Fifth Semester

Total: 200 Marks

Chem H 501

100 Marks

PART A Inorganic Theory

38 marks

Unit I

7 marks

(a) Molecular Symmetry: Symmetry elements and symmetry operations: symmetry planes and reflections, inversion center, proper axis and proper rotations, improper axis and improper rotations; molecular point groups; systematic classification of molecules into point groups with examples{(i) linear molecules, ($C_{\infty v}$, D_{∞}h), (ii) molecules with no C_n or S_n,(C_s and C_i only) , (iii) molecules with cubic point group, (T_d and O_h) , (iv) H_2O, NH_3, $XeOF_4$, XeF_4, PF_5, B_2H_6, Cyclohexane (chair and boat forms)}.

(b) Error Analysis: Significant figures; errors. types of error; accuracy and precision; normal distribution of indeterminate errors; propagation of errors – mean and standard deviations; rejection of data – the F-test, t-test and Q-test.

Unit II

8 marks

(a) Complexometric titration (using EDTA), metal ion indicators, masking and demasking reagents; principles of argentometric titrations, estimation of chloride using adsorption indicators; principles of gravimetric estimation of chloride, theory of precipitation, co-precipitation, post-precipitation and digestion of the precipitate.

(b) Organic Reagents in Inorganic Analysis: Basic qualities of the reagents and conditions; advantages of organic precipitants and their limitations; study of Oxine, α-nitroso β-naphthol, cupferron, cupron, and dimethylglyoxime.

Unit III

8 marks

***Nucleus and Radioactivity-II*:** Types of radioactive decay; radioactive equilibrium; spontaneous fission, nuclear reactions, Q value, principles of separation of isotopes – gaseous diffusion, electrolysis and electromagnetic separation methods; application of radioisotopes as tracers; detection and measurement of radioactivity.

Stability of nucleus and nuclear forces, magic number concept, nuclear binding energy; Basic principles and types of nuclear reactors; India's Nuclear Energy Programme.

7 marks

Unit IV

Crystal Field Theory (CFT): (i) d-orbital splitting by electrostatic field (octahedral, tetrahedral and square planar geometry), and (ii) magnetic properties (high spin and low spin complexes); factors affecting crystal field splitting energy (10Dq value) and spectrochemical series; Structural and thermodynamic effects of d-orbital splitting, variation of ionic radii, Jahn-Teller effect, hydration and lattice energies of first row transition metal ions; octahedral vs. tetrahedral coordination; adjusted CFT and molecular orbital theory for octahedral complexes.

8 marks

Unit V

Magnetochemistry: Explanations of diamagnetism, paramagnetism, ferromagnetism and anti-ferromagnetism, origin of paramagnetic moment: electron spin moment and orbital angular moment, magnetic susceptibility, Curie law, Curie-Weiss law, Bohr magneton, magnetic susceptibility measurement by Gouy and Faraday methods; explanation of magnetic behaviour of $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Co(NH_3)_6]Cl_6$, $K_2[Ni(CN)_4]$, $K_3[CoF_6]$, $K_3[MnF_6]$, $Ni(CO)_4$.

PART B Organic Theory

35 Marks

Unit I

9 marks

(a) Organic Acids and Bases: Bronsted-Lowry and Lewis concepts of acids and bases, electro-negativity, polarity of bonds and dipole moment, inductive effect and its role in substituted aliphatic carboxylic acids. Relative strengths of acids and bases [alcohols, phenols, carboxylic acid, dicarboxylic acids, amines, heterocyclic compounds, carbon acids and bases]; pKa concept; effect of resonance, induction, hybridisation, H-bonding and steric effect on acidity and basicity of molecules.

(b) Polynuclear Aromatic Hydrocarbons: Introduction; molecular orbital structure of naphthalene; resonance; Preparations, reactions, mechanism and orientation of electrophilic substitution. Preparations and reactions of α- and β-naphthols (azo-coupling, reactions with HNO_2 and $FeCl_3$. Preparation and reactions of anthracene.

Unit II

9 marks

(a) Organic Stereochemistry-II: Nomenclature of enantiomers (R and S); relative and absolute configuration; inversion, retention, conformation and conformational isomerism in ethane and *n*-butane; conformation of cyclic compounds – cyclohexane, mono-substituted and disubstituted

cyclohexanes with reference to their relative stability; stereochemical aspects of addition of bromine to alkenes.

***(b) Introduction to Dienes*:** Conjugated, isolated and cumulated dienes (allenes); preparations and reactions of conjugated dienes (1,3-butadiene and isoprene). Addition reaction of 1,3–dienes (1,2 and 1,4).

***(c) Polymers*:** Types of polymers and polymerization processes. Addition (chain-growth) polymerization; free radical vinyl polymerization; ionic vinyl polymerization [Ziegler–Natta polymerisation]. Condensation (step-growth) polymerization, polyesters, polyamides, urea-formaldehyde resins, polyurethanes. Natural and synthetic rubbers.

Unit III *9 marks*

***(a) Introduction to Organic Synthesis*:** Formation of carbon-carbon bond, electrophilic and nucleophilic carbon species, acid-assisted reaction (Friedel Crafts alkylation and acylation, Gatterman-Koch formylation), base assisted condensations (Knoevenagel, Michael, Wittig reaction, Claisen reaction, Claisen-Schmidt reaction, Mannich reaction).

Formation and acid-assisted cleavage of acetals and ketals. mechanisms of formation and hydrolysis of esters and amides (acyclic and cyclic).

***(b) Rearrangements*:** Carbocation rearrangements – pinacole-pinacolone, Wagner-Meerwein, dienone-phenol. Beckmann, Wolff, Hofmann, Curtius, Lossen, Schmidt, benzil-benzilic acid, benzidine-semidene, Favorskii, Fries and Claisen rearrangements.

***(c) Inorganic Reagents in Organic Synthesis*:** $NaBH_4$, $LiAlH_4$, B_2H_6, Na/liq.NH_3, aluminium isopropoxide, $KMnO_4$, $K_2Cr_2O_7$, HIO_4, Lead tetraacetate, peracids.

Unit IV *10 marks*

***(a) Heterocyclic Compounds-II*:** Introduction to condensed five- and six-membered heterocycles, preparation and reactions of indole, quinoline and isoquinoline with special reference to Fischer-Indole synthesis, Skraup and Bischler-Napieralski syntheses.

***(b) Green Chemistry*:** Definition, goals, principles and techniques (brief discussions); Applications to common reactions. Solvent free reactions. Ultrasound reactions, Microwave assisted reactions, Reactions in aqueous and ionic media.

(c) Interconversions: Interconversion involving following functional groups (mechanism not required): -OH. –CHO, -CO, -COOH, -COOR,-$CONH_2$, -NH_2, NHR, -NO_2, -CN, SO_3H, X(Cl, Br, I). (Aliphatic to aliphatic and aromatic to aromatic)

Chem H 502

100 Marks

PART A Physical Theory

50 Marks (13:37)

Unit I: Gaseous State-II

9 marks

Maxwell's distribution law of molecular speeds, molecular speeds and energy distribution as a function of temperature, calculation of the most probable, average and root mean square speeds of molecules, Maxwell-Boltzmann distribution, degrees of freedom of motion, principle of equipartition of energy, collision diameter, collision cross-section, collision frequency and mean free path, viscosity of gases, Boyle temperature, critical phenomena-critical constants, p-v isotherm of carbon dioxide, continuity of state, law of corresponding states and reduced equation of state, vapour density and limiting density.

Unit II: Liquid State-II

6 marks

Determination of surface tension, viscosity and refractive index of liquids. Physical properties and chemical constitution- additive and constitutive properties, molar volume, parachor, specific and molar refraction. Polar and non-polar liquids, dielectric constant, dipole moment, structure of molecules, polarization, Clausius-Mossotti equation.Dipole induced dipole and vander Waals interactions in molecules.

Unit III: Crystalline State-II

6 marks

Symmetry elements in crystals-plane of symmetry, axis of symmetry, centre of symmetry, seven crystal systems, Law of symmetry, Bravais lattices, X-ray diffraction of crystals, Bragg's law, crystal structure determination-Laue's method and powder method, Frenkel and Schottky defects.

Unit IV: Thermodynamics-III

7 marks

Thermodynamic scale of temperature, , Maxwell's relations, definition of chemical potential., concept of chemical potential, equilibrium between different phases, derivation of phase rule from the concept of chemical potential, partial molal quantities, variation of chemical potential with temperature and pressure, chemical potential of a component in an ideal mixture, Gibbs-Duhem equation.

Nernst heat theorem, third law of thermodynamics and its application to the determination of entropy, concept of residual entropy.

Unit V: Chemical Kinetics-II 9 marks

Catalyzed reactions – homogeneous catalysis, acid-base catalysis, enzyme catalysis - Michaelis-Menten equation; Theory of Reaction rates – collision theory, transition state theory of unimolecular and bimolecular reactions.

Complex reactions – opposite, parallel, consecutive and chain reactions, rate determining step, steady state approximation and derivation of rate laws of complex reactions.

Chem H 502 PART B (Practical – Organic) 25 Marks (7: 18)

Laboratory Course (Organic)

Total Time for Practical Exams: 6 hours

1. Separation of Mixtures 4 marks

(a) Separation of binary organic mixtures based on acid-base concept

(b) Determination of melting points

2. Organic Preparation 6 marks

(a) Preparation of the following compounds

(i) Phthalimide (from phthalic anhydride)

(ii) m-Dinitrobenzene (from benzene)

(iii) Picric acid (from phenol)

(iv) p-Bromoacetanilide (from acetanilide)

(v) Benzilic acid (from benzil)

(vi) Methyl Orange (from sulphanilic acid)

3. Viva Voce 5 marks

4. Laboratory Record (Internal Assessment) 3 marks

Chem H 502 PART C (Practical – Physical) 25 Marks

Laboratory Course (Physical)

Total Practical Examination Time: **6 hours**

The following experiments are to be carried out in the class. In the examination, each student should be asked to do any **one** experiment

List of Experiments

1. Conductometric titrations of an acid by a base.
2. Acid-base titration using potentiometer.
3. Verification of Beer-Lambert's law using copper sulfate or $K_2Cr_2O_7$ solution colorimetrically and determination of the concentration of the supplied solution
4. Determination of velocity constant for the decomposition of hydrogen peroxide using ferric chloride as catalyst; and to determine the activation energy.
5. Determination of the heat of solution of solid calcium chloride and to determine lattice with the help of Born-Haber cycle.
6. Determination of the critical solution temperature of the phenol-water system.
7. Study on the kinetics of the reaction between potassium persulfate and potassium iodide at two temperatures with determination of activation energy
8. Study of the adsorption of oxalic acid on charcoal and verification of Freundlich's adsorption isotherm.
9. Determination of surface tension of a liquid/solution by drop-weight method.
10. To obtain the viscosity–composition (v/v) curve of ethanol-water/ glycerol-water/ methanol-water system and to determine the composition (v/v) of a given unknown mixture.
11. Determination of partition coefficient of a solute between two immiscible solvents (e.g. iodine in water/organic solvent; benzoic acid in water/benzene).
12. Determination of pKa value of different sets of buffer by pH-metric titration using glass electrode

(*cont'd* .....

Distribution of marks:

Viva Voce : 05 Marks

Laboratory Record: 03 Marks

Experiment: 10 Marks