

2023-24

408 - CHEMISTRY

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Syllabus for Ph.D. Entrance Examination: Chemistry – 2018

SECTION A: Research Methodology

Science and Technology- developments and their applications and effects in everyday life,

Achievements of Indians in science & technology, Indigenization of technology and developing new technology, General Science, General issues on Environmental Ecology, Bio-diversity and Climate Change, Conservation, environmental pollution and degradation, environmental impact assessment

Role of science and technology in: democracy, social movements, health, agriculture, Security, Architecture, disaster

Awareness in the fields of: Information Technology, Space, Computers, Robotics, Human machine mixing, Nanotechnology, Biotechnology, Issues relating to intellectual property right

Interdisciplinary topics

1. Chemistry in nanoscience and technology.
2. Catalysis and green chemistry.
3. Medicinal chemistry.
4. Supramolecular chemistry.
5. Environmental chemistry.

SECTION B: Subject: Chemistry

Inorganic Chemistry

Structure of Atom, Periodicity and Bonding: Plank's Quantum Theory, Bohr's Atomic model, Hydrogen spectra and its explanation by Bohr's atomic model, wave- particle duality, De-Broglie's equation, photoelectric effect, Heisenberg uncertainty principle, Schrodinger wave equation, definition wave function and operator, radial and angular wave function, quantum numbers, pauli exclusion principle and Hund's rule, electronic configuration, modern periodic table and periodicity in properties like ionization energy, electronegativity, ionic/ covalent radii etc. Type of chemical bonds, Lewis structure, explanation of bond formation (ionic bond through energy consideration and covalent bonds through orbital overlap), VSEPR theory, concept of hybridization, molecular orbital theory, molecular diagram for homonuclear diatomic molecules, Walsh diagram and shape of the molecules, δ - π bonds, Bent rule and energetics of hybridization, some simple reactions of covalently bonded molecules, percent ionic character, Fajan's rule, properties of ionic and covalent bond, molecular forces.

Chemistry of Group elements: General principles and methods of extraction, trends in physical and chemical properties of s- and p- block elements, especially for hydrides, oxides, hydroxides, halides and oxoacids of elements of different groups. Diagonal relationship, concept of allotrope and catenation, preparation and properties of borax, boric acid, silicones, silicates, zeolites and interhalogen compounds, d and f- block elements: General trends in properties of first row transition metals- metallic character, electronic configuration trends in properties in lanthanoids and actinoids, lanthanide

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interaction and its consequence. IUPAC nomenclature, isomerism and general properties of coordination compounds, different bonding theories like (Werner's theory, VBT and CFT) for explaining bonding and associated properties of coordination compounds, Limitation of Crystal field theory, molecular orbital theory, octahedral, tetrahedral and square planar complexes, π bonding and molecular orbital theory. (MOT). Metal carbonyls, metal nitrosyls, structure and bonding & important reactions of metal carbonyls; preparation, bonding structure and important reactions of transition metal nitrosyl; dinitrogen and di oxygen complexes; tertiary phosphine as ligand, metal olefin complexes – structure and bonding. Metal ions in biological systems: Essential and trace metals; Na^+/K^+ Pump, Role of metal ions in biological processes. Bioenergetics and ATP Cycle, metal complexes in transmission of energy, chlorophylls, photosystem I and photosystem II in cleavage of water, model systems. Nitrogenase; Biological nitrogen fixation, molybdenum nitrogenase, spectroscopic and other evidence, other nitrogenase model systems. Transport and Storage of Dioxygen: heme proteins and oxygen uptake, structure and function of Haemoglobin, Myoglobin, Hemocyanins and Hemerythrin, model synthetic complexes of Iron, cobalt and copper. Electron Transfer in Biology: Structure and function of metalloproteins in electron transport process – cytochromes and Iron – sulphur proteins, synthetic models.

Stepwise and overall formation constants and their interaction, trends in stepwise constants, factors affecting the stability of metal complexes, determination of binary formation constants by spectrophotometry. Energy profile of a reaction, reactivity of metal complexes, inert and labile complexes, kinetic application of valence bond and crystal field theories, kinetics of octahedral substitution, acid hydrolysis, factors affecting acid hydrolysis, base hydrolysis, conjugate base

mechanism, direct and indirect evidence in favor of conjugate mechanism, anation reactions, reactions without metal ligand bond cleavage. Substitution reactions in square planar complexes, the trans effect, mechanism of the substitution reaction; Redox reactions, electron transfer reactions, mechanism of one electron transfer reactions, outer-sphere type reactions, cross reactions and Marcus-Hush theory, inner sphere type reactions.

Recent Advances in Organometallics and Catalysis: Homogenous catalysis- alkene isomerization, alkene, and allyl mechanism, alkene hydrogenation oxidative addition, directing effect and asymmetric catalysis, reversibility, chiral poisoning, heterolytic and homolytic H_2 activation, alkene hydroformylation, hydrocyanation of butadiene, Insertion Reactions, study of Co mechanism reaction, study of mechanism insertion reaction of CO into $\text{CH}_3\text{Mn}(\text{CO})_5$, Coupling reaction, Tsuji-Trost reaction, Mizoroki-Heck reaction, Miyaura-Suzuki coupling, Stille Coupling, Buchwald-Hartwig amination, Surface Organometallics Chemistry, Polymer-Bound organometallic and its applications, alkene metathesis, dimerization, oligomerization and polymerization, types of catalyst, Green-Rooney mechanism, Brookhart catalyst, Grubb's catalyst, SHOP oligomerization, Reppe reaction, Activation of CO, CO_2 and CH activation, Agostic interaction. Alkyls and Aryls of Transition Metals, Compounds of Transition Metal-Carbon Multiple Bonds, Transition Metal π -Complexes, Ziegler-Natta polymerization of olefins, catalytic reactions involving carbon monoxide such as hydrocarbonylation of olefins (oxo reaction), oxopalladation reactions, activation of C-H bond.

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Group Theory and Inorganic spectroscopy: Symmetry elements and Symmetry operations, definitions of group, subgroups, relationship between orders of finite group and its subgroup. Schonflies symbols, representations of groups by matrices (representation for the C_{2v} , C_{3v} , C_{4v} etc groups to be worked out explicitly). Character of a representation. The great orthogonality theorem (without proof) and its importance. Character tables and their use in spectroscopy. Basic Principle of IR spectroscopy. Mode of bonding of ligand with metal ions, Application of resonance Raman spectroscopy particularly for the study of active sites of metalloproteins, Electronic Spectra of transition metal complexes: Selection rules and band width, Band intensities, factors influencing band widths, variation of $10 Dq$, vibrational structure, spin orbit coupling, low symmetry components- Jahn-Teller effect, electronic spectra of octahedral and tetrahedral $d^1 - d^9$ metal ions, calculation of $10 Dq$ and B with and without the use of Tanabe Sugano diagrams, low spin complexes of Mn^{3+} , Mn^{2+} , Fe^{3+} , Co^{3+} , Fe^{2+} , comment on the spectra of second and third transition series, nephelauxetic effect and spectrochemical series, Charge Transfer Spectra: CT Bands, MLCT and LMCT bands, CT bands in $KMnO_4$ and K_2MnO_4 .

NMR Spectroscopy: Theory of NMR spectroscopy, Mechanism of electron shielding and factors contributing to the magnitude of the chemical shift, Spin-spin splitting, Spin-spin coupling mechanism for transmitting nuclear spins, Applications of spin-spin coupling to structure determination, Applications involving the magnitude of coupling constants, Complex spectra obtained when $J \sim \Delta$, Chemical exchange and other factors affecting line width, Effect of chemical exchange on spectra and the evaluation of reaction rates for fast reactions, Consequences of nuclei with quadrupole moments in NMR, Double resonance technique, NMR studies of exchange reactions between ligands and metal ions of fluxional molecules, NMR of

paramagnetic complexes-contact shift, Miscellaneous applications of NMR to inorganic problems. Electron Spin Resonance Spectroscopy: Introduction, Hyperfine splitting in some

simple systems, Hyperfine splittings in various structures, factors affecting the magnitude of the g -values, Zero-field splitting and Kramer's degeneracy, Anisotropy in the hyperfine coupling constant, Nuclear quadrupole interaction, miscellaneous applications to transition metal complexes, Interpretation of spectra for single electron systems (d^1 , d^5 -low spin and d^9 system) and multi-electron systems (d^1 , d^5 -high spin and d^7 -high spin system). Mossbauer Spectroscopy: Basic principles, Recoil energy, Resonance line shifts from change in electronic environment, Quadrupole and Magnetic interactions, Simple spin states ($1/2$, $3/2$), Higher spin states, Spectral parameters and spectrum display. Magnetism: Contributions to magnetic properties, effect of ligand field on spin-orbit coupling, Measurement of magnetic properties, Some applications of magnetic data, Temperature dependence of magnetism.

Organic Chemistry

IUPAC Nomenclature of organic molecules including regio-and stereoisomers.

Principles of Stereochemistry: Configurational and conformational isomerism in acyclic and cyclic compounds; stereogenicity, stereoselectivity, enantioselectivity, diastereoselectivity; Optical activity and

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Chirality, Conformational analysis. Elements of symmetry, Asymmetric synthesis: Chiral auxiliaries, methods of asymmetric induction-reagent and catalyst controlled reactions, determination of enantiomeric and diastereomeric excess, resolution, methods of resolution-optical and kinetic.

Nature of Bonding in Organic Molecules

Delocalized chemical bonding, aromaticity in benzenoid and non-benzenoid compounds, anti-aromaticity, homo-aromaticity, alternant and non-alternant hydrocarbons, Huckel's rule, annulenes, energy level of π -molecular orbitals, annulenes, PMO approach, Bonds weaker than covalent bond, hydrogen bonding, crown ether complexes, cryptands, inclusion compounds, cyclodextrins.

Organic Reactive Intermediates and Reaction Mechanism: Generation, stability and reactivity of carbocations, carbanions, free radicals, carbenes, benzyne and nitrenes. Organic reaction mechanism involving addition, elimination and substitution reactions with electrophilic, nucleophilic or radical species. Energetics, kinetics and the investigation of reaction mechanism, isotope effects, Hard and soft acids and bases. Hammond's postulate, Curtin-Hammett principle, Effect of structure on reactivity-resonance and field effects, steric effect, The Hammett equation and linear free energy relationship, Substituent and reaction constants, Taft equation.

Common Name Reactions and Rearrangements

General mechanistic considerations- nature of migration, migratory aptitude, memory effects. A detailed study of the following name reaction and rearrangements: Wittig reaction, Diels-Alder, various condensation reactions, Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and

Stobbe reactions, Grignard reaction, Hydroboration. Michael addition and Robinson annelation, Sharpless asymmetric epoxidation. Shapiro reaction etc. Rearrangement reactions: Pinacol-pinacolone, Wagner-Meerwein, Demjanov, Benzil-Benzilic acid, Favorskii, Arndt-Eistert synthesis, Neber, Beckmann, Hofman, Curtius, Schmidt, Baeyer-Villiger, Claisen and Cope rearrangements etc. and their applications in organic synthesis.

Concepts in Organic Synthesis: Retrosynthesis, disconnection, synthons, linear and convergent synthesis, umpolung of reactivity and protecting groups, Functional group interconversion including oxidations and reductions; common catalysts and reagents (organic, inorganic, organometallic and enzymatic). Chemo, regio and stereoselective transformations.

Pericyclic Reactions – Principles and applications of electrocyclic reaction, cycloaddition, sigmatropic rearrangements and other related concerted reactions. Woodward-Hoffmann correlation diagrams; FMO and PMO approach; 2+2 addition of ketenes and 1,3 dipolar cycloadditions and ene reaction.

Photochemistry: Introduction and basic principles, types of photochemical reaction, Photochemistry of carbonyl compounds, alkene, dienes, aromatic compounds, photo substitution reactions. photo rearrangements, photo reduction and photo oxidation, photochemistry in nature and applied photochemistry.

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Organometallic Reagents: Principle, preparations, properties and applications of the following in organic synthesis with mechanistic details: Group I and II metal organic compounds: Li, Mg, Zn and Ce compounds; Transition metals: Cu, Fe, Rh, Ru, Pd, Pt and Ti compounds and other elements Si and B and metallocenes.

Heterocyclic Chemistry: Nomenclature of heterocycles, Synthesis and reactivity of Small ring heterocycles compounds: Three-membered, four-membered, five membered heterocycles, Six-membered heterocycles, Seven and large-membered heterocycles containing one or two heteroatoms (O, N, S), Aromatic heterocycles, Non-aromatic heterocycles, synthesis and reactions, Heterocyclic ring system containing P, As, Sb and B, their nomenclature, synthesis and characteristics of 5-and 6-membered ring systems.

Chemistry of Natural Products: Carbohydrates, amino acids, lipids, proteins and peptides, fatty acids, nucleic acids. Classification, nomenclature, occurrence, isolation, general methods of structure determination terpenes, carotenoids, steroids and alkaloids, plant pigments, porphyrins. Synthesis of important natural products: Citral, Geraniol, Farnesol, Phytol, Abietic acid and β -Carotene, Juvabione, Ephedrine, Nicotine, Atropine, Quinine and Morphine, Cholesterol, Testosterone, Progesterone, Hemoglobin and Chlorophyll, Cortisone, Vitamin-D. Biosynthesis of of terpenoids and alkaloids.

Medicinal Chemistry: Concept of drug design, structure-activity relationship (SAR), Quantitative structure activity relationship (QSAR), pharmacokinetics, pharmacodynamics, antineoplastic agents, cardiovascular drugs, Local anti-infective drugs, psychoactive drugs, antibiotics.

Structure Determination of Organic Compounds: Structure determination of organic compounds by IR, UV-Vis, ^1H & ^{13}C NMR, DEPT, Mass and other spectroscopic techniques. Two dimension NMR spectroscopy-COSY, NOESY.

Physical Chemistry

Quantum mechanics: Schrodinger wave equations, operators, postulates, particle-in-a-box, harmonic oscillator, rigid and non-rigid rotor, angular momentum, Schrodinger equations for hydrogen like atoms, shapes of atomic orbitals; orbital and spin angular momenta; tunneling, variational principle; perturbation theory up to second order in energy; applications; atomic spectra and selection Rules, term symbols; many-electron systems and antisymmetry principle, variational method, Hartree-Fock Self-consistent Field Method, The Born-Oppenheimer Approximation, elementary concepts of MO and VB theories; Huckel theory for conjugated π -electron systems.

Group theory: Symmetry elements and symmetry operations, identification of point groups of molecules, character tables, selection rules

Spectroscopy: Rotational and vibrational spectra of diatomic molecules; Fourier Transforms, electronic spectra, Franck-Condon Principle; IR and Raman activities - selection rules; basic principles of nuclear

magnetic resonance The Chemical Shift, Internuclear Spin-Spin Coupling, Spin-Spin Splitting in AX and AB Systems, Nuclear Magnetic Relaxation, Two-Dimensional NMR, electron spin resonance.

Chemical thermodynamics: State and path functions and their applications, Law of Thermodynamics, Work and Heat, Internal Energy, Exact and Inexact Differentials, Various Kinds of Work, thermodynamic description of various types of processes, Enthalpy and Change of State at Constant Pressure, entropy as a state function, entropy changes in reversible processes and irreversible processes, entropy of mixing ideal gases, entropy and statistical probability, heat engines, Gibbs energy, fugacity and activity, chemical potential, partial molar properties, Gibbs-Duhem Equation, Maxwell Relations, thermodynamics of ideal and non-ideal gases, and solutions, Equilibrium Constants, Effect of Temperature on the Equilibrium Constant, Le Chatelier principle, Degrees of Freedom and the Phase Rule, The Clausius-Clapeyron Equation, elementary description of phase transitions;

Electrochemistry: Standard electrode potentials, Nernst equation, redox systems, electrochemical cells; Determination of pH, Fuel cell, membrane potential. Debye-Huckel

theory; electrolytic conductance – Kohlrausch's law and its applications; ionic equilibria; conductometric and potentiometric titrations.

Statistical thermodynamics: Boltzmann distribution; kinetic theory of gases; translational partition functions, rotational partition functions, vibrational partition functions, electronic partition functions and their relation to thermodynamic quantities. equipartition,

Chemical kinetics: Empirical rate laws and temperature dependence; complex reactions; steady state approximation; Mechanisms of Chemical Reactions; collision and transition state theories of rate constants; unimolecular reactions; bimolecular Reactions, Unbranched Chain Reactions, Branched Chain Reactions, enzyme kinetics; kinetic salt effects; homogeneous catalysis; photochemical reactions.

Colloids and surface dynamics: Stability and properties of colloids; Physisorption and Chemisorption, isotherms and surface area; Theory of Surface Reactions, Heterogeneous Catalysis

Solid state: Classification of crystal structures; crystal planes, Bragg's law, cubic lattices, scattering of X-rays from a unit cell, packing in crystals, band structure of solids.

Polymer chemistry: Size and shape of macromolecules, molar masses and experimental determination, kinetics of polymerization.

Data analysis: Mean and standard deviation; absolute and relative errors; linear regression; covariance and correlation coefficient.

Signature of Chairman Board of Studies