

SYLLABUS FOR GSAT-2019
FOR ADMISSION TO M.Sc. Chemistry (Analytical/Organic)
(TEST CODE NO: 103)

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 m_l and m_s . 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 (3d series)

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 (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).

Aliphatic Hydrocarbons

Functional group approach for the following reactions (preparations & reactions) to be studied.

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). *Reactions:* *cis*-addition (alk. KMnO_4) and *trans*-addition (bromine), Addition of HX (Markownikoff's and anti-Markownikoff's addition), Hydration, Ozonolysis.

Alkynes: (Upto 5 Carbons) *Preparation:* Acetylene from CaC_2 and conversion into higher alkynes; by dehalogenation of tetra halides and dehydrohalogenation of vicinal-dihalides. *Reactions:* formation of metal acetylides, addition of bromine and alkaline KMnO_4 , ozonolysis and oxidation with hot alk. KMnO_4 .

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). Side chain oxidation of alkyl benzenes (upto 4 carbons on benzene).

Alkyl Halides

Preparation: from alkenes and alcohols. *Reactions:* hydrolysis, nitrite & nitro formation, nitrile & isonitrile formation. Williamson's ether synthesis: Elimination vs substitution.

Aryl Halides *Preparation:* (Chloro, bromo and iodo-benzene case): from phenol, Sandmeyer &

Gattermann reactions. *Reactions (Chlorobenzene)*: Aromatic nucleophilic substitution (replacement by –OH group) and effect of nitro substituent. Benzyne Mechanism: KNH_2/NH_3 (or $\text{NaNH}_2/\text{NH}_3$).

Alcohols: *Preparation*: Preparation of 1°, 2° and 3° alcohols: using Grignard reagent, Ester hydrolysis, Reduction of aldehydes, ketones, carboxylic acid and esters. *Reactions*: With sodium, HX (Lucas test), esterification, oxidation (with PCC, alk. KMnO_4 , acidic dichromate, conc. HNO_3). Oppeneauer oxidation *Diols*: (Upto 6 Carbons) oxidation of diols. Pinacol-Pinacolone rearrangement.

Phenols: (Phenol case) *Preparation*: Cumene hydroperoxide method, from diazonium salts. *Reactions*: Electrophilic substitution: Nitration, halogenation and sulphonation. Reimer-Tiemann Reaction, Gattermann-Koch Reaction, Houben–Hoesch Condensation, Schotten – Baumann Reaction.

Ethers (aliphatic and aromatic): Cleavage of ethers with HI.

Aldehydes and ketones (aliphatic and aromatic): (Formaldehyde, acetaldehyde, acetone and benzaldehyde) *Preparation*: from acid chlorides and from nitriles. *Reactions* – Reaction with HCN, ROH, NaHSO_3 , $\text{NH}_2\text{-G}$ derivatives. Iodoform test. Aldol Condensation, Cannizzaro's reaction, Wittig reaction, Benzoin condensation. Clemensen reduction and Wolff Kishner reduction. Meerwein-Ponndorf Verley reduction.

Carboxylic acids and their derivatives

Carboxylic acids (aliphatic and aromatic) *Preparation*: Acidic and Alkaline hydrolysis of esters. *Reactions*: Hell – Vohlard - Zelinsky Reaction.

Carboxylic acid derivatives (aliphatic): (Upto 5 carbons)

Preparation: Acid chlorides, Anhydrides, Esters and Amides from acids and their interconversion. *Reactions*: Comparative study of nucleophilicity of acyl derivatives. Reformatsky Reaction, Perkin condensation.

Amines and Diazonium Salts

Amines (Aliphatic and Aromatic): (Upto 5 carbons) *Preparation*: from alkyl halides, Gabriel's Phthalimide synthesis, Hofmann Bromamide reaction.

Reactions: Hofmann vs. Saytzeff elimination, Carbylamine test, Hinsberg test, with HNO_2 , Schotten – Baumann Reaction. Electrophilic substitution (case aniline): nitration, bromination, sulphonation.

Diazonium salts: *Preparation* from aromatic amines *Reactions*: conversion to benzene, phenol, dyes.

Amino Acids, Peptides and Proteins:

Preparation of Amino Acids: Strecker synthesis using Gabriel's phthalimide synthesis. Zwitterion, Isoelectric point and Electrophoresis. *Reactions of Amino acids*: ester of –COOH

group, acetylation of $-\text{NH}_2$ group, complexation with Cu^{2+} ions, ninhydrin test. Overview of Primary, Secondary, Tertiary and Quaternary Structure of proteins.

Determination of Primary structure of Peptides by degradation Edmann degradation (Nterminal) and C-terminal (thiohydantoin and with carboxypeptidase enzyme). Synthesis of simple peptides (upto dipeptides) by N-protection (t-butyloxycarbonyl and phthaloyl) & activating groups and Merrifield solid-phase synthesis.

Carbohydrates: Classification, and General Properties, Glucose and Fructose (open chain and cyclic structure), Determination of configuration of monosaccharides, absolute configuration of Glucose and Fructose, Mutarotation, ascending and descending in monosaccharides. Structure of disaccharides (sucrose, cellobiose, maltose, lactose) and polysaccharides (starch and cellulose) excluding their structure elucidation.

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 – Kirchoff's equation. Statement of Third Law of thermodynamics .

Chemical Equilibrium:

Free energy change in a chemical reaction. Thermodynamic derivation of the law of chemical equilibrium. Le Chatelier's principle. Relationship between K_p , and K_c

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.

Phase Equilibrium

Phases, components and degrees of freedom of a system, criteria of phase equilibrium. Gibbs Phase Rule and its thermodynamic derivation. Derivation of Clausius – Clapeyron equation and its importance in phase equilibria. Phase diagrams of one-component systems (water) and two component systems involving eutectics, congruent and incongruent melting points (lead-silver only).

Conductance

Conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Kohlrausch law of independent migration of ions. Transference number and its experimental determination using Hittorf and Moving boundary methods. Ionic mobility. Applications of conductance measurements: determination of degree of ionization of weak

electrolyte, solubility and solubility products of sparingly soluble salts, ionic product of water, hydrolysis constant of a salt. Conductometric titrations (only acid-base).

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.

Temperature dependence of these distributions. Most probable, average and root mean square velocities (no derivation). Collision cross section, collision number, collision frequency, collision diameter and mean free path of molecules. Viscosity of gases and effect of temperature and pressure on coefficient of viscosity (qualitative treatment only).

Liquids

Surface tension and its determination using stalagmometer. Viscosity of a liquid and determination of coefficient of viscosity using Ostwald viscometer. Effect of temperature on surface tension and coefficient of viscosity of a liquid (qualitative treatment only).

Solids

Forms of solids. Symmetry elements, unit cells, crystal systems, Bravais lattice types. Miller indices. X-Ray diffraction by crystals, Bragg's law. Structures of NaCl, KCl and CsCl (qualitative treatment only). Defects in crystals.

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. Theories of Reaction Rates: Collision theory and Activated Complex theory of bimolecular reactions.
