M.Sc. Chemistry Entrance Test syllabus (2019-20)

PART A. INORGANIC CHEMISTRY

- I. Atomic Structure Idea of de Broglie matter waves, Heinsenberg's uncertainty principle, atomic orbitals, quantum numbers, radial and angular wave functions, normal and orthogonal wave functions, significance of Ψ and $\Psi 2$, probability distribution curves, shapes of s, p, d, f orbitals, Aufbau and Pauli exclusion principles, Hund's multiplicity rules, Electronic configuration of elements, effective nuclear charge, Slater's rules.
- II. Periodic table and atomic properties Classification of periodic table into s, p, d, f blocks, atomic and ionic radii, ionisation energy, electron affinity and electronegativity definition, methods of determination or evaluation, trend in periodic table (in s and p-block elements), Pauling , Mulliken, Allred Rachow and Mulliken Jaffe's electronegativity scale, Sanderson's electron density ratio.
- III. Covalent Bond Valence bond theory (Heitler-London and Pauling approach) and its limitation, directional characteristics of covalent bond, various type of hybridisation and shapes of simple inorganic molecules and ions (BeF₂, BF₃, CH₄, PF₅, SF₆, IF₇, SO₄²⁻, ClO₄⁻¹, NO₃⁻¹) valence shell electron pair repulsion (VSEPR) theory to NH₃, H₃O⁺, SF4, ClF₃, H₂O, SnCl₂, ClO₃⁻¹ and ICl₂⁻¹. Molecular orbital theory of Homonuclear (N₂, O₂) Heteronuclear (CO and NO) diatomic molecules and ions, bond energy, bond angle, bond length and dipole moments, percentage ionic character from dipole moment and electronegativity difference.
- IV. Ionic Solids Ionic structures (NaCl, CsCl, ZnS (Zinc blende), CaF₂) size effects, radius ratio rule and its limitations, Madelung constant, Stoichiometric and Non stoichiometric defects in crystals, Lattice energy (Mathematical derivation excluded) and Born Haber cycle, Solvation energy and its relation with solubility of Ionic solids, Polarizing power and Polarisability of ions, Fajan's rule.
- Wetallic Bond and semiconductors Metallic bond Qualitative idea of valence bond and Band theories of metallic bond (conductors, semiconductors, insulators). Semiconductors – Introduction, types and applications.
- VI. **S-Block elements** Comparative study of the elements including diagonal relationship, Anomalous behaviour of Lithium and Beryllium compared to other elements in the same group, salient features of hydrides, oxides, halides, hydroxides (methods of preparation excluded), behaviour of solution in liquid NH3.
- VII. **P-Block elements**: Electronic configuration, atomic and ionic size, metallic character, melting point, ionization energy, electron affinity, Electronegativity, inert pair effect and diagonal relationship. Chemistry of Noble Gases General physical properties, low chemical reactivity, chemistry of xenon, structure and bonding in fluorides, oxides and oxyfluorides of xenon.
- VIII. Chemistry of d-Block elements Definition of transition elements, position in the periodic table, General characteristic properties of d-Block elements, Comparison of properties of 3d elements with 4d and 5d elements with reference only to ionic radii, oxidation state, magnetic and spectral properties and stereo chemistry. Stability of various oxidation states and e.m.f (Latimer and Frost diagrams), Structure and properties of some compounds of transition elements- TiO₂, VOCl₂, FeCl₃, CuCl₂ and Ni(CO)₄.

- IX. Chemistry of f-Block elements Lanthanides: Electronic structure, oxidation states, magnetic properties, complex formation, colour, ionic radii and lanthanide contraction, occurrence, separation of lanthanides, Lanthanide compounds. Actinides: General characteristics of actinides, chemistry of separation of Np, Pu and Am from uranium, Transuranic elements, comparison of properties of Lanthanides and actinides with transition elements.
- X. **Theory of Qualitative and Quantitative Analysis** Chemistry of analysis of various groups of basic and acidic radicals, chemistry of identification of acid radicals in typical combination, chemistry of interference of acid radicals including their removal in the analysis of basic radicals, common ion effect, solubility product, theory of precipitation, co-precipitation, post precipitation, purification of precipitates.
- XI. Coordination Chemistry: Metal- Ligand Bonding in Transition Metal complexes Limitations of valence bond theory, an elementary idea of crystal field theory, crystal field splitting in octahedral, tetrahedral and square planer complexes, factors affecting the crystal field parameters. Thermodynamics and Kinetic Aspects of metal complexes. Thermodynamic stability of metal complexes and factors affecting the stability, Irving William Series, substitution reactions of square planer complexes of Pt[II], Trans effect. Magnetic properties of Transition metal complexes Types of magnetic materials, magnetic susceptibility, method of determining magnetic susceptibility, spin only formula, L-S coupling, correlation of µs and µeff values, orbital contribution to magnetic moments, application of magnetic moment data for 3d metal complexes. Electronic spectra of Transition metal complexes Selection rules for d-d transition, spectroscopic ground states,

Transition metal complexes Selection rules for d-d transition, spectroscopic ground states, spectrochemical series, orgel energy level diagram for d^1 and d^9 states, discussion of electronic spectrum of $[Ti(H_2O)_6]^{+3}$ complex ion.

- XII. Acids and Bases Arrhenius, Bronsted-lowry, Lux-flood, solvent system and Lewis concept of acids and bases, relative strength of acids and bases, levelling solvents, hard and soft acids and bases(HSAB), Applications of HSAB principle.
- XIII. **Organometallic chemistry** Definition, classification and nomenclature of organometallic compounds, preparation, properties and bonding of alkyls of Li, Al, Hg and Sn, concept of hapticity of organic ligand, Structure and bonding in metal-ethylenic complexes, Structure of Ferrocene, classification in metal carbonyls, preparation, properties and bonding in mononuclear carbonyls.
- XIV. **Bio inorganic chemistry** Metal ions present in biological system, classification on the basis of action (essential, non essential, trace, toxic), Metalloporphyrins with special reference to haemoglobin and myoglobin. Biological role of Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺ ions, Cooperative effect, Bohr effect.

PART B: PHYSICAL CHEMISTRY

- I. **Gaseous States**: Kinetic Molecular Theory of Gases, Maxwell's distribution of velocities and energies (derivation excluded) Calculation of root mean square velocity, average velocity and most probable velocity. Collision diameter, collision number, collision frequency and mean free path (Derivations excluded), Deviation of Real gases from ideal behavior, Derivation of Vander Waal's Equation of State, its application in the calculation of Boyle's temperature (compression factor)
- II. Critical Phenomenon: Critical temperature, Critical pressure, critical volume and their determination. PV isotherms of real gases, continuity of states, the isotherms of Vander Waal's equation, relationship between critical constants and Vander Waal's constants. Critical compressibility factor. The Law of corresponding states.

Liquid States: Structure of liquids, Properties of liquids – surface tension, refractive index, viscosity, vapour pressure and optical rotation.

Solid State: Classification of solids, Laws of crystallography – (i) Law of constancy of interfacial angles (ii) Law of rationality of indices (iii) Miller indices, (iv) Law of symmetry. Symmetry elements of crystals. Definition of unit cell & space lattice. Bravais lattices, crystal system. X-ray diffraction by crystals, Determination of Avogadro's number. Derivation of Bragg equation. Laue method, Powder method, rotating crystal method

- III. Kinetics: Rate of reaction, rate equation and its types, factors influencing the rate of a reaction concentration, temperature, pressure, solvent, light, catalyst. Order of a reaction, integrated rate expression for zero order, first order, second and third order reaction. Half-life period of a reaction. Effect of temperature on the rate of reaction Arrhenius equation. Theories of reaction rate Simple collision theory for unimolecular collision. Transition state theory of bimolecular reactions.
- Electrochemistry: Electrolytic conduction, factors affecting electrolytic conduction, IV. specific, conductance, molar conductance, equivalent conductance and relation among them, their variation with concentration. Arrhenius theory of ionization, Ostwald's Dilution Law. Debye- Huckel – Onsager's equation for strong electrolytes (elementary treatment only), Application of Kohlrausch's Law in calculation of conductance of weak electrolytes at infinite dilution. Applications of conductivity measurements: determination of degree of dissociation, determination of Ka of acids determination of solubility product of sparingly soluble salts, conductometric titrations. Definition of pH and pKa, Buffer solution, Buffer action, Henderson – Hazel equation, Buffer mechanism of buffer action. Electrolytic and Galvanic cells - reversible & Irreversible cells, conventional representation of electrochemical cells. Calculation of thermodynamic quantities of cell reaction (\blacktriangle G, \blacktriangle H & K). Types of reversible electrodes – metal- metal ion gas electrode, metal -insoluble salt- anion and redox electrodes. Electrode reactions, Nernst equations, derivation of cell EMF and single electrode potential. Standard Hydrogen electrode, reference electrodes, standard electrodes potential, sign conventions, Concentration cells

with and without transference, liquid junction potential and its measurement. Applications of EMF measurement in solubility product and potentiometric titrations using glass electrode. More stress on numerical problems.

V. **Thermodynamics:** Definition of thermodynamic terms: system, surrounding etc. Types of systems, intensive and extensive properties. State and path functions and their differentials. Thermodynamic process. Thermodynamic equilibrium Concept of heat and work.

First law of thermodynamics: statement, definition of internal energy and enthalpy. Heat capacity, heat capacities at constant volume and pressure and their relationship. Joule– Thomson coefficient for ideal gas and real gas: and inversion temperature. Calculation of w.q. dU & dH for the expansion of ideal gases under isothermal and adiabatic conditions for reversible process, Second law of thermodynamics, need for the law, different statements of the law, Carnot's cycles and its efficiency, Carnot's theorm, Thermodynamics scale of temperature. Concept of entropy – entropy as a state function, entropy as a function of V & T, entropy as a function of P & T, entropy change in physical change, entropy as a criteria of spontaneity and equilibrium. Third law of thermodynamics: Nernst heat theorem, statement of concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, G as criteria for thermodynamic equilibrium and spontaneity, its advantage over entropy change. Variation of G with P, V and T.

- VI. **Chemical Equilibrium:** Equilibrium constant and free energy, concept of chemical potential, Thermodynamic derivation of law of chemical equilibrium. Temperature dependence of equilibrium constant; Clausius–clapeyron equation and its applications.
- VII. Distribution Law: Nernst distribution law its thermodynamic derivation, Applications of distribution law: (i) Determination of degree of hydrolysis and hydrolysis constant of aniline hydrochloride. (ii) Determination of equilibrium constant of potassium tri-iodide complex and (iii) Process of extraction. More stress on numerical problems.
- VIII. Quantum Mechanics: Black-body radiation, Plank's radiation law, photoelectric effect, postulates of quantum mechanics, quantum mechanical operators, commutation relations, Hamiltonian operator, Hermitian operator, average value of square of Hermitian as a positive quantity, Role of operators in quantum mechanics, To show quantum mechanically that position and momentum cannot be predicated simultaneously, Determination of wave function & energy of a particle in one dimensional box.
 - IX. Physical Properties and Molecular Structure: Optical activity, polarization (clausius Mossotti equation- derivation excluded). Orientation of dipoles in an electric field, dipole moment, included dipole moment, measurement of dipole moment-temperature method and refractivity method, dipole moment and structure of molecules, Magnetic permeability, magnetic susceptibility and its determination. Application of magnetic susceptibility, magnetic properties paramagnetism, diamagnetism and ferromagnetics.
 - X. **Spectroscopy:** Introduction: Electromagnetic radiation, regions of spectrum, basic features of spectroscopy, statement of Born-oppenheimer approximation, Degrees of freedom.

Rotational Spectrum: Diatomic molecules. Energy levels of rigid rotator (semi-classical principles), selection rules, spectral intensity distribution using population distribution (Maxwell-Boltzmann distribution), and determination of bond length and isotope effect.

Vibrational spectrum: Infrared spectrum: Energy levels of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies, idea of vibrational frequencies of different functional groups.

Raman Spectrum: Concept of polarizibility, pure rotational and pure vibrational Raman spectra of diatomic molecules, selectin rules, Quantum theory of Raman spectra. More stress on numerical problems.

- **XI. Photochemistry:** Frank-Condon Principle. Introduction to statistical mechanics. Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry: Grotthus-Drapper law, Stark-Einstein law (law of photochemical equivalence) Jablonski diagram depiciting various processes occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing), quantum yield, photosensitized reactions-energy transfer processes (simple examples).
- XII. Solutions Dilute Solutions and Colligative Properties: Ideal and non-ideal solutions, methods of expressing concentrations of solutions,. Dilute solution,Colligative properties, Raolut's law, relative lowering of vapour pressure, molelcular weight determination, Osmosis law of osmotic pressure and its measurement, determination of molecular weight from osmotic pressure. Elevation of boiling point and depression of freezing point, Thermodynamic derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Abnormal molar mass, degree of dissociation and association of solutes.
- XIII. Phase Equilibrium: Statement and meaning of the terms phase, component and degree of freedom, thermodynamic derivation of Gibbs phase rule, phase equilibria of one component system –Example water system.

Phase equilibria of two component systems solid-liquid equilibria, simple eutectic Example Pb-Ag system, desilerisation of lead

PART C. ORGANIC CHEMISTRY

- I. **Structure and Bonding:** Localized and delocalized chemical bond, van der Waals interactions, resonance: conditions, resonance effect and its applications, hyperconjugation, inductive effect, Electromeric effect & their comparison.
- II. Stereochemistry of Organic Compounds: Concept of isomerism. Types of isomerism. Optical isomerism — elements of symmetry, molecular chirality, enantiomers, stereogenic centre, optical activity, properties of enantiomers, chiral and achiral molecules with two stereogenic centres, diastereomers, threo and erythro diastereomers, meso compounds, resolution of enantiomers, inversion, retention and racemization.

Relative and absolute configuration, sequence rules, R & S systems of nomenclature.

Geometric isomerism — determination of configuration of geometric isomers. E & Z system of nomenclature, Conformational isomerism — conformational analysis of ethane and n-butane, conformations of cyclohexane, axial and equatorial bonds,. Newman projection and Sawhorse formulae, Difference between configuration and conformation.

III. Mechanism of Organic Reactions: Curved arrow notation, drawing electron movements with arrows, half-headed and double-headed arrows, homolytic and heterolytic bond breaking. Types of reagents – electrophiles and nucleophiles. Types of organic reactions. Energy considerations.

Reactive intermediates — carbocations, carbanions, free radicals, carbenes,(formation, structure & stability).

IV. Alkanes and Cycloalkanes: IUPAC nomenclature of branched and unbranched alkanes, the alkyl group, classification of carbon atoms in alkanes. Isomerism in alkanes, sources, methods of formation (with special reference to Wurtz reaction, Kolbe reaction, Corey-House reaction and decarboxylation of carboxylic acids), physical properties.

Mechanism of free radical halogenation of alkanes: reactivity and selectivity.

Cycloalkanes — nomenclature, synthesis of cycloalkanes and their derivatives – photochemical (2+2) cycloaddition reactions, , dehalogenation of α , ω -dihalides, , pyrolysis of calcium or barium salts of dicarboxylic acids, Baeyer's strain theory and its limitations., theory of strainless rings.

V. **Alkenes:** Nomenclature of alkenes, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides,. The Saytzeff rule, Hofmann elimination, physical properties and relative stabilities of alkenes.

Chemical reactions of alkenes — mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikoff's rule, hydroboration–oxidation, oxymercuration-reduction, ozonolysis, hydration, hydroxylation and oxidation with KMnO₄,

VI. Arenes and Aromaticity: Nomenclature of benzene derivatives:. Aromatic nucleus and side chain. Aromaticity: the Huckel rule, aromatic ions, annulenes up to 10 carbon atoms, aromatic, anti - aromatic and non - aromatic compounds. Aromatic electrophilic substitution — general pattern of the mechanism, mechansim of nitration, halogenation,

sulphonation, and Friedel-Crafts reaction. Energy profile diagrams. Activating , deactivating substituents and orientation.

- VII. Dienes and Alkynes: Nomenclature and classification of dienes: isolated, conjugated and cumulated dienes. Structure of butadiene,. Chemical reactions 1,2 and 1,4 additions (Electrophilic & free radical mechanism), Diels-Alder reaction, Nomenclature, structure and bonding in alkynes. Methods of formation. Chemical reactions of alkynes, acidity of alkynes. Mechanism of electrophilic and nucleophilic addition reactions, hydroboration-oxidation of alkynes,
- VIII. Alkyl and Aryl Halides: Nomenclature and classes of alkyl halides, methods of formation, chemical reactions. Mechanisms and stereochemistry of nucleophilic substitution reactions of alkyl halides, S_N2 and S_N1 reactions with energy profile diagrams. Methods of formation and reactions of aryl halides, The addition-elimination and the elimination-addition mechanisms of nucleophilic aromatic substitution reactions. Relative reactivities of alkyl halides vs allyl, vinyl and aryl halides.
 - IX. Alcohols and Phenols : Monohydric alcohols nomenclature, methods of formation by reduction of aldehydes, ketones, carboxylic acids and esters. Hydrogen bonding. Acidic nature. Reactions of alcohols.

Dihydric alcohols — nomenclature, methods of formation, chemical reactions of vicinal glycols, oxidative cleavage [Pb(OAc)₄ and HIO₄] and pinacol-pinacolone rearrangement. **Phenols:** Nomenclature, structure and bonding. Preparation of phenols, physical properties and acidic character. Comparative acidic strengths of alcohols and phenols, resonance stabilization of phenoxide ion. Reactions of phenols — electrophilic aromatic substitution, Mechanisms of Fries rearrangement, Claisen rearrangement, Reimer-Tiemann reaction, Kolbe's reaction and Schotten and Baumann reactions.

- **X. Epoxides:** Synthesis of epoxides. Acid and base-catalyzed ring opening of epoxides, orientation of epoxide ring opening, reactions of Grignard and organolithium reagents with epoxides.
- XI. Ultraviolet (UV) absorption spectroscopy: Absorption laws (Beer-Lambert law), molar absorptivity, presentation and analysis of UV spectra, types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated enes and enones, Woodward- Fieser rules, calculation of λ_{max} of simple conjugated dienes and α,β -unsaturated ketones. Applications of UV Spectroscopy in structure elucidation of simple organic compounds.
- XII. Carboxylic Acids & Acid Derivatives: Nomenclature of Carboxylic acids, structure and bonding, physical properties, acidity of carboxylic acids, effects of substituents on acid strength. Preparation of carboxylic acids. Reactions of carboxylic acids. Hell-Volhard-Zelinsky reaction. Reduction of carboxylic acids. Mechanism of decarboxylation.

Structure, nomenclature and preparation of acid chlorides, esters, amides and acid anhydrides. Relative stability of acyl derivatives. Physical properties, interconversion of acid derivatives by nucleophilic acyl substitution.

Mechanisms of esterification and hydrolysis (acidic and basic).

- XIII. **Infrared (IR) absorption spectroscopy:** Molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, measurement of IR spectrum, fingerprint region, characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds. Applications of IR spectroscopy in structure elucidation of simple organic compounds.
- XIV. Amines: Structure and nomenclature of amines, physical properties. Separation of a mixture of primary, secondary and tertiary amines. Structural features affecting basicity of amines. Preparation of alkyl and aryl amines (reduction of nitro compounds, nitriles, reductive amination of aldehydic and ketonic compounds. Gabriel-phthalimide reaction, Hofmann bromamide reaction. electrophilic aromatic substitution in aryl amines, reactions of amines with nitrous acid.
- XV. **Diazonium Salts:** Mechanism of diazotisation, structure of benzene diazonium chloride, Replacement of diazo group by H, OH, F, Cl, Br, I, NO₂ and CN groups, reduction of diazonium salts to hyrazines, coupling reaction and its synthetic application.
- XVI. Aldehydes and Ketones: Nomenclature and structure of the carbonyl group. Synthesis of aldehydes and ketones with particular reference to the synthesis of aldehydes from acid chlorides, advantage of oxidation of alcohols with chromium trioxide (Sarett reagent) pyridinium chlorochromate (PCC) and pyridinium dichromate., Physical properties. Comparison of reactivities of aldehydes and ketones. Mechanism of nucleophilic additions to carbonyl group with particular emphasis on benzoin, aldol, Perkin and Knoevenagel condensations. Condensation with ammonia and its derivatives. Wittig reaction. Mannich reaction.Oxidation of aldehydes, Baeyer–Villiger oxidation of ketones, Cannizzaro reaction. MPV, Clemmensen, Wolff-Kishner, LiAlH4 and NaBH4 reductions.
- XVII. **NMR Spectroscopy:** Principle of nuclear magnetic resonance, the PMR spectrum, number of signals, peak areas, equivalent and nonequivalent protons positions of signals and chemical shift, shielding and deshielding of protons, proton counting, splitting of signals and coupling constants, magnetic equivalence of protons. Discussion of PMR spectra of the molecules: ethyl bromide, n-propyl bromide, isopropyl bromide, 1,1-dibromoethane, 1,1,2-tribromoethane, ethanol, acetaldehyde, ethyl acetate, toluene, benzaldehyde and acetophenone..Simple problems on PMR spectroscopy for structure determination of organic compounds.

- XVIII. Carbohydrates: Classification and nomenclature. Monosaccharides, mechanism of osazone formation, interconversion of glucose and fructose, chain lengthening and chain shortening of aldoses. Configuration of monosaccharides. Erythro and threo diastereomers. Conversion of glucose into mannose. Formation of glycosides, ethers and esters. Determination of ring size of glucose and fructose. Open chain and cyclic structure of D(+)-glucose & D(-) fructose. Mechanism of mutarotation. Structures of ribose and deoxyribose. An introduction to disaccharides (maltose, sucrose and lactose) and polysaccharides (starch and cellulose) without involving structure determination.
 - XIX. **Organometallic Compounds:** Organomagnesium compounds: the Grignard reagentsformation, structure and chemical reactions. Organozinc compounds: formation and chemical reactions. Organolithium compounds: formation and chemical reactions.
 - XX. **Organic Synthesis via Enolates:** Acidity of α -hydrogens, alkylation of diethyl malonate and ethyl acetoacetate. Synthesis of ethyl acetoacetate: the Claisen condensation. Keto-enol tautomerism of ethyl acetoacetate.
 - XXI. Heterocyclic Compounds: Introduction: Molecular orbital picture and aromatic characteristics of pyrrole, furan, thiophene and pyridine. Methods of synthesis and chemical reactions with particular emphasis on the mechanism of electrophilic substitution. Mechanism of nucleophilic substitution reactions in pyridine derivatives. Comparison of basicity of pyridine, piperidine and pyrrole.

Introduction to condensed five and six- membered heterocycles. Prepration and reactions of indole, quinoline and isoquinoline with special reference to Fisher indole synthesis, Skraup synthesis and Bischler-Napieralski synthesis. Mechanism of electrophilic substitution reactions of, quinoline and isoquinoline.

- XXII. Amino Acids, Peptides& Proteins: Classification, of amino acids. Acid-base behavior, isoelectric point and electrophoresis. Preparation of α-amino acids.
 Structure and nomenclature of peptides and proteins. Classification of proteins. Peptide structure determination, end group analysis, selective hydrolysis of peptides. Classical peptide synthesis, solid–phase peptide synthesis. Structures of peptides and proteins: Primary & Secondary structure.
- XXIII. **Synthetic Polymers:** Addition or chain-growth polymerization. Free radical vinyl polymerization, ionic vinyl polymerization, Ziegler-Natta polymerization and vinyl polymers. Condensation or step growth polymerization. Polyesters, polyamides, phenol formaldehyde resins, urea formaldehyde resins, epoxy resins and polyurethanes. Natural and synthetic rubbers.