SEMESTER II

Paper: CHM801C (Core)
Inorganic Chemistry II
Credits: 3+1+0=4

Theory: 60Lectures

Unit 1: E**lectronic spectra of Transition metal complexes**

d-d transition, charge transfer transition, colour, intensity and origin of spectra, term symbols and splitting of terms in different geometries, selection rules for electronic transitions, correlation, Orgel and Tanabe-Sugano diagrams, calculation of Dq and Racah parameters, Nephelauxetic series.

(15 lectures)

Unit 2: Inorganic Reaction Mechanisms

Kinetic and thermodynamic stability, Lability and inertness, Stability Constants, Mechanisms of Substitution reactions in octahedral and square planer complexes, Trans effect and its application to the synthesis of metal complexes. Inner sphere and outer sphere mechanisms of Redox Reactions, MarcusTheory, Concept of Photochemical Reactions.

(15 lectures)

Unit 3: Magnetic Properties

Ferro and antiferro-magnetism, temperature independent paramagnetism, magnetic susceptibility - Van Vleck equation, experimental measurement, magnetic moment - orbital contribution, quenching of contribution, effect of spin orbit coupling, spin crossover. Temperature dependence of magnetic susceptibility, exchange coupling effects. Magnetic properties of second and third transition series.

(15 lectures)

Unit 4: Organometallic Chemistry

18-Electron rule, metal alkyl, metal carbonyl, metal-olefin and metal carbene complexes, synthesis, structure and bonding in metallocenes, Fluxionality in organometallic complexes, Types of organmetallic reactions, Homogeneous catalysis - Hydrogenation, hydroformylation, acetic acid synthesis, metathesis and olefin oxidation. Heterogeneous catalysis - Fischer-Tropsch reaction, Ziegler-Natta polymerization.

(15 lectures)

Paper: CHM802C (Core)
Organic Chemistry II
Credits: 3+1+0=4

Theory: 60Lectures

Unit1: Reaction intermediates and related reactions: I

Carbanions: enolates and enamines, Kinetic and thermodynamic enolates, lithium and boron enolates and silyl enol ethers in aldol reactions (Zimmerman-Traxler model), conjugate addition, Michael reactions, Robinson annulation, alkylation and acylation of enolates; name reactions under carbanion chemistry - Claisen, Dieckmann, Knoevenegal, Stobbe, Darzen, Acyloin condensations, Shapiro reaction, Julia olefination, Brook rearrangement, Sakurai reaction, Henry reaction, Kulinkovich reaction, Nef reaction, Baylis-Hillman reaction.

Ylids: Chemistry of phosphorous and sulfur ylids - Wittig and related reactions, Peterson olefination

Carbocation: structure and stability of carbocations, classical and non-classical carbocations, neighbouring group participation and rearrangements including Wagner-Meerwein, pinacol-pinacolone, semi-pinacol rearrangement, Fries rearrangement, C-C bond formation involving carbocations, oxymercuration, halo-lactonisation,Tishchenko reaction, Ritter reaction, Prins reaction.

(20 Lectures)

Unit 2: Reaction intermediates and related reactions: II

Carbenes: Structure of carbenes, generation of carbenes, addition and insertion reactions, rearrangement reactions of carbenes such as Wolff rearrangement, generation and reactions of ylids by carbenoid decomposition (existence of O and N based ylids),

Nitrenes: Structure of nitrene, generation and reactions of nitrene and related electron deficient nitrogen intermediates, Curtius, Lossen, Hoffmann, Schmidt, Beckmann rearrangement, Tebbe olefination reactions.

Radicals: Generation of radical intermediates and its (a) addition to alkenes, alkynes (inter & intramolecular) for C-C bond formation and Baldwin‘s rules (b) fragmentation and rearrangements. Name reactions involving radical intermediates such as Barton deoxygenation and decarboxylation, McMurry coupling.

Benzyne: Generation and reactions involving benzyne.

(12 Lectures)

Unit 3: Bioorganic chemistry

Prokaryotic and eukaryotic cells; structure of plant and animal cells; intracellular organelles and their functions; metabolic processes- catabolism and anabolism; Constituents of cell nucleus, structure of chromosomes; composition and functions biological membranes- lipids and lipoproteins. **(3 Lectures)**

Nucleic acid chemistry- structure and functions of DNA and RNA, the double helical structure of DNA; unusual DNA structure- DNA hairpins, triple helix, G-quadruplex; stability of the double helix- thermal denaturation and renaturation of DNA double helix; chemical and enzymatic hydrolysis of nucleic acids; DNA replication, RNA transcription and translation of genetic information; chemical basis of heredity.
(6 Lectures)

Carbohydrate metabolism- glycolysis, gluconeogenesis and Kreb's cycle, oxidative phosphorylation. **(4 Lectures)**

Biochemistry of lipids- biosynthesis of fatty acids, triacylglycerols, phospholipids, cholesterol and related steroids; prostaglandins. **(4 Lectures)**

Protein biochemistry- amino acids, biosynthesis of amino acids, activation of amino acids, mechanism of translation, sequencing of amino acids in polypeptides; protein structure- primary, secondary, tertiary and quaternary structure of proteins, post-translational modifications and protein folding. **(6 Lectures)**

Enzymes- classification and catalytic behavior, enzyme kinetics, mechanism of action, factors affecting enzyme activity, enzyme regulators and inhibitors, enzyme models- host-guest chemistry, biotechnological applications of enzymes. **(5 Lectures)**

(28 Lectures)

Paper: CHM803C (Core)
Physical Chemistry II
Credits: 3+1+0=4

Theory: 60 Lectures

Unit 1: Kinetics

Theories of reaction rate: Collision theory, basic ideas of potential energy surfaces, Eyring equation, its thermodynamic and statistical thermodynamic formulation. Theory of unimolecular reactions, Lindemann mechanism, Hinshelwood treatment.

Solution kinetics: Factors effecting reaction rates in solutions, Effects of solvent and ionic strength (primary salt effect) on the rate constant, secondary salt effects.

Oscillating reactions: Belousov-Zhabotinski reaction, concept of chemical chaos.

Fast reaction kinetics: Introduction to relaxation and flow methods, idea of relaxation kinetics and stopped flow technique.

Kinetics of heterogeneous catalysis – Langmuir-Hinselwood and Eley-Riedel models.

(20 Lectures)

Unit 2: Homogeneous catalysis

Atom transfer and electron transfer processes. Role of transition metal ions with special reference to Cu, Pd, Pt, Co, Ru and Rh, catalysis in non-aqueous media. Rates of homogeneously catalysed reactions, turnover number and frequency. Catalysis of isomerisation, hydrogenation, oxidation and polymerisation reactions. Metal clusters in catalysis, phase-transfer catalysis.

(10 Lectures)

Unit 3: Dynamic Electrochemistry

Ion-solvent interactions: The Born model – thermodynamic parameters of ion-solvent interactions. Structural treatment: the ion-dipole model – its modifications.

Primary solvation – determination of hydration number, compressibility method and viscosity method.

Debye-Húckel theory of ion-ion interactions – derivation, validity and limitations; extended Debye-Húckel-Onsager equation.

The random walk model of ionic diffusion - Einstein-Smoluchowski relation.

(15 Lectures)

Unit 4: Data Analysis

Errors and deviations in measurements of physical quantities: accuracy and precision. Absolute, relative and mean errors. Relative and mean deviation, standard deviation. Significant figures in reporting measurements and calculation results, its relation to precision. Types of errors: determinate and indeterminate errors, various types of determinate errors.

Propagation of errors in calculations. Uncertainty in measurement of physical quantities and in universal constants.

Regression analysis – linear least-square fitting of experimental data-points. Correlation analysis – positive, nil and negative correlations, calculation of Pearson’s correlation coefficient.

Tests of significance: Concept of confidence level and confidence interval. Reliability of results – Dixon’s Q Test. Comparison of results – Student’s t test and the F test.

(15 Lectures)

Paper: CHM804C (Core)
Quantum Chemistry and Molecular Spectroscopy
Credits: 3+1+0=4

Theory: 60 Lectures

(The answers to the two parts must be written in separate answer-scripts)

Part A: Quantum Chemistry

Unit 1: Basic principles of quantum mechanics

Review of the postulates of quantum mechanics and of Schrödinger wave equation – both time dependent and time independent forms. Wave functions of one-particle and many-particle systems, their Born interpretation. Well-behaved functions and normalized functions. Orthogonal functions – Schmidt's orthogonalisation technique.

Physical observables and corresponding quantum mechanical operators. Eigenvalues and eigenfunctions of quantum mechanical operators, the physical significance of the eigenvalues. Expectation values of observable properties. Hermitian operators and the theorems they obey. Concept of degeneracy. Compatible observables and compatibility theorem, incompatible observables and the (generalised) uncertainty principle (derivation not required).

Basic ideas about the theory of angular momenta – spin and orbital angular momenta, ways of their coupling. Conservation of angular momenta.

(15 lectures)

Unit 2: Some Model Systems with Exact Solutions

Solutions of the Schrödinger time-independent equations for:

(i) Particle in a one-dimensional box and in a three-dimensional box.
(ii) Linear harmonic oscillator, vibrational energy levels of diatomic molecules.
(iii) Rectangular potential barrier problems, quantum mechanical tunnelling.
(iv) Problem of two interacting particles: separating centre of mass and relative motion.

(v) The two-particle rigid rotor problem, rotational energy levels of a diatomic molecule.
(vi) The hydrogen atom: representation and solution of the Schrodinger equation for electronic motion in spherical polar coordinate system. Radial solution: radial wavefunction and radial probability distribution function. Angular solution: the angular wavefunction and the representation of the shapes of atomic orbitals.

(15 lectures)

Part B: Molecular Spectroscopy II

Unit 3: Spin Resonance Spectroscopy

Basic Concepts, Chemical Shift, splitting patterns of signals; coupling constant and its distinction from chemical shift – use of coupling constant in structural elucidation. Simplification of spectra by use of shift reagents and high magnetic fields, Integration and its use in proton count and molecular ratios- determination of enantiomeric excess. Deuterium exchange technique in the determination of labile hydrogen, spin-decoupling and NOE, 2D NMR (^{1}H- ^{1}H and ^{1}H – ^{13}C COSY), DEPT. Complexity of ^{13}C NMR spectra and use of spin decoupling in its simplification; CINDP and its applications., Simple worked out examples using application of NMR. A brief introduction to solid state NMR.

(12 lectures)

Unit 4: ESR and NMR Spectroscopy

Applications of NMR spectroscopy to diamagnetic and paramagnetic inorganic compounds; paramagnetic shifts, ^{11}B, ^{14}N, ^{19}F, and ^{31}P NMR in inorganic compounds.

Electron Spin Resonance (ESR spectroscopy): Basic principles, factors affecting g-tensors, hyperfine splitting in free radicals and metal complexes, zero field splitting, application of ESR for d^1 and d^9 complexes.

(8 lectures)

Unit 5: Mass Spectrometry

Basic Principle of mass spectrometry, Instrumentation: Ionization methods, Mass Analysers, Base peak, molecular ion peak and isotope peak. Nominal mass and exact mass, determination of molecular formula, McLafferty Rearrangement, Metastable peak, The Nitrogen Rule, General fragmentation modes, Important features of the mass spectra of aliphatic, aromatic and cyclic hydrocarbons, primary alcohols and carbonyl compounds, Analyzing Mass Spectrum and solving simple problems in Mass Spectra.

(6 lectures)

Unit 6: Mössbauer Spectroscopy

Basic principles, isomer shift, quadrupole splitting and effect of magnetic field. Mössbauer Spectra of high-spin and low-spin iron complexes.

(4 lectures)

Paper: CHM805L (Lab Course)
Inorganic and Physical Chemistry Practical
Credits: 0+0+4=4

Practicals: 120 Hours

Unit 1: Inorganic Chemistry Practical **90 Hours**

(Each Student should perform one experiment from each unit during end semester examination)

A. Quantitative analysis

(a) Separation and determination of two metal ions Cu-Ni, Ni-Zn, Cu-Fe, etc. involving volumetric and gravimetric methods.

(b) Analysis of ores/alloys, cement and steel, etc.

Ores: Hematite, Limestone, Dolomite, Cement, Pyrolusite and other ores.

Alloys: Brass, Gunmetal, Cupronickel, Solder, Bronze, Phosphor Bronze, Steel, Copper-Nickel, other alloys.

(c) Determination of hardness of water

B. Preparation and Characterization of Inorganic Complexes

Preparation of selected inorganic complexes (Linkage isomers, Cis-Trans isomers etc.) and their physico-chemical characterization by elemental analysis, IR and electronic spectrophotometry, magnetic susceptibility measurements, magnetic resonance spectroscopy, and solution conductivity measurements wherever appropriate and possible.

Unit 2: Physical Chemistry Practical **30 Hours**

(1) Study of the inversion of sucrose in presence of two acids polarimetrically using Guggenheim plots and hence determination of the relative strengths of the acids.

(2) Verification of the proportionality of the rate constant for acid-catalysed hydrolysis of methyl acetate to the concentration of the mineral acid catalyst (linear least square fitting method is to be used for calculation of the rate constants instead of the common graphical method).

(3) Study of the progress of the autocatalytic reaction between oxalic acid and $KMnO_4$ with time and identification of its autocatalytic nature.

(4) Study of the dependence of the rate constant of the ionic reaction $S_2O_8^{2-} + 2\ I^- = 2\ SO_4^{2-} + I_2$ on the ionic strength of the aqueous reaction medium in presence of varying concentrations of NaCl.

(5) Verification of the Debye-Huckel-Onsager equation for aqueous solutions of a strong electrolyte.

(Any new experiments may be added from time to time)