

P G DEPARTMENT OF CHEMISTRY

M.Phil. / Ph.D. Entrance Test-2010.

Subject: Chemistry.

(Note: Equal Weightage shall be given to all sections.)

Note:- The question paper shall comprise of two parts :

Part (I) Subjective part containing Six questions of which Four questions must be attempted (40 Marks);

Part (II) Multiple choice objective part containing 30 questions are to be attempted (30 Marks).

SECTION-A

INORGANIC CHEMISTRY

Unit I:

Stereochemistry and Bonding in Main Group Compounds and Metal clusters

Valence bond theory- Energy changes taking place during the formation of diatomic molecules; factors affecting the combined wave function. Bent's rule and energetics of hybridization. Resonance: Conditions, Resonance energy and examples of some inorganic molecules/ions. Molecular orbital theory- Variation of electron density with internuclear distance; overlap integral. . Molecular orbitals and molecular structure - Walsh diagrams (tri- and tetra-atomic molecules). Delocalized molecular orbitals:- Butadiene, cyclopentadiene and benzene. VSEPR: Shape of molecules and ions; limitations Hydrogen bond: Detection, theories, effect on properties and π -hydrogen bonding. Odd electron bonds: Types, properties and molecular orbital treatment. Metal Clusters. Introduction to metal clusters; Dinuclear species; trinuclear clusters; metal-metal multiple bonds. Tetranuclear metal clusters.

Unit II:

Chemistry of coordination compounds including organometallic compounds:

Metal- Ligand Equilibria in Solution

Stepwise and overall formation constants. Factors affecting stability of complexes with respect to the nature of metal ion and ligands. Stability of uncommon oxidation states. Determination of formation constants by pH- metry and spectrophotometry. Metal Chelates: Characteristics and detection of chelates; the chelate effect and the factors affecting stability of metal chelates. Applications of metal chelates in chemical analysis and medicine. Complexes of macrocyclic ligands:- Crown ethers and cryptands.

Metal-Ligand Bonding

Structural (ionic radii) and thermodynamic (hydration and lattice energies) effects of crystal field splitting. Jahn -Teller distortion, spectrochemical series and the nephleuxetic effect. Evidence of covalent bonding in transition metal complexes; Adjusted crystal field theory. Molecular orbital theory of bonding in octahedral complexes- composition of ligand group orbitals; molecular orbitals and energy level diagram for sigma bonded ML_6 ; effect of π -bonding. Molecular orbital and energy level diagram for square-planar and tetrahedral complexes.

π - Complexes of Transition Metals

Transition Metal Carbonyls: Carbon Monoxide as a ligand; synthesis, reactions, structures and bonding of mono- and poly-nuclear binary carbonyls. Vibrational spectra of metal carbonyls for structural diagnosis. Preparation, reactions, structure, bonding of transition metal Nitrosyls, and Dinitrogen and Dioxygen complexes of transition metals. Tertiary phosphine as ligand.

Organometallic Compounds

Definition, nomenclature and classification of organometallic compounds. Effective atomic number (18-electron) rule. Stability of organometallic compounds towards heat, oxidation and hydrolysis. Preparation, properties, structure and bonding, and applications of alkyls and aryls of Li, B, Al and Sn. Synthesis, structure and bonding of metal-alkene complexes with special reference to Zeise's salt. Homogeneous hydrogenation.

Unit III:

Reaction Mechanism in coordination complexes and their spectral/magnetic Properties:

Magnetic Properties and Electronic Spectra of Transition Metal Complexes

Types of magnetic behaviour, magnetic susceptibility and magnetic moment; methods of determining magnetic susceptibility; spin-only formula; L-S coupling, correlation of λ and μ_{eff} values; orbital contribution to magnetic moments; applications of magnetic moment data in investigation of nature of bonding and stereochemistry of first row transition metal complexes. High spin- low spin crossover. Electronic spectra of Transition metal complexes:- General features; Types of electronic transitions, theoretical aspects of d-d spectra, selection rules; spectral terms of d1 - d10 metal ions. Selected examples of d-d spectra. Spectra of distorted octahedral and square planar complexes. Charge transfer spectra.

Mechanisms of Ligand substitution reactions in Octahedral Metal Complexes

Energy profile of a reaction; reactivity of metal complexes; inert and labile complexes. Types of substitution reactions; mechanistic classification of substitution reactions:-Dissociative, Associative, Dissociative conjugate base and Interchange. Empirical criteria to differentiate the mechanism of substitution. Substitution in octahedral complexes- Classification of metal ions based on water exchange rates. Metal-complex formation- the Eigen-Wilkins mechanism. Anation reactions. Hydrolysis reactions; Simple Acid hydrolysis, Acid catalysed and Base hydrolysis. Stereochemical changes in octahedral substitution reactions. Substitution reactions without metal-ligand bond breaking.

Ligand substitution reactions in square-planar complexes

Significance of the two-term rate law, mechanism, and steric course of the substitution reaction. Factors affecting the rate of substitution - entering and leaving groups; nucleophilicity of entering group and the pK_a scale, central metal ion, solvent, and the non-leaving groups. The Trans Effect-theories, applications in synthesis. Cis-Trans isomerization in square planar complexes.

Electron Transfer Reactions in coordination Complexes

Complementary and non-complementary reactions. Classification as outer sphere and inner sphere redox reactions. Mechanism of outer sphere and inner sphere electron transfer reactions-the elementary steps involved; formation of precursor and successor complexes; rate laws. Characterization of redox processes as outer and inner sphere. Factors affecting the rate of electron transfer- Chemical activation; sigma and pi nature of donor/ acceptor orbitals; electron configuration of oxidant/reductant. Bridging ligand effects in inner-sphere reactions. Oxidative addition, reductive elimination and migration (insertion) reactions.

Unit IV:

Bioinorganic Chemistry:

Metal—Ions in Biological Systems

Classification of elements in human systems. Concept of essentiality and evolution of essential elements. Distribution and biological role of essential trace and ultra trace elements like V, Cr,

Mn, Ni, P, and halogens. Effects of deficiency of essential trace elements in biological systems and its treatment. Antagonism and Synergism among essential trace elements. Role of alkali and alkaline earth metal—ions in biological systems and their mechanism of transport in cell membrane. The Sodium / Potassium pump. Lithium and the mental health. Chlorophyll and its role in Photosynthesis.

Transport and Storage of Dioxygen

Porphyryns: Introduction, Characteristic absorption spectrum and Salient features. Haemoglobin and Myoglobin: Structure, Bohr effect; Cooperative interaction in haemoglobin. Mechanism of oxygen transport in human body. Hemerythrin and Hemocyanin: Structure, Metal binding groups and Dioxygen binding. Synthetic Oxygen Carriers: Vaska's iridium complex; Cobalt complexes with micro-, and macrocyclic ligands; salen and acacen ligands. Biological Nitrogen Fixation: Dinitrogen complexes and their reactivity; Nitrogenase enzyme; fixation via nitride formation.

Unit V:

Physical characterization of Inorganic compounds by spectroscopic techniques:

IR, Raman and EPR Spectroscopy

Symmetry of IR and Raman active normal vibrational modes of AB₂, AB₃, AB₄, AB₅, and ABe type molecules. Metal Isotope Technique, Normal Coordinate Analysis (introductory idea). Mode of bonding of ambidentate ligands: ethylenediamine and diketonato complexes. Raman Spectroscopy particularly for the study of active sites of Metalloproteins. EPR: Hyperfine coupling, Fermi contact, Spin polarization effects, Dipolar coupling, McConnell equation and calculation of spin densities in inorganic radicals such as CO₂⁻, CH₃⁻, BH₃⁻ and F₂⁻. Spin orbit coupling and significance of g tensors.

Mossbauer Spectroscopy

Basic principles, Spectral parameters such as isomer shift, quadrupole splitting and magnetic splitting, spectrum display. Application of the technique to the studies of i) bonding and structure of Fe²⁺ and Fe³⁺ compounds including those of intermediate spin, ii) Sn²⁺ and Sn⁴⁺ compounds— nature of M—L bond, coordination number and structure, iii) detection of oxidation state and inequivalent MB atoms.

SECTION-B

Organic Chemistry

Unit-VI:

Delocalised Chemical bonding

Conjugation, Cross conjugation, rules of resonance, steric inhibition of resonance.

Aromaticity: Huckel rule and concept of aromaticity, Molecular orbital description of aromaticity and antiaromaticity. Relation between NMR and aromaticity. Annulenes (Two to more than ten π -electron systems), Aromaticity of hetero annulenes and fullerenes (C-60). Homoaromaticity. **Hyperconjugation:** Explanation of hyperconjugative effect, isovalent and sacrificial hyperconjugations. **Tautomerism:** Different types including valence tautomerism. **Reactive Intermediates:** Generation, Structure, fate and stability of carbocations, (Classical and non-classical) carbanions, free radicals, carbenes, nitrenes and radical ions.

Stereochemistry

Elements of symmetry, Chirality due to chiral centre, molecules with more than one chiral centre, threo and erythro isomers optical activity in the absence of chiral carbon

(biphenyls, allenes and spirans). Chirality due to helical shape. Enantiotopic and diastereotopic atoms, groups and faces. Asymmetric synthesis, Stereospecific reactions (Diels Alder reaction, anti addition of halogens, enzyme catalysed reactions and Rhodium complex reaction). Stereoselective synthesis of ephedrine and epiandrosterone and pheromone. Conformational analysis of cycloalkanes and decalines. Effect of conformation and reactivity in acyclic and cycloalkanes. Conformation of sugars, steric strain due to unavoidable crowding.

Unit -VII

Reaction Mechanism/ Structure and reactivity

Types of mechanisms. Types of reactions, thermodynamic and kinetic requirements, Hammond postulate, Curtin-Hammett principle. Potential energy diagrams, transition states and intermediates. Methods of determining reaction mechanism, isotope effects. **Effect of structure on reactivity:** Resonance and field effects, steric effect, quantitative treatment. The Hammett equation and linear free energy relationship, substituent and reaction constants. Taft equation.

Aliphatic Electrophilic Substitutions

General mechanism of S_E1 , S_E2 and S_{Ei} reactions. Mechanisms of reactions involving migration of double bond. Effect of substrate, leaving group and solvent on reactivity. Stork-enamine reaction.

Aliphatic Nucleophilic Substitution

Mechanisms and stereochemical implications of S_N2 , S_N1 , S_{Ni} and neighbouring group participation (by π and σ -bonds) reactions. Effect of substrate structure, attacking nucleophile, leaving group and solvent on the rates of S_N1 and S_N2 reactions. Mixed S_N1 and S_N2 reactions. Nucleophilic substitution at allylic, aliphatic trigonal and vinylic carbon.

Elimination reactions:

Discussion of $E1$, $E2$, $E1cB$ and $E2C$ mechanisms. Effect of substrate structure base and the leaving group on reactivity. Competition between substitution and elimination reactions. Stereochemistry and orientation of $E2$ elimination. Mechanism and orientation in pyrolytic eliminations, Shapiro reaction.

Aromatic Electrophilic Substitution

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The ortho/para ratio, ipso attack. Orientation of substitution in benzene rings having more than one substituents. Orientation in other ring systems. Mechanisms of diazonium coupling, Vilsmeier-Haack and Gattermann-Koch reactions and Fries rearrangement.

Aromatic Nucleophilic substitution

Discussion of different mechanism (S_N1 , S_NAr , Benzyne and $s_{rn}!$). Structure reactivity relationships. Effect of leaving group and attacking nucleophile. Mechanisms of Vortmeyer, Sommelet-Hauser and Smiles rearrangements and Chichibabin reaction.

Free Radical Substitution

Free radical substitution mechanisms. Mechanism at an aromatic substrate, neighbouring group assistance, reactivity for aliphatic and aromatic substrates. Reactivity in the attacking radical. Effect of solvent on reactivity. Allylic halogenation (NBS), oxidation of aldehydes to carboxylic acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmeyer reaction, free radical rearrangement and Hunsdiecker reaction.

Unit –VIII:

Addition to carbon Hetero multiple bonds,

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagent, organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds. Wittig reaction. Mechanisms of condensations involving enolates: Aldol, Robinson annulation, Knoevenagel, Claisen, Dieckmann, Mannich, Benzoin, Perkin and Stobbe reactions. Hydrolysis of esters, amides and ammonolysis of esters.

Addition to carbon --Carbon multiple bonds

General mechanism, reactivity, orientation and stereochemical implications of additions reactions involving electrophiles, nucleophiles and free radicals. Addition to cyclopropane ring. Hydrogenation of double/triple bonds and aromatic rings. Hydroboration, Ene-reaction, Michael reaction and Sharpless asymmetric epoxidation.

Molecular Rearrangements

General mechanistic treatment of nucleophilic, electrophilic and free radical rearrangements. Nature of migration and migratory aptitude and memory effect. Detailed study of following rearrangement: Wagner-Meerwein, Pinacol- Pinacolone, Demjanov, Benzil-Benzilic acid, Favorskii, Arndt-Eistert, Neber, Hofmann, Curtius, Lossen, Schmidt, Beckmann, and Baeyer-Villiger.

Unit –IX

Pericyclic reactions

Molecular orbital symmetry, Frontier orbitals of ethene, 1,3-butadiene, 1,3,5-hexatriene and allylic system. HOMO, LUMO concept, FMO approach. Classification of pericyclic reactions, Woodward-Hoffmann rules for the following pericyclic reactions. Cycloadditions: Thermal and Photochemical 2+2 and 4+2 cycloadditions. Suprafacial and antarafacial cycloaddition. Electrocyclic Reactions: Thermal and Photo-induced Electrocyclic reactions of $4n$ and $4n + 2$ systems and their stereochemistry. Conrotatory and disrotatory motions. Sigmatropic rearrangements: Classification, [1,3], [1,5] and [3,3] sigmatropic shifts. Cope and Claisen rearrangement. Suprafacial and antarafacial shifts of hydrogen atom.

Photochemical Reactions

Interaction of electromagnetic radiation with matter. Types of excitations. Singlet and triplet states and their lifetimes. The fate of excited molecule. (Physical and chemical processes). Transfer of excitation energy: Sensitization and Quenching, Quantum yield, types of photochemical reactions.

Photochemistry of alkenes

Geometrical isomerisations, cyclisation and dimerisation reactions. Photochemical reactions of 1,3-butadiene (excluding pericyclic reactions). Rearrangement of 1,4 and 1,5-dienes.

Photochemistry of saturated carbonyl compounds

Intramolecular reactions of saturated acyclic and cyclic carbonyl compounds. (Norrish type-I and Norrish type-II processes). Intermolecular cycloaddition reactions (Paterno-Buchi reaction).

Photochemistry of unsaturated carbonyl compounds

Photochemical reactions of α,β -unsaturated carbonyl compounds. (H-Abstraction and isomerisation to β, γ -unsaturated carbonyl compounds). Photolysis of cyclic α,β -unsaturated ketones (dimerisation and lumiketone rearrangement) and cyclohexadienones.

Photochemistry of Aromatic compounds

Photoinduced isomerisations of benzene and its alkyl derivatives. 1,2 ; 1,3 and 1,4 photoaddition reactions of benzene. Nucleophilic photosubstitution reactions in aromatic compounds. Photo Fries-rearrangement of aryl esters and anilides.

Miscellaneous Photochemical reaction

Photolysis of organic nitrites and their synthetic utility (Barton reaction). Photochemistry of vision.

Unit -X

Ultraviolet Spectroscopy

Ultraviolet absorption spectra of enones, dienes (homo and heteroannular) carbonyl compounds, aromatic and heteroaromatic compounds. Effect of conjugation on ultraviolet spectra, Woodward-Fieser rules, application and limitation. Kuhn's rule, application to conjugated polyenes.

Infrared Spectroscopy

Introduction, instrumentation and sample handling, characteristic vibrational frequencies of hydrocarbons, alcohols, ethers, phenols, amines, aldehydes, ketones, acids, anhydrides, esters, lactones, amides and conjugated carbonyl compounds. Effect of hydrogen bonding on vibrational frequencies in IR spectra. Overtones, combination bands and Fermi resonance, FT-IR.

Mass Spectrometry

Introduction, instrumentation, a typical mass spectra, molecular ion peak. Ion production, EI, CI, FD and FAB methods. Role of isotopes in mass spectrometry. Fragmentation pattern of various classes of organic compounds. Metastable peak, McLafferty rearrangement, nitrogen rule, high resolution mass spectrometry.

Nuclear magnetic resonance spectroscopy

General Introduction and definition, chemical shift, spin-spin interaction, shielding mechanism, mechanism of measurement, chemical shift values and correlation for protons bonded to carbon (aliphatic, olefinic, aldehydic and aromatic) and other nuclei (alcohols, phenols, enols, carboxylic acids, amines, amides and mercapto). Chemical exchange, effect of deuteration, complex spin-spin interactions between two three, four and five nuclei (first order spectra) virtual coupling, stereochemistry, hindered rotation Karplus curve variation of coupling constant with dihedral angle. Simplification of complex spectra, nuclear magnetic double resonance, contact shift reagents, solvent effect. Fourier transform technique, nuclear overhauser effect (NOE)

Carbon-13 NMR Spectroscopy

General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroaromatic and carbonyl carbon), coupling constant. Structure determination of organic compounds based on their spectral data (uv, ir, nmr and mass). Problem based exercises.

SECTION-C

Physical Chemistry

Unit-XI:

Quantum Chemistry

Exact quantum mechanical results:

Time-independent and time-dependent Schrodinger equation. Postulates of quantum mechanics. Operator concept, quantum mechanical operators in Cartesian and Spherical polar co-ordinate systems, some properties of quantum mechanical operators. Review of particle in a box problem. The solution of problems of harmonic oscillator & the rigid rotator. Tunneling effect. Born-Oppenheimer approximation. Solution of the Hydrogen-like atom problem- radial and angular wave functions.

Angular momentum and electronic structure of atom

General theory of angular momentum. Eigen functions and Eigen values of angular momentum operators. Ladder operators. Spin angular momentum, antisymmetry and Pauli's principle. Wave functions of poly-electron atoms, Slater determinant. Atomic term symbols, term separation of pn and dn configurations, spin-orbit coupling, Zeeman splitting.

Approximation methods

The Variation theorem, linear variation principle, application to hydrogen atom and helium atom. Perturbation theory -first order(non-degenerate & degenerate). Application of perturbation method to helium atom.

Chemical Bonding

LCAO-MO approximation, H₂⁺ molecular ion, brief introduction to H₂. Molecular term symbols. Valence bond treatment of H₂, comparison of MO and VB methods in the light of H₂ molecule. Hybridization of orbitals (sp, sp² & sp³). Huckel's Pi-MO theory of conjugated systems; Application to linear and cyclic polyenes. Pi-electron charge and bond-order. Alternant hydrocarbons, heteroatomic conjugated systems. Limitations of Huckel theory and improvement.

Unit-XII:

Thermodynamics of electrolyte solutions

Ion solvent Interactions: Non structural (Born) treatment and an introduction to structural (Ion-dipole, Ion-quadrupole) treatments of ion-solvent interactions.

Ion-Ion Interactions: Activity and activity co-efficients. Debye-Huckel theory of activity coefficients of electrolyte solutions; derivation of Debye-Huckel limiting law, validity and extension to high concentrations; ion-pair formation-Bjerrum model. Debye-Huckel-Onsager conductance equation and brief idea of its extension.

Statistical Thermodynamics

Concept of distribution, thermodynamic probability and most probable distribution. Sterling approximation. Derivation of Boltzmann distribution law. Bose-Einstein and

Fermi-Dirac distribution equations (without derivation) and comparison of the three statistics. Partition function & its significance. Translational, rotational, vibrational and electronic partition functions. Calculation of thermodynamic properties in terms of partition functions, application to ideal monoatomic & diatomic gases. Equilibrium constant in terms of partition functions.

Irreversible Thermodynamics

Irreversible processes and uncompensated heat, degree of advancement, reaction rate & affinity. Gibbs' equation, entropy production, entropy production due to matter flow, heat flow, charge flow & chemical reactions. Concept of forces & fluxes, Onsager's theory of irreversible processes- phenomenological laws, their domain of validity. Chemical reactions near equilibrium. Transformation properties of forces and fluxes. Electrokinetic phenomena.

Unit-XIII:

Electrochemistry

Electrified interface, concept of surface excess. Thermodynamics of electrified interface, Lippman equation, electrocapillary curves. Methods for determination of surface excess. Structural models of metal-electrolyte interface: Helmholtz-Perrin, Gouy-Chapman and Stern models. Ionic Adsorption at electrodes – isotherms for adsorption (Langmuir, Frumkin and Temkin isotherms) Adsorption of organic molecules – an introduction. Electron transfer at electrified interface at and away from equilibrium. Derivation of Butler-Volmer equation, low and high field approximations, Introduction to corrosion mechanism and types of corrosion, corrosion current and corrosion potential. Electrode kinetics of corrosion in absence of oxide layer, monitoring of corrosion, and inhibiting corrosion.

Unit-XIV:

Chemical kinetics

General features of fast reactions, study of fast reactions by flow method, relaxation method and flash photolysis. Activated complex theory of reaction rates, statistical & thermodynamic formulations, comparison with collision theory. Dynamics of unimolecular reactions (Lindman-Hinshelwood, RRK and RRKM theories), Introduction to potential energy surfaces. Surface Reactions: Unimolecular & bimolecular surface reactions [Langmuir-Hinshelwood & Langmuir-Riedel mechanism], classical & statistical treatments. Ionic Reactions: Single & double sphere models of ionic reactions. Diffusion controlled reactions (partial & full microscopic diffusion control) Chain Reactions: Thermal Hydrogen-Bromine reaction, explosive reactions, oscillatory reactions (BZ reaction)

Unit-XV:

Crystal defects and solid state reactions

Various classifications of crystal defects. Thermodynamics of Schottky & Frankel defects. Dislocations- their types. Colour centers. Solid state reactions - general principles. Experimental procedures. Kinetics of Solid-state reactions (Solid-Solid & Solid-Gas reactions)

Electronic Properties & Band Theory

Free electron theory of metallic solids, Band theory of solids .Semiconductors- Intrinsic & extrinsic semiconductor (n-type & p-type). Doping semiconductors, p-n junction. Super conductors- characteristic properties and applications. Magnetic properties of solids: origin of magnetism in solids, Diamagnetism, paramagnetism – ferromagnetism, antiferromagnetism and ferrimagnetism. Temperature dependence of magnetization.

Surface Chemistry

Pressure difference across curved surfaces (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, BET equation and its use in estimation of surface area, catalytic activity at surfaces. Determination of molecular mass of colloidal particles through-Sedimentation, Viscosity and light scattering methods.

Hydrophobic interactions, Micellization, factors affecting the Micellization, Thermodynamics of micellization - phase separation and mass action models, Regular solution theory for mixed micellization
