyls of acetaldehyde and benzaldehyde by thin layer chromatography (using benzene: petroleum ether = 3:1).

- 12.Separation of a mixture of dyes by thin layer chromatography (using cyclohexane: ethyl acetate = 8.5:1.5).
- 13. Separation of a mixture of 2,4-dinitro phenyls of acetaldehyde and benzaldehyde by thin layer chromatography (using toluene: petroleum ether).

16 Laboratory sessions

Marks: 50

### **Exercise II: Physical Chemistry experiments**

### **10 Laboratory sessions**

- 1. To determine dissociation constant of weak acid by conductometry.
- 2. To determine dissociation constant of weak acid by potentiometry.
- 3. To study potentiometric titration of KCl and AgNO<sub>3</sub>.
- 4. To determine dissociation constant of dibasic acid by pH-metry.
- 5. To verify Beer's Lambart's law using KMnO<sub>4</sub>/K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.
- 6. To determine pH of a soil sample by pH-meter.
- 7. To determine solubility and solubility product of sparingly soluble salts conductometrically.
- 8. To study strong acid and strong base titration by pH-metry.