

Syllabus for GAT-2021 - Chemical Sciences

For Admission to M.Sc. Chemistry (Analytical/Organic)

SECTION- A

Inorganic Chemistry

Atomic Structure: Review of: Bohr's theory and its limitations, dual behaviour of matter and radiation, de Broglie's relation, Heisenberg Uncertainty principle. What is Quantum mechanics? Time independent Schrodinger equation and meaning of various terms in it. Significance of ψ and ψ^2 , Schrödinger equation for hydrogen atom. graphical representation of $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ orbitals. Significance of quantum numbers, orbital angular momentum and quantum numbers ml and ms . Shapes of s , p and d atomic orbitals, nodal planes. Rules for filling electrons in various orbitals, Electronic configurations of the atoms. Stability of half-filled and completely filled orbitals, concept of exchange energy. Relative energies of atomic orbitals, Anomalous electronic configurations.

Chemical Bonding and Molecular Structure

Ionic Bonding: General characteristics of ionic bonding. Energy considerations in ionic bonding, lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds. Statement of Born-Landé equation for calculation of lattice energy, Born-Haber cycle and its applications, polarizing power and polarizability. Fajan's rules, ionic character in covalent compounds, bond moment, dipole moment and percentage ionic character. *Covalent bonding:* VB Approach: Shapes of some inorganic molecules and ions on the basis of VSEPR and hybridization with suitable examples of linear, trigonal planar, square planar, tetrahedral, trigonal bipyramidal and octahedral arrangements. MO Approach: Rules for the LCAO method, bonding and antibonding MOs and their characteristics for $s-s$, $s-p$ and $p-p$ combinations of atomic orbitals, nonbonding combination of orbitals, MO treatment of homonuclear diatomic molecules of 1st and 2nd periods (including idea of $s-p$ mixing) and heteronuclear diatomic molecules such as CO, NO and NO^+ .

Transition Elements

General group trends with special reference to electronic configuration, variable valency, colour, magnetic and catalytic properties, ability to form complexes and stability of various oxidation states (Latimer diagrams) for Mn, Fe and Cu. Lanthanoids and actinoids: Electronic configurations, oxidation states, colour, magnetic properties, lanthanide contraction, separation of lanthanides by ion exchange method only.

Coordination Chemistry

Valence Bond Theory (VBT): Inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu(Coordination numbers 4 and 6). Structural and stereoisomerism in complexes with coordination numbers 4 and 6. Drawbacks of VBT. IUPAC system of nomenclature.

Crystal Field Theory

Crystal field effect, octahedral symmetry. Crystal field stabilization energy (CFSE), Crystal field effects for weak and strong fields. Tetrahedral symmetry.

SECTION- B

Organic Chemistry

Fundamentals of Organic Chemistry: Physical Effects, Electronic Displacements: Inductive Effect, Electromeric Effect, Resonance and Hyperconjugation. Cleavage of Bonds: Homolysis and Heterolysis. Structure, shape and reactivity of organic molecules: Nucleophiles and electrophiles. Reactive Intermediates: Carbocations, Carbanions and free radicals. Strength of organic acids and bases: Comparative study with emphasis on factors affecting pK values. Aromaticity: Benzenoids and Hückel's rule.

Stereochemistry: Conformations with respect to ethane, butane and cyclohexane. Interconversion of Wedge Formula, Newmann, Sawhorse and Fischer representations. Concept of chirality (upto two carbon atoms). Configuration: Geometrical and Optical isomerism; Enantiomerism, Diastereomerism and Meso compounds). Threo and erythro; D and L; *cis* - *trans* nomenclature; CIP Rules: R / S (for upto 2 chiral carbon atoms) and E / Z Nomenclature (for upto two C=C systems).

Alkanes: (Upto 5 Carbons). *Preparation:* Catalytic hydrogenation, Wurtz reaction, Kolbe's synthesis, from Grignard reagent. *Reactions:* Free radical Substitution: Halogenation.

Alkenes: (Upto 5 Carbons) *Preparation:* Elimination reactions: Dehydration of alkenes and dehydrohalogenation of alkyl halides (Saytzeff's rule); cis alkenes (Partial catalytic hydrogenation) and trans alkenes (Birch reduction). Addition of HX (Markownikoff's and anti-Markownikoff's addition). **Alkynes:** (Upto 5 Carbons) *Preparation:* Acetylene from CaC₂ and conversion into higher alkynes; by dehalogenation of tetra halides and dehydrohalogenation of vicinal-dihalides.

Aromatic hydrocarbons: *Preparation* (Case benzene): from phenol, by decarboxylation, from acetylene, from benzenesulphonic acid. *Reactions:* (Case benzene): Electrophilic substitution: nitration, halogenation and sulphonation. Friedel-Craft's reaction (alkylation and acylation) (upto 4 carbons on benzene).

Alcohols: *Preparation:* Preparation of 1°, 2° and 3° alcohols: using Grignard reagent, Esterhydrolysis, Reduction of aldehydes, ketones, carboxylic acid and esters. *Reactions:* With sodium, HX (Lucas test), esterification, oxidation (with PCC, alk. KMnO₄, acidic dichromate, conc. HNO₃).

Aldehydes and ketones (aliphatic and aromatic): (Formaldehyde, acetaldehyde, acetone and benzaldehyde) *Preparation:* from acid chlorides and from nitriles. *Reactions – Reaction with HCN, ROH, NaHSO₃, NH₂-G derivatives. Iodoform test. Aldol Condensation, Cannizzaro's reaction, Wittig reaction, Benzoin condensation. Clemensen reduction.*

Carboxylic acids and their derivatives: Carboxylic acids (aliphatic and aromatic) *Preparation:* Acidic and Alkaline hydrolysis of esters.

Reactions: Hell – Vohlard - Zelinsky Reaction.

SECTION- C

Physical Chemistry

Chemical Energetics

Review of thermodynamics and the Laws of Thermodynamics. Important principles and definitions of thermochemistry. Concept of standard state and standard enthalpies of formations, integral and differential enthalpies of solution and dilution. Calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data. Variation of enthalpy of a reaction with temperature – Kirchhoff's equation. Statement of Third Law of thermodynamics .

Ionic Equilibria:

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions. Solubility and solubility product of sparingly soluble salts

Solutions

Thermodynamics of ideal solutions: Ideal solutions and Raoult's law, deviations from Raoult's law – non-ideal solutions. Vapour pressure-composition and temperature-composition curves of ideal and non-ideal solutions. Distillation of solutions. Lever rule. Azeotropes.

Electrochemistry

Reversible and irreversible cells. Concept of EMF of a cell. Measurement of EMF of a cell. Nernst equation and its importance. Types of electrodes. Standard electrode potential. Electrochemical series. Thermodynamics of a reversible cell, calculation of thermodynamic properties: G , H and S from EMF data. Calculation of equilibrium constant from EMF data. Concentration cells with transference and without transference. Liquid junction potential and salt bridge.

Kinetic Theory of Gases

Postulates of Kinetic Theory of Gases and derivation of the kinetic gas equation. Deviation of real gases from ideal behaviour, compressibility factor, causes of deviation. van der Waals equation of state for real gases. Boyle temperature (derivation not required). Critical phenomena, critical constants and their calculation from van der Waals equation. Maxwell Boltzmann distribution laws of molecular velocities and molecular energies (graphic representation – derivation not required) and their importance.

Chemical Kinetics

The concept of reaction rates. Effect of temperature, pressure, catalyst and other factors on reaction rates. Order and molecularity of a reaction. Derivation of integrated rate equations for zero, first and second order reactions (both for equal and unequal concentrations of reactants). Half-life of a reaction. General methods for determination of order of a reaction. Concept of activation energy and its calculation from Arrhenius equation.