Department of Chemistry

University of Kashmir

(NAAC Accredited A++)

PG Entrance Test Syllabus
For 2-year PG Program in Chemistry under NEP-2020

Unit 1

Basics: Effective nuclear charge and its calculation by Slater rules. Solvation energy and factors affecting solubility of ionic solids. VSEPR theory of simple molecules (AX_4, AX_4E_2, AX_5, AX_5E, AX_3E_2, AX_6) MO treatment of heteronuclear diatomic molecules (CO and NO). Multicenter bonding in electron deficient molecules.

***Acid base theories**:* Arrhenius, Bronsted-Lowry, Lewis, Lux-Flood and Usanovich. HSAB-principle, concept and applications. Differentiating and leveling solvents. Non aqueous solvents: comparison with aqueous solvents.

s-Block Elements: Chemical reactivity of s-block elements towards water, oxygen, hydrogen, and halogens. Chemical characteristics of the compounds of alkali and alkaline earth metals (oxides, hydrides, hydroxides carbonates, nitrates, sulphates). EDTA complexes of calcium and magnesium. Alkali metal ion batteries.

Molecular Symmetry: Symmetry elements and operations. Identity. Proper axis of rotation, order of axis, and principal axis. Reflection plane: horizontal, vertical and dihedral planes. Inversion centre. Improper axis of rotation. Combination of symmetry operations-General considerations, group multiplication tables. Symmetry subgroups and classes. Mathematical requirements of a group. Point groups-Schoenflies notation of point groups.

Unit 2

***Boranes**:* topological classification, bonding in diborane. STYX convention of bonding in boron clusters. Chemical behavior, structure and bonding in Boron-Nitrogen (Borazine) and Nitrogen-Phosphorus compound (phosphonitrilic halides). Structure and bonding in silicates (rings, chains, sheets and network). Chemical behavior of oxides and oxoacids of phosphorus, sulphur and chlorine, peroxoacids of sulphur. Structure of Pseudohalogens, polyhalides, interhalogen compounds. Structure and bonding in fluorides, oxides and oxyfluorides of xenon.

Transition elements: Characteristic properties of Transition elements: variable oxidation states, anomalous electronic configurations. Trends in ionic radii, hydration and lattice energy of 3d series. Complexing ability, Catalytic properties (. Acidic/Basic character of transition metal compounds in various oxidation states. Stabilization of unusual oxidation states. Chemistry of selected transition metal compounds (Potassium ferricyanide and sodium nitroprusside). Magnetic properties: calculation of magnetic moment value (spin only). Spectral properties (d-d bands and charge transfer transitions).

Unit 3

Coordination Chemistry: Experimental verification of Werner's Theory. Effective atomic number and its significance, Geometrical and optical isomerism of MA_4B_2, MA_3B_3 and MABCD type complexes. Bonding models in coordination complexes: Limitations of VBT, Crystal field theory of octahedral tetrahedral and square planar complexes. Stability of coordination compounds (Thermodynamic and Kinetic) and factors affecting stability. Chelate and Macrocyclic effect. Spectrochemical series. Magnetic properties of transition metal complexes. Limitations of Crystal field theory. Analytical applications of coordination compounds.

Inner transition elements: Electronic configuration, oxidation states, f-orbital's. Complexing behavior of inner transition elements (Stereochemistry and stability). Spectral and Magnetic Properties (comparison with transition metals). Consequences of Lanthanide contraction (case studies). Separation of Lanthanides by ion–exchange and solvent extraction methods. Homo and hetero dinuclear coordination compounds, coordination polymers of lanthanide ions.

Unit 4

***Environmental Chemistry*:** Segments of Environment; Macro and Micronutrients in Soil. Acid--Base and Ion exchange reactions in Soil. Factors determining composition of water bodies (thermal stratification, acid-base, pE concept). Water quality parameters: Dissolved oxygen, Metals, Content of Chloride, Phosphate and Nitrate. Vertical profile of atmosphere, Chemical and Photochemical Reactions in Atmosphere, Photochemical Smog formation, Green House Effect; Acid Rain: chemistry and control.

***Organometallic Chemistry*:** Definition and classification of organometallic compounds. hapticity concept, Applications of 18-electron rule. Decomposition pathways (Beta elimination reaction). Comparison of main group and transition metal organometallic compounds. Preparation, structure and bonding in Zeise's salt. Homogenous and heterogenous catalysis,catalytic efficiency: TON and TOF.Mechanism of Alkene hydrogenation and Hydroformylation reactions using transition metal catalysts.

Unit 5

Basics: Electron displacements: Inductive, electromeric, conjugative and hyperconjugative effects. Tautomerism. Nucleophiles and electrophiles. Arrow formalism. Reactive intermediates: Introduction, structure, generation, fate and stability of carbocations, carbanions, free- radicals and carbenes

Stereochemistry: Conformations of ethane, butane and cyclohexane. Interconversions: Wedge Formula, Newmann, Sawhorse and Fischer representations. Geometrical and Optical isomerism, concept of chirality, Enantiomerism, Diastereomerism and Meso compounds). Threo and erythro, Absolute Configuration; D and L; R/ S (upto two chiral centers), *cis - trans* and E / Z systems of nomenclature.

Aromaticity: Requirements of aromaticity. Huckel's rule and its significance. Explanation using molecular orbital diagram of benzene. Homo and Antiaromaticity, Aromaticity of non-benzenoid compounds like pyrrole, thiophene, furan and aromatic ions (3, 5 and 7-membered rings).

Unit 6

***Substitution and elimination reactions of alkyl halides and alcohols*:** Mechanistic details of S_N1 and S_N2; E1 and E2 reactions. Hoffman and Saytzev's rules, Effects of structure of alkyl halides/ alcohols, nature of nucleophiles, leaving groups and effect of solvent. Substitution versus Elimination. Mitsunobu reaction.

Addition Reactions of alkenes and alkynes: Mechanistic details including regioselectivity and stereochemical implications of halogenation, hydrohalogenation, hydroboration, epoxidation, Prevost and Woodward hydroxylation. Acidic character, hydration and Catalytic/ metal-ammonia reductions of alkynes.

Aromatic electrophilic substitution: General mechanism; formation of sigma and pi complexes. The second substitution: role of activating and deactivating groups, orientation of benzene. Mechanisms of Gattermann, Huben-Hoesch, Veils-Meir Haack and Riemer-Tieman reactions.

Aromatic nucleophilic substitution:

Discussion of S_N –unimolecular, S_N2Ar and benzyne mechanisms.

Unit 7

Alcohols: Synthesis of 1, 2 diols and trihydric alcohols (Glycerol). Periodic acid and lead tetra acetate oxidations of 1,2-diols. Reactions of glycerol with Na, PCl_5, Acetylation, Oxalic acid, HI, Dehydration, HCl, and oxidation reactions, Noble Oil.

Phenols: Comparative study of acidic character of substituted phenol and Napthols, Nitration and sulphonation on α and β napthols, Mechanisms of, Kolbe's–Schmidt reactions, Fries and Claisen rearrangements.

Nucleophillic addition reactions of aldehydes/ketones: Reaction with HCN, ROH, $NaHSO_3$ and amines, Aldol, Perkin Condensation, Cannizzaro's and Wittig reaction. Clemensen, Wolff Kishner, Meerwein-Pondorff Verley and Bouvaelt-Blanc Reduction. Baeyer Villeger oxidation.

Additions and elimination reactions: Nucleophilic additions to carbonyls and stereochemical aspects through various models (Cram, Cram chelation) for acyclic systems. Stereochemical control in addition of nucleophiles to cyclic carbonyl compounds. Formation and stability of enolates and enamines. Mechanism and stereochemical aspects of Aldol reactions (Controlling aldol reactions, intramolecular Aldol reaction and Cross Aldol condensation). Addition of Phosphorus and sulfur ylids. Wittig-Horner reaction. Michael addition.

Unit 8

Molecular Rearrangements: Introduction, Mechanism, stereochemical implications and applications of rearrangement reactions. Migration to Electron-Deficient Carbon: Wagner-Meerwein, Pinacol and Semipinacol Rearrangements, Dienone-Phenol Rearrangements. Migration to Electron-Deficient Nitrogen: Beckmann Rearrangement, Hofmann Degradation. Migration to Electron-Deficient Oxygen: The Baeyer-Villiger rearrangement Anionic Rearrangements: Benzil-Benzylic acid rearrangement, Favorskii Rearrangement

Green Chemistry: Need for Green Chemistry and the role of chemists. Principles of Green Chemistry. E-Factor. Tools of Green Chemistry: Selection of starting materials, Catalysts, Alternative Solvents: Supercritical fluids, ScO2, H2O, Ionic Liquids, Appropriate reagents, atom economy. Alternative energy sources: Microwaves, Sonication, Mechanical and Visible light. Chemicals from Renewable Raw Materials: Ethanol, Biodiesel, Ethylene glycol, and Glycerol.

Unit 9

States of matter: *Gaseous State:* Kinetic molecular theory of gases, Root mean square, average and most probable velocities; qualitative discussion of Maxwell's distribution of molecular velocities. Deviation of gases from ideal behaviour, van der Waal's equation of state. PV isotherms of real gases, continuity of states, van der Waal's equation isotherms. Relationship between critical constants and van der Waal's constants, the law of corresponding states, reduced equation of state.

Liquid State: Viscosity and surface tension of liquids, factors affecting viscosity and surface tension. Surface tension, the pressure difference across curved surfaces (Laplace equation), the vapor pressure of droplets (Kelvin equation), and Capillary condensation. Thermodynamics of Interfaces: Surface excess, surface tension and thermodynamic parameters, Gibbs adsorption isotherm.

Solid State: General characteristics of solids, Symmetry elements in crystals, Crystal lattice and unit cell, number of atoms in the unit cell, close-packed structures, packing efficiency, and Characteristic structures of ionic solids (NaCl, CaF_2, ZnS).

Surface chemistry: *Surfactants:* Introduction, types, cmc and micellization, vesicles and bilayers.

Solid surfaces: Adsorption at solid surfaces, adsorption models; Langmuir adsorption isotherm, BET adsorption isotherm. Solid liquid interface: Contact angle, young's equation, wetting, Wetting as contact angle phenomena.

Unit 10

Thermodynamics: *Thermodynamic functions*: State and path functions and their differentials. Thermodynamic processes. Concept of heat and work.

First law of thermodynamics: The formulation of the first law of thermodynamics, Heat capacity, heat capacities at constant volume and constant pressure and their relationship. Calculation of ΔU & ΔH for the expansion of ideal gases under isothermal and adiabatic conditions. Joule's law, Joule-Thomson coefficient and inversion temperature. Temperature dependence of enthalpy, Kirchhoff's equation. Bond dissociation energy and its calculation from thermo-chemical data with applications.

The second *law of thermodynamics:* Need for the law, and different statements of the law. Carnot cycle and its efficiency, Carnot theorem. The thermodynamic scale of temperature.

Concept of entropy, entropy as a function of V&T, and as a function of P&T. Clausius inequality; entropy as criteria for spontaneity and equilibrium. Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, ΔG & ΔA as criteria for thermodynamic equilibrium and spontaneity. Variation of A and G with Temperature, pressure and Composition, Gibbs-Helmholtz equation, Entropy change in physical processes, ideal gas expansion and entropy of mixing of ideal gases, Gibb's paradox, Maxwell's relations and thermodynamic equations of state.

Third law of thermodynamics: Nernst heat theorem, third law of thermodynamics, concept of residual entropy. The molecular interpretation of entropy, The calorimetric measurement of entropy, residual entropy.

Phase Equilibria: Meaning of the terms: phase, component and degree of freedom, statement and derivation of Gibbs phase rule. Reaction isotherm and reaction isochore, Clapeyron equation and Clausius-Clapeyron equation, applications. Phase diagrams of one-component systems (water and sulphur) and two-component systems involving eutectics, congruent and incongruent melting points (lead-silver, $FeCl_3$-H_2O and Na-K only).

Unit 11

Chemical Kinetics: Reaction Order and Rate constants: Order of reaction, derivation of rate equations for second (two reactants) and third order reactions. Determination of order of reaction by differential rate, integration, half-life period and isolation methods. Temperature dependence of reaction rates:-Arrhenius equation, concept of activation energy.

Theories of chemical kinetics: Simple collision theory based on hard sphere model, estimation of rate constants of atomic reactions, extension to molecular reactions, limitations.

Catalysis: Introduction, mechanism of action of catalysts, Acid-Base catalysis*:* Generalized and specific acid-base catalysis, pH dependence of reaction rate.

Heterogenous Catalysis: Kinetics of Surface Reactions, Unimolecular& bimolecular surface reactions [Langmuir-Hinshelwood & Langmuir- Riedel mechanism], classical & statistical treatments. Enzyme Catalysis: Introduction to enzyme-catalyzed reactions, Michaelis-Menton equation, effect of temperature and pH. Enzyme inhibition. Specially Catalysed Reactions: Fischer-Tropsch process, Haber-Bosch process, Photocatalysis, reactions, Photocatalytic breakdown of water.

Unit 12

Electrochemistry: *Ionic Conductors:* Electrolytes as conductors, Migration of ions and Kohlrausch's law, ionic mobility, Debye-Huckel-Onsager's equation for strong electrolytes (Approximations and predictions, no derivation). Transport number, definition and determination by Hittorf's and moving boundary methods.
Application of conductivity measurements: determination of the degree of dissociation and dissociation constants of acids, solubility product of a sparingly soluble salt, conductometric titrations.
Electrochemical Cells: electrode types, electrode potential and its measurement,
Nernst equation and cell E.M.F and its measurement. Electrochemical series and its significance.
Concentration cells: electrolyte concentration cells without transport.
Application of EMF measurements: Determination of thermodynamic functions of cell reactions (ΔG, ΔH and K.), potentiometric acid-base titrations (pH and pKa determination).
Photochemistry*:* Interaction of radiation with matter, the difference between thermal and photochemical processes. Laws of photochemistry: Lambert-Beer Law, Grothus-Drapper law, and Stark-Einstein law. Jablonski diagram depicting 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).
Kinetics of photochemical reactions: Photochemical decomposition of hydrogen iodide. Hydrogen-chlorine and hydrogen-bromine reactions, Comparison with thermal decomposition reactions.