

Chemistry Syllabus for PG Entrance

- 1. Redox Reactions and precipitation reactions:** Ion-electron method of balancing equation of redox reaction. Elementary idea on standard redox potentials with sign conventions, Nernst equation (without derivation). Influence of complex formation, precipitation and change of pH on redox potentials; formal potential. Feasibility of a redox titration, redox potential at the equivalence point, redox indicators. Redox potential diagram (Latimer and Frost diagrams) of common elements and their applications. Disproportionation and comproportionation reactions (typical examples). Theoretical principles involved in analysis of cations and anions and Solubility product principle, common ion effect and their applications to the precipitation and separation of common metallic ions as hydroxides, sulfides, phosphates, carbonates, sulfates and halides. Interfering anions (fluoride, borate, oxalate and phosphate) and need to remove them after group II.
- 2. Molecular Orbital Theory:** Necessity of Molecular Orbital Theory (MOT), features of MOT, formation of molecular orbitals (MO's) by LCAO principle, rules of LCAO combination, different types of combination of Atomic orbital (AO's): σ , π and δ MOs, Non-bonding combination of orbitals (formation of NBMO), M.O. energy level diagram for homonuclear and heteronuclear molecules, bond order and existence of molecule from bond order.
- 3. Ionic Solids:** Crystalline and amorphous solids, crystal structures, simple cubic, body centered cubic and face centered cubic, properties of ionic solids, packing arrangements of anions in an ionic solids, voids in crystal structure, tetrahedral and octahedral, ionic radius, radius ratio effect, Lattice energy, Born-Landé equation, Schottky and Frenkel defect.
- 4. Bioinorganic Chemistry Elements of life:** essential and beneficial elements, major, trace and ultratrace elements. Basic chemical reactions in the biological systems and the role of metal ions (specially Na^+ , K^+ , Mg^{2+} , Ca^{2+} , $\text{Fe}^{3+/2+}$, Cu^{2+} , and Zn^{2+}). Metal ion transport across biological membrane Na^+/K^+ -ion pump. Dioxygen molecule in life. Dioxygen management proteins: Haemoglobin, Myoglobin, Hemocyanine and Hemerythrin. Electron transfer proteins: Cytochromes and Ferredoxins. Hydrolytic enzymes: carbonate bicarbonate buffering system and carbonic anhydrase and carboxyanhydrase A. Biological nitrogen fixation, Photosynthesis: Photosystem-I and Photosystem-II. Toxic metal ions and their effects, chelation therapy, Pt and Au complexes as drugs, metal dependent diseases.
- 5. Organometallic Chemistry:** Definition and classification of organometallic compounds on the basis of bond type. Concept of hapticity of organic ligands. 18-electron and 16-electron rules (pictorial MO approach). Applications of 18-electron rule to metal carbonyls, nitrosyls, cyanides. General methods of preparation of mono and binuclear carbonyls of 3d series. Structures of mononuclear and binuclear carbonyls. π -acceptor behaviour of CO, synergic effect and use of IR data to explain extent of back bonding. Zeise's salt: Preparation, structure, evidences of synergic effect. Ferrocene: Preparation and reactions (acetylation, alkylation, metallation,

Mannich Condensation). Reactions of organometallic complexes: substitution, oxidative addition, reductive elimination and insertion reactions.

Catalysis by Organometallic Compounds

Study of the following industrial processes

1. Alkene hydrogenation (Wilkinson's Catalyst) 2. Hydroformylation 3. Wacker Process 4. Synthetic gasoline (Fischer Tropsch reaction) 5. Ziegler-Natta catalysis for olefin polymerization.

6. Chemistry of Nano Materials including Graphene. Syntheses, characterization and applications. Plasmonic materials, Semiconductor, Band gap, Types of Semiconductors, Colour Centres.
7. **Magnetism and Colour:** Orbital and spin magnetic moments, spin only moments of d^n ions and their correlation with effective magnetic moments, including orbital contribution; quenching of magnetic moment: super exchange and antiferromagnetic interactions (elementary idea with examples only); d-d transitions; L-S coupling; qualitative Orgel diagrams for $3d^1$ to $3d^9$ ions. Racah parameter. Selection rules for electronic spectral transitions; spectrochemical series of ligands; charge transfer spectra (elementary idea).
8. **Radioactivity:** Nuclear stability and nuclear binding energy. Nuclear forces: meson exchange theory. Nuclear models (elementary idea): Concept of nuclear quantum number, magic numbers. Nuclear Reactions: Artificial radioactivity, transmutation of elements, fission, fusion and spallation. Nuclear energy and power generation. Separation and uses of isotopes. Radio chemical methods: principles of determination of age of rocks and minerals, radio carbon dating, hazards of radiation and safety measures.
9. **Inorganic Polymers:** Types of inorganic polymers, comparison with organic polymers, synthesis, structural aspects and applications of silicones and siloxanes. Borazines, silicates and phosphazenes.
10. **Coordination Chemistry:** Coordinate bonding: double and complex salts. Werner's theory of coordination complexes, Classification of ligands, Ambidentate ligands, chelates, Coordination numbers, IUPAC nomenclature of coordination complexes (up to two metal centers), Isomerism in coordination compounds, constitutional and stereo isomerism, Geometrical and optical isomerism in square planar and octahedral complexes. VB description and its limitations. Elementary Crystal Field Theory: splitting of d^n configurations in octahedral, square planar and tetrahedral fields, crystal field stabilization energy (CFSE) in weak and strong fields; pairing energy. Spectrochemical series. Jahn- Teller distortion. Octahedral site stabilization energy (OSSE). Metal-ligand bonding (MO concept, elementary idea), sigma- and pi-bonding in octahedral complexes (qualitative pictorial approach) and their effects on the oxidation states of transitional metals (examples).
11. **Relative and absolute configuration:** D/L and R/S descriptors; *erythro/threo*; *pref/parf* and *meso* nomenclature of compounds; *syn/anti* nomenclatures for aldols; E/Z descriptors for C=C, conjugated diene, triene, C=N and N=N systems; combination of R/S- and E/Z- isomerisms.

12. Optical activity of chiral compounds: optical rotation, specific rotation and molar rotation; racemic compounds, racemisation (through cationic, anionic, radical intermediates and through reversible formation of stable achiral intermediates); resolution of acids, bases and alcohols via diastereomeric salt formation; optical purity and enantiomeric excess; invertomerism of chiral trialkylamines.

13. Carbonyl and Related Compounds: *Addition to C=O:* structure, reactivity and preparation of carbonyl compounds; mechanism (with evidence), reactivity, equilibrium and kinetic control; Burgi-Dunitz trajectory in nucleophilic additions; formation of hydrates, cyano hydrins and bisulphite adduct; nucleophilic addition-elimination reactions with alcohols, thiols and nitrogen-based nucleophiles; reactions: benzoin condensation, Cannizzaro and Tischenko reactions, reactions with ylides: Wittig and Corey-Chaykovsky reaction; Rupe rearrangement, oxidations and reductions: Clemmensen, Wolff-Kishner, LiAlH_4 , NaBH_4 , MPV, Oppenauer, Bouveault-Blanc, acyloin condensation; oxidation of alcohols with PDC and PCC; periodic acid and lead tetraacetate oxidation of 1,2-diols.

Exploitation of acidity of α -H of C=O: formation of enols and enolates; kinetic and thermodynamic enolates; reactions (mechanism with evidence): halogenation of carbonyl compounds under acidic and basic conditions, Hell-Volhard-Zelinsky (H. V. Z.) reaction, nitrosation, SeO_2 (Riley) oxidation; condensations (mechanism with evidence): Aldol, Tollens', Knoevenagel, Claisen-Schmidt, Claisen ester including Dieckmann, Stobbe; Mannich reaction, Perkin reaction, Favorskii rearrangement; alkylation of active methylene compounds; preparation and synthetic applications of diethyl malonate and ethyl acetoacetate; specific enol equivalents (lithium enolates, enamines, aza-enolates and silyl enol ethers) in connection with alkylation, acylation and aldol type reaction.

Nucleophilic addition to α,β -unsaturated carbonyl system: general principle and mechanism (with evidence); direct and conjugate addition, addition of enolates (Michael reaction), Stetter reaction, Robinson annulation.

Substitution at sp^2 carbon (C=O system): mechanism (with evidence): $B_{AC}2$, $A_{AC}2$, $A_{AC}1$, $A_{AL}1$ (in connection to acid and ester); acid derivatives: amides, anhydrides & acyl halides (formation and hydrolysis including comparison).

Elementary ideas of Green Chemistry: Twelve (12) principles of green chemistry; planning of green synthesis; common organic reactions and their counterparts: reactions: Aldol, Friedel-Crafts, Michael, Knoevenagel, Cannizzaro, benzoin condensation and Dieckmann condensation.

14. Heterocyclic compounds: 5- and 6-membered rings with one heteroatom; reactivity, orientation and important reactions (with mechanism) of furan, pyrrole, thiophene and pyridine; synthesis (including retrosynthetic approach and mechanistic details): pyrrole: Knorr synthesis, Paal-Knorr synthesis, Hantzsch; furan: Paal-Knorr synthesis, Feist-Benary synthesis and its variation; thiophenes: Paal-Knorr synthesis, Hinsberg synthesis; pyridine: Hantzsch synthesis; **benzo-fused 5- and 6-membered rings with one heteroatom:** reactivity, orientation and important reactions (with mechanistic details) of indole, quinoline and isoquinoline; synthesis (including retrosynthetic

approach and mechanistic details): indole: Fischer, Madelung and Reissert; quinoline: Skraup, Doebner- Miller, Friedlander; isoquinoline: Bischler-Napieralski synthesis.

15. Cyclic Stereochemistry: Alicyclic compounds: concept of I-strain; conformational analysis: cyclohexane, mono and disubstituted cyclohexane; symmetry properties and optical activity; topomerisation; ring-size and ease of cyclisation; conformation & reactivity in cyclohexane system: consideration of steric and stereoelectronic requirements; elimination (E2, E1), nucleophilic substitution (SN1, SN2, SNi, NGP), merged substitution-elimination; rearrangements; oxidation of cyclohexanol, esterification, saponification, lactonisation, epoxidation, pyrolytic syn elimination and fragmentation reactions

16. Pericyclic reactions: Mechanism, stereochemistry, regioselectivity in case of

- (i) Electrocyclic reactions: FMO approach involving 4π - and 6π -electrons (thermal and photochemical) and corresponding cycloreversion reactions. (ii) Cycloaddition reactions: FMO approach, Diels-Alder reaction, photochemical cycloadditions. (iii) Sigmatropic reactions: FMO approach, sigmatropic shifts and their order; [1,3]- and [1,5]-H shifts and [3,3]-shifts with reference to Claisen and Cope rearrangements.

17. Nucleic acids: pyrimidine and purine bases; nucleosides and nucleotides corresponding to DNA and RNA; mechanism for acid catalysed hydrolysis of nucleosides (both pyrimidine and purine types); comparison of alkaline hydrolysis of DNA and RNA; elementary idea of double helical structure of DNA (Watson-Crick model); complimentary base-pairing in DNA.

18. Dyes: Classification, Colour and constitution; Mordant and Vat Dyes; Chemistry of dyeing; Synthesis and applications of: Azo dyes – Methyl Orange and Congo Red (mechanism of Diazo Coupling); Triphenyl Methane Dyes - Malachite Green, Rosaniline and Crystal Violet; Phthalein Dyes – Phenolphthalein and Fluorescein; Natural dyes –structure elucidation and synthesis of Alizarin and Indigotin; Edible Dyes with examples.

19. Rearrangements: Mechanism with evidence and stereochemical features for the following:

Rearrangement to electron-deficient carbon, Rearrangement to electron-deficient nitrogen, Rearrangement to electron-deficient oxygen and Rearrangement reactions by green approach.

20. **Retrosynthetic** analysis including ring synthesis, asymmetry synthesis.

21. Principles and applications of **IR**, **UV** and **¹H-NMR** spectroscopy for identification of simple organic molecules.

22. **Chemical Thermodynamics:** Zeroth and 1st law of Thermodynamics: Intensive and extensive variables; state and path functions; isolated, closed and open systems; zeroth law of thermodynamics; Concept of heat, work, internal energy and statement of first law; enthalpy, H ; relation between heat capacities, calculations of q , w , U and H for reversible, irreversible and free expansion of gases (ideal and van der Waals) under isothermal and adiabatic conditions; Joule's experiment and its consequence.

23. **Thermochemistry:** Standard states; Heats of reaction; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications; Laws of

thermochemistry; bond energy, bond dissociation energy and resonance energy from thermochemical data, Kirchhoff's equations and effect of pressure on enthalpy of reactions; Adiabatic flame temperature; explosion temperature

24. **Second Law:** Need for a Second law; statement of the second law of thermodynamics; Concept of heat reservoirs and heat engines; Carnot cycle; Physical concept of Entropy; Carnot engine and refrigerator; Kelvin – Planck and Clausius statements and equivalence of the two statements with entropic formulation; Carnot's theorem; Values of $\delta Q/T$ and Clausius inequality; Entropy change of systems and surroundings for various processes and transformations; Entropy and unavailable work; Auxiliary state functions (G and A) and their variation with T, P and V. Criteria for spontaneity and equilibrium. Thermodynamic relations: Maxwell's relations; Gibbs- Helmholtz equation, Joule-Thomson experiment and its consequences; inversion temperature; Joule-Thomson coefficient for a van der Waals gas; General heat capacity relations.
25. **Partial properties and Chemical potential:** Chemical potential and activity, partial molar quantities, relation between Chemical potential and Gibb's free energy and other thermodynamic state functions; variation of Chemical potential (μ) with temperature and pressure; Gibbs-Duhem equation; fugacity and fugacity coefficient; Variation of thermodynamic functions for systems with variable composition; Equations of states for these systems, Change in G, S H and V during mixing for binary solutions.
26. **Chemical kinetics:** Rate law, order and molecularity: Introduction of rate law, Extent of reaction; rate constants, order; Forms of rates of First, second and nth order reactions; Pseudo first order reactions (example using acid catalyzed hydrolysis of methyl acetate); Determination of order of a reaction by half-life and differential method; Opposing reactions, consecutive reactions and parallel reactions (with explanation of kinetic and thermodynamic control of products; all steps first order)
27. **Role of T and theories of reaction rate:** Temperature dependence of rate constant; Arrhenius equation, energy of activation; Rate-determining step and steady-state approximation – explanation with suitable examples; Collision theory; Lindemann theory of unimolecular reaction; outline of Transition State theory (classical treatment)
28. Homogeneous catalysis: Homogeneous catalysis with reference to acid-base catalysis; Primary kinetic salt effect; Enzyme catalysis; Michaelis-Menten equation, Lineweaver-Burk plot, turn-over number Autocatalysis; periodic reactions.
29. **Electromotive Force:** Quantitative aspects of Faraday's laws of electrolysis, rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry; Chemical cells, reversible and irreversible cells with examples; Electromotive force of a cell and its measurement, Nernst equation; Standard electrode (reduction) potential and its application to different kinds of half-cells. Application of EMF measurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass and $\text{SbO/Sb}_2\text{O}_3$ electrodes Concentration cells with and without transference, liquid junction potential; determination of activity

coefficients and transference numbers; Qualitative discussion of potentiometric titrations (acidbase, redox, precipitation)

30. **Quantum Chemistry:** Beginning of Quantum Mechanics: Wave-particle duality, light as particles: photoelectric and Compton effects; electrons as waves and the de Broglie hypothesis; Uncertainty relations (without proof) Wave function: Schrodinger time-independent equation; nature of the equation, acceptability conditions imposed on the wave functions and probability interpretations of wave function Concept of Operators: Elementary concepts of operators, eigen-functions and eigenvalues; Linear operators; Commutation of operators, commutator and uncertainty relation; Expectation value; Hermitian operator; Postulates of Quantum Mechanics Particle in a box: Setting up of Schrodinger equation for one-dimensional box and its solution; Comparison with free particle eigenfunctions and eigenvalues. Properties of PB wave functions (normalisation, orthogonality, probability distribution); Expectation values of x , x^2 , p_x and p_x^2 and their significance in relation to the uncertainty principle; Extension of the problem to two and three dimensions and the concept of degenerate energy levels Simple Harmonic Oscillator: setting up of the Schrodinger stationary equation, energy expression (without derivation), expression of wave function for $n = 0$ and $n = 1$ (without derivation) and their characteristic features
31. **Angular momentum:** Commutation rules, quantization of square of total angular momentum and z component; Rigid rotator model of rotation of diatomic molecule; Schrödinger equation, transformation to spherical polar coordinates; Separation of variables. Spherical harmonics; Discussion of solution
32. **Qualitative treatment of hydrogen atom and hydrogen-like ions:** Setting up of Schrödinger equation in spherical polar coordinates, radial part, quantization of energy (only final energy expression); Average and most probable distances of electron from nucleus; Setting up of Schrödinger equation for many-electron atoms (He, Li)
33. **Molecular Spectroscopy:** 1. Interaction of electromagnetic radiation with molecules and various types of spectra; Born-Oppenheimer approximation 2. **Rotation spectroscopy:** Selection rules, intensities of spectral lines, determination of bond lengths of diatomic and linear triatomic molecules, isotopic substitution 3. **Vibrational spectroscopy:** Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies; Diatomic vibrating rotator, P, Q, R branches, 4. **Raman spectroscopy:** Qualitative treatment of Rotational Raman effect; Effect of nuclear spin, Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion 5. **Nuclear Magnetic Resonance (NMR) spectroscopy:** Principles of NMR spectroscopy, Larmor precession, chemical shift and low resolution spectra, different scales, spin-spin coupling and high resolution spectra, interpretation of PMR spectra of organic molecules 6. **Electron Spin Resonance (ESR) spectroscopy:** Its principle, hyperfine structure, ESR of simple radicals.