PG ENTRANCE EXAMINATION SYLLABUS FOR CHEMISTRY/ORGANIC CHEMSITRY

UNIT-I

Bohr's theory, its limitations and atomic spectrum of hydrogen atom. Wave mechanics: de Broglie equation, Heisenberg's Uncertainty Principle and its significance, Schrödinger's wave equation, significance of ψ and ψ^2. Quantum numbers and their significance.
Shapes of s, p, d- and f-orbitals.
Pauli's Exclusion Principle, Hund's rule of maximum multiplicity, Aufbau's principle and its limitations- Electronic configurations of the elements (Z=1-30), effective nuclear charge, shielding/screening effect, Slater's rules Problems. Periodic Table and periodic properties.

The ionic bond: Structures of ionic solids. Radius ratio rules, Calculation of some limiting radius ratio values, Coordination number 3 (planar triangle), Coordination number 4 (tetrahedral and square planar), Coordination number 6 (octahedral), Close packing.

Classification of ionic structures:
Ionic compounds of the type AX (ZnS, NaCl, CsCl), Ionic compounds of the type AX_2 (Calcium fluoride (fluorite) and Rutile structure Layer structures CdI_2, Cadmium iodide structure. Limitations of radius ratio concept
Lattice energy and Born-Haber cycle, Derivation of Born-Lande equation and its drawbacks, Kapustinskii equation, solvation energy and solubility of ionic solids, polarizing power and polarizability, Fajan's rules with applications.

UNIT-II

Covalent bond: Valence bond theory, The Lewis theory, The octet rule, Exceptions to the octet rule, Sidgwick- Powell theory. Valence shell electron pair repulsion (VSEPR) theory, Effect of lone pairs, electronegativity, isoelectronic principle, Examples using VSEPR theory: BF_3 and BF^-, NH_4 and NH_3^+, H_2O, PCl_5, ClF_3, SF_4, I_3^- and I_4^+, SF_3, and IF_7. [6]
Concept of resonance, resonance energy, hybridization, types of hybridization, sp, sp^2, sp^3 dsp^2, dsp^3, d^2sp^3, sp^3d^2 with one example each, and energetics of hybridization. Bent's rule, Limitations of Valence Bond Theory.

Molecular Orbital theory: LCAO concept: s-s, s-p, p-p, p-d and d-d combinations of orbitals, bonding, nonbonding and antibonding molecular orbitals, non-bonding combinations of orbitals, Rules for linear combination of atomic orbitals.
Examples of molecular orbital treatment for homonuclear diatomic molecules: H_2 molecule, H_2^+ molecule ion, He_2 molecule, He_2^+ molecule ion, Li_2 molecule, Be_2 molecule, B_2 molecule, C_2 molecule, N_2 molecule, N_2^+ molecule ion, O_2 molecule, O_2^- and O_2^{2-} molecule ions.

M.O. Energy diagrams of heteronuclear diatomic molecules with examples (NO, NO+, CO and HCl). Calculation of bond order, relationship between bond order, bond energy, and bond length, magnetic properties based on MOT.

UNIT-III

Coordination compounds: Ligands, classification of ligands, and chelation, physical methods in the study of complexes-change in conductance, color and pH. Nomenclature of co-ordination compounds, Inner metallic polynuclear and bridged complexes, Preparation of complexes-by simple addition reactions, substitution reactions and oxidation-reduction reactions. Geometries of complexes with coordination number 3 to 8. **Isomerism in co-ordination complexes:** Structural isomerism- Ionization, Hydrate, linkage, Ligand isomerism. Stereoisomerism – Geometrical and optical isomerism exhibited by co-ordination compounds of co-ordination number 4 and 6.

Metal-ligand bonding: Valence bond theory: Salient features, formation and magnetic properties of octahedral complexes $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[CoF_6]^{3-}$ $[Cr(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$. Formation and magnetic properties of tetrahedral and square planar complexes $[Ni(CO)_4]$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$ and $[PtCl_4]^{2-}$, limitations of VBT.

Crystal field theory: Salient features, splitting of d-orbitals in octahedral, tetrahedral, and square planar geometry. Applications - colors of transition metal complexes, magnetic properties of octahedral complex, CFSE and their uses. Factors affecting CFSE: Geometry of complexes, nature of the central metal ion, nature of ligand, and spectrochemical series. Limitations of CFT. Experimental evidence for metal-ligand covalent bonding in complexes, nephelauxetic effect. **MO theory**: tetrahedral and octahedral complexes (including p-bonding).

UNIT-IV

Classification and nomenclature of organic compounds, Hybridization, Shapes of organic molecules, Influence of hybridization on bond properties. Nature of bonding in Organic molecules. Formation of Covalent bond, Types of chemical bonding, localized and delocalized, conjugation and cross conjugation, concept of resonance, electronic displacements: Inductive effect, Electromeric effect, Resonance and Hyper conjugation, cross conjugation explanation with examples. Concept of resonance, aromaticity, Huckel rule, anti-aromaticity explanation with examples. Strengths of Organic acid and bases: Comparative study with emphasis on factors effecting pK values. Relative strength of aliphatic and aromatic carboxylic acids-Acetic acid and chloroacetic acid, acetic acid and propionic acid, acetic acid and Benzoic acid. Steric effect- Relative stability of *trans* and *cis*-2-butene.

Mechanisms of Organic Reactions

Notations used to represent electron movements and directions of reactions- curly arrows, formal charges. Types of bonds breaking- homolytic and heterolytic.Types of Reagents-Electrophiles, nucleophiles, nucleophilicity and basicity.Types of organic

reactions- substitution, addition, elimination, rearrangement and pericyclic reactions, explanation with examples.
Chemistry of Aliphatic hydrocarbons, Carbon-Carbon Sigma bonds. Chemistry of alkanes: Formation of alkanes, Wurtz reaction, Wurtz-Fittig reaction, Free radical substitution, Halogenation- relative reactivity and selectivity. Carbon-carbon pi bonds. Formation of alkenes and alkynes by elimination reaction.Mechanism of E1, E2, E1cb reaction.Saytzeff and Hofmann eliminations. Addition of HBr to propene, Free radical addition of HBr to propene.Addition of halogens to alkenes-carbocation and halonium ion mechanism.Stereospecificity of halogen addition.Ozonolysis mechanism - ozonolysis of propene.Addition of hydrogen halides to alkenes, mechanism, regioselectivity and relative rates of addition. Hydrogenation, hydration, hydroxylation and epoxidation of alkenes, explanation with examples, 1,2 and 1,4- addition reactions in conjugated dienes. Diels-Alder reaction, Allylic and benzylicbromination and mechanism in propene, 1-butene, 1-toluene and ethylbenzene.

UNIT-V

Nucleophilic substitution at saturated carbon. Mechanism of $SN_1$and SN_2 reactions with suitable examples. Energy profile diagrams, Stereochemistry and factors effecting SN1 and SN_2 reactions.Aromatic Electrophilic substitution reactions, Mechanisms, σ- and π-complexes, Halogenation, Nitration,Sulphonation, Friedel Crafts alkylation and acylation with their mechanism. Activating and deactivating groups. Orientation influence, Ortho-para ratio. Aromatic nucleophilic substitution reaction: SN Ar and Benzyne mechanism with suitable examples.

Reaction Intermediates: Generation, structure, stability and reactions involving;

i. **Carbocations**: Dienone-phenol and Pinacol-Pinacolone Rearrangement.
ii. **Carbanions**: Perkin Reaction, Aldol condensation, Claisen-Schmitt condensation.
iii. **Free Radicals**: Chlorination of methane, formation of gammaxene (lindane).
iv. **Carbenes**: Singlet and triplet states, their relative stability. Riemer-Tieman, and Wolffrearrangement.
v. **Nitrenes**: Singlet and triplet states, their relative stability. Hoffman and Curtius reactions.
vi. **Arynes**: Formation, detection. Bromobenzene to aniline, (4+2) cycloaddition reaction.

Aromaticity, Homo-aromaticity of azulene, tropone, tropolone, annulenes, benzenoids, meso-ionic compounds. Alternant and non-alternant hydrocarbons, Energy levels in odd and even-alternant hydrocarbons.

UNIT-VI

Carbohydrates: Introduction. Monosaccharides-Open and ring structure of glucose, mutarotation, epimerization. Interconversion reactions (aldose to ketose, ketose to aldose, chain elongation-Killiani-Fischer method, and chain degradation-Ruff's method), Determination ring size of glucose (methylation). Determination of configuration and conformational analysis of monosaccharides (glucose, galactose). Amino sugars: Structural formulae and conformations of α- and β- (glucosamine, galactosamine). Disaccharides- Structure elucidation of sucrose. Polysaccharides- partial structural formulae of starch and cellulose. Application of starch in titrimetric analysis.

Heterocyclic compounds: Definition, classification and nomenclature.
Furan-synthesis (from pentasan), reactions (nitration, acylation). Thiophene-synthesis (from sodium succinate), reactions (sulphonation, chlorination). Pyrrole-synthesis (from furan), reactions (diazotization, Riemer-Tiemann). Pyridine-synthesis (from acetylene), reactions (bromination, with $NaNH_2$). Aromaticity and basicity of pyrrole and pyrimidine. Indole: Synthesis (Fischer), reactions (Br_2/HOAc, $CHCl_3$/NaOH). Quinoline: Synthesis (Skraup), reactions (nitration, with $NaNH_2$, with $KMnO_4$/NaOH). Pyrazole: Synthesis (Fromacetyl acetone and hydrazine), reactions (nitration, bromination).

Aromatic Electrophilic Substitution Reactions: Quantitative treatment of reactivity in substrates and electrophiles. Amination, sulfonylation, diazonium coupling, Vilsmeier-Haackreaction, Gatterman reaction, Gatterman-Koch reaction and Hoesch reaction.
Aromatic Nucleophilic substitution reactions: The Goldberg reaction, Bucherer reaction, Schiemann reaction, von Richter reaction, and Sommelet-Hauser reactions.

Addition Reactions: Addition reactions of cyclopropane ring. Addition reactions of carbon- heteroatom multiple bonds: Mechanism of metal hydride reduction (NaH, LiH, $LiAlH_4$, $NaBH_4$), Grignard reagent (CH_3MgBr) and organolithium (CH_3Li) of saturated and unsaturated carbonyl compounds. Hydrolysis of nitriles with mechanism. Wittig, Mannichand Stobbe reactions.

Elimination Reactions: Effects of substrate structure, attacking base, the leaving group andthe medium on elimination reactions. Chugaev reaction

UNIT-VII

Gaseous State: Elementary aspects of kinetic theory of gases, Ideal and real gases. Boyle temperature (derivation not required), Molecular velocity, collision frequency, collision diameter, Collision cross section, collision number and mean free path and coefficient of viscosity, calculation of σ and η, variation of viscosity with temperature and pressure.Maxwell's Boltzmann distribution law of molecular velocities (Most probable, average and root mean square velocities).Relation between RMS, average and most probable velocity and average kinetic energies. (Mathematical derivation not required), law of equipartition of energy.Behaviour of real gases: Deviation from ideal gas behaviour. Compressibility factor (Z) and its variation with pressure for different gases. Causes of deviation from ideal behaviour, vander Waals equation of stat (No derivation) and application in explaining real gas behaviour. Critical phenomena - Andrews isotherms of CO_2, critical constants and their calculation from van der Waals equation, Continuity of states, Law of corresponding states. Numerical problems.

Liquid State: Surface Tension: Definition and its determination using stalagmometer, effect of temperature and solute on surface tension. Viscosity: Definition, Coefficient of viscosity. Determination of viscosity of a liquid using Oswald viscometer.Effect of temperature, size, weight, shape of molecules and intermolecular forces.

Refraction: Specific and molar refraction- definition and advantages. Determination of refractive index by Abbes Refractometer. Additive and constitutive properties.

Parachor: Definition, Atomic and structure parachor, Elucidation of structure of benzene and benzoquinone. Viscosity and molecular structure.Molar refraction and chemical constitution.

First Law of Thermodynamics: Introduction, system, surroundings, types of systems. Thermodynamic Processes (isothermal, adiabatic, isochoric, isobaric and cyclic), Nature of Heat and Work, Internal Energy, First Law of Thermodynamics, Enthalpy of a System, Work done in isothermal and adiabatic expansion of an ideal gas, Numerical problems, Joule - Thomson Expansion, Relation between Joule- Thomson coefficient and other thermodynamic parameters.

Second law of Thermodynamics: Limitations of first law of thermodynamics. Reversible and Irreversible Processes, Concept of entropy, thermodynamic scale of temperature, Statements of the Second Law of Thermodynamics, molecular and statistical interpretation of entropy, Calculation of entropy change for reversible and irreversible processes, Free Energy Functions: Gibbs and Helmholtz energy, variation of S, G, A with T, V and P, Numerical problems, Free energy change and spontaneity, Gibbs-Helmholtzequation.

Third Law of Thermodynamics: Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules.

DistributionLaw: Nernst Distribution Law - Statement and its derivation. Distribution constant, factors affecting distribution constant, validity of Distribution Law, Modification of distribution law when molecules undergo a) Association b) Dissociation. Application of Distribution Law in Solvent extraction. Derivation for simple and multiple extraction. Principles of distribution law in Parkes Process of desilverisation of lead.

UNIT-VIII

Chemical Kinetics: Introduction, rate of reaction, order and molecularity with examples. Rate constant-definition and explanation. Differential and integrated form of rate expressions up to second order reactions, Derivation of expression of rate constant of second order reaction (a=b and a ≠ b), Problems on rate constant (a=b), Methods of determination of order of a reaction (half-life method, isolation method), temperature dependence of reaction rates; Arrhenius equation, activation energy, Numerical problems on Arrhenius equation in calculating energy of activation and rate constants. Collision theory of reaction rates, Lindemann's mechanism, qualitative treatment of the theory of absolute reaction rates. Experimental determination of kinetics of (i) inversion of cane sugar by polarimetric method (ii) spectrophotometric method for the reaction between potassium persulphate and potassium iodide.

Chemical Dynamics: Arrhenius equation-characteristics, Significance of energy of activation, Temperature coefficient and its evaluation. Thermodynamical formulation of reaction rates (Thermodynamic parameters).

Surface Chemistry Adsorption: Introduction, types of adsorptions with examples. Types of adsorption isotherms. Freundlich adsorption isotherm (only equation), its limitations. Langmuir adsorption isotherm (derivation to be done) and BET equation (derivation not included).

Colligative properties: Definition and examples.

Lowering of vapour pressure: Raoult's law (to be derived), relationship between relative lowering of vapour pressure and molar mass (to be derived). Experimental determination of molar mass of the solute by Dynamic method (Numerical problems).

Elevation in boiling point: Definition, its relation to lowering of vapour pressure and molar mass (to be derived). Ebullioscopic constant of the solvent and its relation to the boiling point (only equation). Experimental determination of molar mass of the solute by Walker-Lumsden method (Numerical problems).

Depression in freezing point: Definition, its relation to lowering of vapour pressure and molar mass (to be derived). Cryoscopic constant and its relation to melting point (only equation), Determination of molar mass of non-volatile solute by Rast method (Numerical problems).

Semipermeable membrane: Definition, types with examples. Preparation of artificial semipermeable membrane (copper ferrocyanide) by Morse-Frazer method.

Osmotic pressure: Definition of osmosis, reverse osmosis and osmotic pressure. Determination of osmotic pressure by Berkely-Hartley's method (Numerical problems). Applications of osmotic pressure (mention only).

Osmotic laws and analogy with gas laws: Relationship between molar mass and osmotic pressure (to be derived). Isotonic solutions, plasmolysis and haemolysis. Abnormal molecular mass, causes, vant Hoff's factor.

Phase equilibria: Definition of the terms-phase, component and degree of freedom with examples. Statement of Gibb's phase rule and its thermodynamic derivation. Applications: (a) one component system (water system); (b) reduced phase rule and reduced system, two component system (Silver-lead system, eutectic type), desilverization of lead and FeCl3-H2O system (congruent melting point). Freezing mixtures: Definition and examples, explanationbased on KI-water system.

UNIT-IX

Ionic equilibria: Ionic equilibria in aqueous solutions, strong and weak electrolytes-definition and examples. Ostwald's dilution law (to be derived) and its limitations. Debye-Huckel theory of strong electrolytes (relaxation time, electrophoretic effect and viscous effect). Activity and activity coefficient-definition and their relation. Hydrolysis of salts-Derivation of hydrolysis constant and degree of hydrolysis of the salt of weak acid and weak base (ammonium acetate as an example), effect of temperature on degree of hydrolysis. (Numerical problems).

Electrochemistry – I: Introduction, strong and weak electrolytes, definition with examples. Arrhenius theory of electrolytic dissociation. Merits and Demerits, Conductance, Specific conductance, equivalent and molar conductivity and their variation with dilution. Molar conductivity at infinite dilution. Numerical problems.
Kohlrausch's law of independent migration of ions and its applications, Debye-Hückel-Onsager equation. Ionic mobilities and their determinations, transference numbers and their relation to ionic mobility's, determination of transference numbers using Hittorf and Moving Boundary methods.
Applications of conductance measurement: (i) Degree of dissociation of weak electrolytes (ii) ionic product of water (iii) solubility and solubility product of sparingly soluble salts (iv) conductometric titrations (acid base titrations only) and (v) Hydrolysis constants of salts.

Electrochemistry-II: Electrolytic and Electro chemical cells (galvanic cells)-Daniel cell (construction, working and cell reaction). Reversible and irreversible cells, rules for representation of a cell, single electrode potential, Standard electrode potential, sign convention for electrode potential, Nernst equation for single electrode potential.

Reference electrodes: Calomel electrode, Ag-AgCl electrode**.** Weston standard cell (Construction, working, reaction and standard emf). Equilibrium constant and free energy of a cell reaction, Concentration cell with transport (example) concentration cell without transport, EMF of concentration cell (derivation). Liquid junction potential. Salt bridge. Application of concentration cell: Valency of ions and solubility product of sparingly solublesalt.

Photo chemistry: Laws of photochemistry: Grothus-Draper's law, Stark-Einstein law of photochemical equivalence. Quantum efficiency: definition, reasons for low quantum yield and high quantum yield with examples (formation of HBr and formation of HCl). Actinometers: Uranyl oxalate actinometer, Potassium ferrioxalate actinometer (Qualitativestudy). (Numerical problems).

Photo physical processes: Jabolonski diagram, photosensitization (mercury as an example), photoinhibition, fluorescence and phosphorescence, mechanism chemiluminescence and bioluminescence (explanation with examples), (qualitative).

UNIT-X

Titrimetric analysis: Basic principle of titrimetric analysis. Classification, Preparation and dilution ofreagents/solutions.Normality, Molarity and Mole fraction. Use of $N_1V_1 = N_2V_2$ formula, Preparation of ppm level solutions from source materials(salts),conversion factors. Quantitative applications – selecting and standardizing atitrant, inorganic analysis-alkalinity, acidity. **Complexometric titrimetry**: Indicators for EDTA titrations - theory of metal ion indicators, titration methods employing EDTA - direct, back, displacement and indirect determinations, Application- determination of hardness of water.

Precipitation titrimetry: Precipitation titrations involving silver nitrate-Volhard's and Mohr's methods and their differences. **Gravimetric Analysis**: Reagents used in gravimetry (8-hydroxyquinoline(oxine) and dimethylglyoxime(DMG).

Qualitative analysis of inorganic mixtures and organic compounds

Fundamentals of chromatography: General description, definition, terms and parameters used in chromatography, classification of chromatographic methods, criteria for selection of stationary and mobile phase and nature of adsorbents. Principles of paper, thin layer, column chromatography. Column efficiency, factors affecting the column efficiency, vanDeemter's equation and its modern version.

Ion exchange chromatography: resins, types with examples- cation exchange and anion exchange resins, mechanism of cation and anion exchange process and applications of ion- exchange chromatography (softening of hard water, separation of lanthanides,industrial applications).

Errors and treatment of analytical data: Errors: Determinate and indeterminate errors, absolute error, relative error, minimization of errors. Statistical treatment of finite samples -mean, median, range, standard deviation and variance. External standard calibration - regression equation (least squares method), correlation coefficient (R^2).