Sixth Semester

Total: 200 Marks

Chem H 601

100 Marks (25:75)

PART A Inorganic Theory

50 Marks

Unit I: Organometallic Chemistry-II

10 marks

Synthesis, properties, nature of bonds, structure and application of organometallic compounds of lithium (alkyl and aryl), magnesium (RMgX and MgR_2), iron (ferrocene) and tin (R_3SnX, R_2SnX_2 types); metal-ethylenic complexes and homogeneous hydrogenation;

Π-acid ligands, mononuclear and dinuclear carbonyls and nitrosyls and the nature of bonding in them – their uses in metallurgy; Important applications of organometallic compounds in heterogeneous catalysis – hydrogenation of alkenes using Wilkinson's catalyst and synthesis of acetic acid using rhodium carbonyl iodide catalyst.

Unit II: Bioinorganic Chemistry

10 marks

Essential and trace elements in biological processes, criteria of essential elements, pH of biological fluid, metalloporphyrins, structure, and functions of haemoglobin, myoglobin and chlorophyll; role of Fe and Mg in haemoglobin and chlorophyll, role of Co in vitamin B_{12}, Carbonic anhydrase, its characteristics and functions,. Non-complexing cations in biochemical processes, Na^+-K^+ pump; Toxic effects of metal ions with reference to mercury, lead, beryllium and aluminum; deficiency of Fe, Ca, Mg and iodine; Platinum complexes as anti-cancer drugs.

Unit III: Spectroscopic Methods in Inorganic Chemistry

6 marks

Application of the following techniques for Inorganic and Coordination compounds:

(a) UV-Visible Spectroscopy: Free ion terms and their splitting in octahedral symmetry, Selection rules, Orgel diagrams for octahedral/tetrahedral complexes (d^1, d^2, d^8,and d^9 systems).

(b) IR Spectroscopy: Basic principles, spectral studies of coordination compounds containing following molecules or ions as ligands: H_2O, CN, CO, SO_4^{2-}, and halides (F, Cl, Br, I)

Unit IV

6 marks

Reactivity of Coordination Compounds: Thermodynamic stability; Stepwise formation constant, Kinetic lability and inertness, Mechanisms of Ligand displacement reactions in octahedral and square planar complexes, the *trans* effect, Determination of composition of complexes by spectrophotometric method.

6 marks

Unit V

Nanomaterials: General introduction to nanomaterials and emergence of nanotechnology, Types of nano materials, Synthesis of nanoparticles of gold, platinum and silver; properties of nanoparticles; important applications of nanoparticles.

PART B Organic Theory

50 Marks

10 marks

Unit I

(a) ***Carbohydrates-II***: Disaccharides: Maltose and sucrose – their reactions and structure, structure of cellulose and starch (detailed study not required), preparation of cellulose nitrate, cellulose acetate and cellophane.

(b) Natural Products: (i) Terpenoids: Introduction, isoprene rule, classification, isolation, structural elucidation and syntheses of citral and geraniol. (ii) Alkaloids: Introduction, classification, physiological action, extraction and syntheses of nicotine and cocaine.

9 marks

Unit II

(a) Peptides, Proteins and Vitamins: *(i) Peptides* – definition and preparation of di- and tripeptides from α-amino acids. *(ii) Proteins* - introduction, classification, primary, secondary, tertiary and quart-ernary structures of proteins. α- and β-proteins, helical and sheet structures. *(iii) Vitamins* – definition, classification and biological importance of vitamins. Carotenoids – occurrence, isolation and synthesis, β-carotene as a source of vitamin A_1, synthesis of vitamin A_1 and ascorbic acid.

(b) Topics in Biological Chemistry: *(i) Enzymes* – Introduction, nomenclature and characteristics. Mechanism of enzyme action (a general picture); mechanism of action of the enzyme chymotripsin as a peptidase.; co-enzyme, co-enzymes derived from niacin and thiamine, lipoic acid, co-enzyme A, energy production in biological system (role of ATP and ATP-ADP cycle), glycolysis and tricarboxylic acid cycle. *(ii) Nucleic acids*: Structure of purine and pyrimidine bases in nucleic acid (adenine, guanine, cytosine, uracil and thiamine) [no synthesis]. Structure of nucleosides, nucleotides and DNA, replication of DNA.

9 marks

Unit III

(a) Organic Photochemistry: Molecular energy and photochemical energy, excitation of molecules, Franck-Condon principle, dissipation of energy, Jablonski diagram, singlet-triplet

states, fluorescence and phosphorescence, photosensitization and quenching, quantum yield. Introduction to photochemical reactions of carbonyl compounds, photoreduction. Norrish Type I and Type II cleavages. Paterno-Buchi reaction.

(b) Pericyclic Reactions: Definition and scope of pericyclic reactions. *(i) Electrocyclic reactions* – stereochemistry, conrotatory and disrotatory ring closures and ring opening (simple examples like 1,4-disubstituted 1,3-buta-diene, 1,6-disubstituted-1,3.5-hexatriene, 1,8-disubstituted-1,3,5,7-octatetraene). Woodward-Hoffmann rules for electrocyclic reactions, frontier molecular orbital theory (correlation diagram not required). *(ii) Cycloaddition reactions* - Definition of dienes and dienophiles, *supra-supra* and *antara-antara* modes of cycloadditions ($\pi_s^4 + \pi_s^2$, $\pi_s^4 + \pi_a^2$, $\pi_s^2 + \pi_s^2$, $\pi_s^2 + \pi_a^2$) by taking examples of simple dienes and dienophiles.

Unit IV Spectroscopy for Structural Analysis 9 *marks*

(a) Mass Spectrometry – Basic principles, types of ions produced in mass spectrometer, molecular ion peak, base peak and metastable ion, determination of molecular mass of organic compounds.

(b) Ultraviolet and Visible Spectroscopy – Basic principles of UV and visible spectroscopy, application to conjugated polyenes, carbonyl compounds and α,β-unsaturated carbonyl compounds, Woodward rules.

(c) Infrared Spectroscopy - Basic principles, characteristic vibrational frequencies of carbonyl compounds, hydroxyl and amino compounds.

(d) Nuclear Magnetic Resonance Spectroscopy - Basic principles, chemical shifts, shielding and deshielding of protons, chemically equivalent protons, PMR- peak area and proton counting. Characteristics protons - chemical shifts and coupling constants for ethyl bromide, toluene, p-xylene, o-and p-nitrotoluene, anisole, ethyl alcohol, ethyl acetate, acetaldehyde and acetic acid.

H-602

Chem H 602

100 Marks

50 Marks (12 : 38)

PART A Physical Theory

Unit I: Boltzmann Distribution — **5 marks**

Idea of mathematical and thermodynamic probability; entropy and probability; Boltzmann distribution (without derivation) for non-degenerate and degenerate cases; application to barometric distribution formula. Idea of partition functions.

Unit II: Elementary Quantum Mechanics — **10 marks**

Failure of classical mechanics: Black-body radiation, Planck's radiation law, photoelectric effect, Compton effect, heat capacity of solids; Postulates of quantum mechanis; Model systems (with complete derivation of wavefunction & energy expression): Particle-in-a-box, rigid rotor, harmonic oscillator; quantum numbers and their importance.

Unit III: Molecular Spectroscopy — **10 marks**

Introduction: electromagnetic radiation, regions of the spectrum, basic features of different spectrometers, statement of the Born-Oppenheimer approximation, degrees of freedom.

Rotational and Vibrational spectra of diatomic molecules: frequency expressions, selection rules and applications to estimate molecular parameters; isotope effect in vibrational spectrum.

Unit IV: Photochemistry — **5 marks**

Beer-Lambert's law, Einstein's law; Concept of potential energy curves; Frank-Condon principle; primary photophysical processes; Jablonski diagram: Fluorescence and phosphorescence; photochemical reactions and quantum yield, photosensitized reactions.

Unit V: Electrochemistry-III — **8 marks**

Activity and ionic activity coefficient; mean ionic activity. Ion atmosphere; electrophoretic and relaxation effects; Onsager equation (qualitative); Wien and Debye-Falkenhagen effects; Debye-Huckel theory (qualitative) and the limiting law. Solubility of sparingly soluble salts and ionic strength of medium. Standard cells, concentration cells (with and without transport), liquid junction potentials.EMF of a cell and its measurements. Calculation of thermodynamic parameters (ΔH, ΔG, ΔS and K) from cell EMF, polarization and over potential. Applications of Ag/AgCl, quinhydrone and glass electrodes. potentiometric titrations with examples.

Chem H 602 PART B: Practical (Inorganic) — 35 Marks (8:20)

Laboratory Course (Inorganic Quantitative Analysis) — 20 marks

Total Practical Examination Time: **12 hours**

Estimation (volumetric or gravimetric) of metal constituents from mixtures of Iron-Calcium, Iron-Copper, Copper-Zinc, Calcium-Barium, Copper-Nickel (separation of one metal constituent must be carried out).

Sessional Work and Viva Voce

(a) *Sessional Work*: 3 marks

(b) *Viva Voce:* 4 marks

Chem H 602 PART C: Seminar — 15 Marks

The Seminar shall be conducted internally by the Department of Chemistry of the respective colleges. There shall be no external examiner, but the Seminar shall be conducted formally latest by the end of October each year. A Report of the same along with the marks awarded shall be sent to the Examinations Department on or before 30th November each year.

The Topic of the Seminar shall be decided by the Department and informed to the student at least 30 (thirty) days ahead of the exact date of the Seminar. Each student shall choose a topic in consultation with the Department. The topics must be from any of the subjects of contemporary interest in Chemistry. Students must submit a Write-up of the Seminar.

Marks distribution shall be as follows:

1. Write-up and content : 4 marks
2. Presentation : 7 marks
3. Questions/Answers : 4 marks