RAM KRISHNA DHARMARTH FOUNDATION UNIVERSITY, BHOPAL

Ph.D. Entrance Exam

Subject: Chemistry

Syllabus

Unit -I: Inorganic Chemistry

Chemical periodicity: Electronic configuration, Bond parameters, Electronegativity and Magnitude, Fajan's rules. VSEPR Theory - Valence Bond Theory - Structure and bonding of hybridization and MOT Theory. Octet Rule and 18 electron rule.

Concepts of Acids and Bases: Theories (Arrhenius, Bronsted-Lowry, Lewis concept), Oswalt's Dilution Law. HSAB Concept. pH Scale, Buffer solution. Ionization constant. Relation between K_a and K_b, Non-Aqueous Solvents.

Electro covalent co-ordination, octate rule, Hybridization sp, sp2, sp3
DO, BOD, COD and determination, Zeolite Method, Chromatography. Rf

Coordination compounds: Nomenclature of Coordination Compounds. Important terms to co-ordination compound, Isomerism. Structure and Bonding Theories (CFT, LFT and VBT) Jahn-Teller theorem. Spectral and Magnetic Properties of Para, Dia, Ferro and Antiferro magnetism. Reaction Mechanisms - Trans Effect, Square-planar complex, Electron transfer reactions, Carbonyl complexes.

Inner-Transition elements: Electronic Configurations. Physical and Magnetic properties. Atomic and Ionic sizes and Oxidation states.Spectral and Magnetic Properties, Redox chemistry of Lanthanides and Actinides. Analytical applications- Shift Reagents, Separation of Lanthanides- Ion Exchange Method. Important applications.

Bioinorganic Chemistry: Photosystems - Chlorophyll, Porphyrins, Metalloenzymes , Vitamin B-12. Hemoglobin and Myoglobin. Atom Bomb, Electron transfer Reactions - Cytochromes, Iron-Copper, Blue Copper and Ionophores. Nitrogen Fixation- Molybdoterradoxin, Azoterredoxin. Metal Complexes in Medicine.

Nuclear Chemistry: Nuclear energy and Reactions-Transmutation, Chain Reaction, Spallation reaction, thermonuclear energy, Hydrogen bomb, Nuclear Cross Sections. Nuclear Fission and Fusion, Q-Values. Uses of radioactive isotopes. Group Displacement law, Radio isotopes and isobar.

Unit II: Physical Chemistry

Quantum mechanics: Inadequacy of classical mechanics, Black body radiation, Planck's quantum concept, Photoelectric effect. Lamberts Beer's Law, Wave equations, Wave-particle dualism, Uncertainty principle, Schrödinger equation, operator, eigen functions and eigen values, angular momentum operator, Applications of wave mechanics to simple systems – particle in a box, one and three-dimensional, distortion of the box and Jahn-Teller effect, quantum numbers, zero point energy, orthogonalisation and normality, tunneling. The rigid rotator, harmonic oscillator – Hydrogen atom solution, Pauli principle, application to Hydrogen and Helium atoms–Perturbation method for non degenerate systems, VB and MO treatments of hydrogen molecule,

Group theory: Symmetry elements and symmetry operations, Types of Symmetry operations, Assigning Point groups with Illustrative examples, Group multiplication table of

C_{2V} and C_{3V} for NH_3 molecule. Construction of character Tables- C_{2V} and C_{3V} point groups. Great Orthogonality theorem.

Applications of group theory: IR and Raman spectra for water and ammonia – Mutua l exclusion rule for molecules. Applications of SALC procedure to ethylene and butadiene. Electronic spectroscopy for n-π* and π-π* transitions.

Chemical kinetics: Empirical rate laws and temperature dependence; complex reactions; steady state approximation; determination of reaction mechanisms; collision and transition state theories of rate constants; unimolecular reactions; enzyme kinetics; salt effects; homogeneous catalysis. Rarity of higher order reaction.

Colloids and surfaces: Stability and properties of colloids; isotherms and surface area, Heterogeneous catalysis. Tyndall effect, Electrophoric effect, Emulsion.

Unit III: Physical Chemistry and Instrumental methods of analysis

Thermodynamics: Thermodynamics of open systems; Chemical potential; Definition of fugacity, standard state of real gases, the relation between fugacity and pressure; Partial molar quantities, partial molar volume and its determination, thermodynamics of mixing; Activity and activity coefficients.

Boltzman distribution equation, physical significance of partition function, Quantum statistics Bose–Einstein and Fermi–Dirac distribution equation s, comparison of B.E and F.D statistics with Boltzman statistics, Concept of Negative Kelvin Temperature.

Thermodynamic probability and entropy; Boltzman distribution law; Maxwel-Boltzman, Bose-Einstein and Fermi-Dirac statistics; vibrational, rotational and electronic partition functions; calculation of thermodynamic functions and equilibrium constants; Theories of specific heats of
solids; postulates and methodologies of non-equilibrium thermodynamics; linear laws; Gibbs equation. Clausius-Clapeyron Equation, Trouton's rule

Spectroscopy: Basic principles of electronic spectra. Determination of organic and inorganic compounds Structure by FT-IR, UV-Vis, ^{1}H and ^{13}C NMR and Mass spectroscopic techniques.

Unit IV: Organic Chemistry

IUPAC nomenclature: Organic molecules including regio- and stereoisomers. Aliphatic and aromatic hydrocarbons with most important functional groups, poly functional compounds, bicyclic compounds, Spiro compounds. E/Z notation, R – S nomenclature.

Principles of stereochemistry: Configurational isomerism-Enanitomers, Diastereomers. Conformational isomers. Homotopic, enentiotopic, enantioselectivity, diastereoselectivity. Concept of Chirality: Recognition of symmetry elements and chiral structures; diastereoisomerism in acyclic and cyclic systems. Conformational analysis of simple cyclic (chair and boat cyclo hexanes) and acyclic systems. Interconversion of Fischer, Newman and Sawhorse projections.

Aromaticity: Benzenoid and non-benzenoid compounds – Huckle rul e, Aromaticity, antiaromaticity, non aromaticity. Aromatic characters of Annulenes, fullerenes.

Organic reactive intermediates: Generation, stability and reactivity of carbocations, carbanions, free radicals, carbenes, benzynes and nitrenes. Sandmeyer reaction, Gomberg-Bachmann reaction, Pschorr reaction and Ullmann reaction, mechanism of Hunsdiecker reaction.

Organic reaction mechanisms: Addition, elimination E_1, E_2 and substitution reactions with electrophilic, nucleophilic or radical species. Determination of reaction pathways.

Named reactions and rearrangements: Aldol, Perkin, Stobbe, Dieckmann condensations; Holmann, Schmidt, Lossen, Curtius, Backmann and Fries rearrangements; Reimer – Tiemann, Reformatsky and Grignard reactions. Diels – Aider reactions; Clasien rearrangements; Friedeal
– Crafts reactions; Witting reactions; and robinson annulation. Routine functional group transformations and interconversions of simple functionalities. Hydroboration, Oppenaur oxidations; Clemmensen, Wolff-Kishner, Meerwein – P onndorf – Veriey and Birch reductions.

Organic transformations and reagents: Functional group interconversion including oxidations and reductions-Use of the following reagents in organic synthesis and functional group transformations; Complex metal hybrids, Gilman's reagent, lithium dimethycuprate, lithium disopropylamide (LDA) dicyclohexylcarbodimide. 1,3 – Dithiane (reactivity umpolung), trimethysilyl iodide, tri-n-butyltin hybride, Woodward and provost hydroxylation, osmium tetroxide, DDQ, selenium dioxide, phase transfer catalysts, crown ethers and Merrified resin, Peterson's synthesis, Wilkinson's catalyst, Baker y east. Chemo, regio and stereoselective transformations.

Unit V: Organic Chemistry and Polymer Chemistry

Concepts in organic synthesis: Retrosynthesis, disconnection approach of C-C disconnection and C-X disconnection, synthons, linear and convergent synthesis, umpolung of reactivity and protecting groups.

Pericyclic reactions: Electrocyclisation, cycloaddition, sigmatropic rearrangements and other related concerted reactions. 1,3 and 1,5–hydrogen s hifts - Cope and Claisen rearrangements; 1,3 -dipolar additions and Diels - Alder reaction.

Photochemical reactions in organic chemistry: Principles and applications- Jablonski diagram - Photochemical reactions of Ketones - Norrish I and II type reactions - Photoreduction - Paterno-Buchi reaction - Photosensitization - Reactions of alpha beta-unsaturated ketones - isomerization and cycloadditions - cis-trans isomerisation of simple olefins - di-pi-methane rearrangement - Photooxidation - Oxidative coupling - Barton reaction.

Heterocyclic compounds Synthesis and reactivity of common heterocyclic compounds containing one or two heteroatoms (O, N, S). Imidazole, oxazole, thiazole and indole, Anthocyanidins, pyrimidines, purines.

Chemistry of natural products: Carbohydrates, proteins and peptides, fatty acids, nucleic acids, terpenes, steroids and alkaloids, cholesterol and hormones. Function and application of enzymes and coenzymes.

Organometallic compounds: Synthesis, bonding and structure, and reactivity. Organometallics in homogeneous catalysis.

Polymer chemistry: Functionality of monomers, degree of polymerization. Types of polymerization: addition, condensation and copolymerization. Glass transition temperature (Tg), Number average, weight average and viscosity average molecular weight of polymers. Molecular weight determination by light scattering, osmotic, centrifuge and viscosity methods. Gel permeation chromatography. Analysis and testing of polymer by FT-IR, NMR, XRD, SEM, TEM, AFM, TGA/DTA/DSC. Biopolymers and biodegradable polymers and its applications.

Suggested Readings

1) F.A. Cotton, G. Wilkinson, F.A Murillo and M.Bochmann, **Advanced Inorganic Chemistry**, 6th Edition, John Wiley, 2007.

2) J.E. Huheey, E.A. Keiter, R.L. Keiter and O.K.Methi, **Inorganic Chemistry-Principles of structure and reactivity**, 4th ed. 5th Impression, Pearson-Education, 2009.
3) I.L. Finar, **Organic Chemistry Vol. I & II**, 5th ed, Pearson Education, Singapore, 2004.
4) J.M.Coxon and B. Halton, **Organic Photochemistry**, 2nd edition, Cambridge University Press, 2011.
5) Jagdamba Singh, **Photochemistry and Pericyclic Reactions**, 3rd edition, New Age Science, 2009.
6) Gowariker and Viswanathan, **Polymer Science**, Wiley Eastern, 1986
7) S. Glasstone, **Text Book of Physical Chemistry**, D. Von Nostrand Inc., 2006.
8) Willard, Merit Dean and Settle, **Instrumental Methods of Analysis**, CBS Publishers, IV Edn., 1986.
9) R.T. Morrison and R. N. Boyd's, **Organic Chemistry**, 6thed., Spring 2008.
10) I.L. Finar, **Organic Chemistry Vol. I & II**, 5th ed, Pearson Education, Singapore, 2004.
11) Micheal B.Smith and Jerry March, **March's Advanced Organic Chemistry Reactions, Mechanishms and Structure**, 6thed., JohnWiley&Sons Inc., New Jersey, 2007.
12) Peter Skyes, **A Guide book to Mechnism in Organic Chemistry**, Orient Longman Private Limited., New Delhi, 2003
13) Peter Atkins, **Physical Chemistry**, 8th ed., Oxford University Press, New Delhi, 2007.
14) K.J. Laidler, **Chemical Kinetics,** 3rd ed., Pearson Education Inc, New Delhi, 2008.