Syllabus for Ph.D. Entrance Test in Chemistry

UNIT – I

Errors in Analytical Measurements: Measurement errors, absolute and relative error, determinate and indeterminate errors. Assessment of accuracy and precision. Significance testing-t-F-and Q-tests, Calibration and linear regression. Acid-base titrations - indicators and applications. Complexation, precipitation and redox titrations. Gravimetry - conditions of precipitation, co-precipitation and post-precipitation, PFHS, Organic precipitating agents, Examples of gravimetric analysis.

Potentiometric Electrodes and Potentiometry: Indicator and reference electrodes, glass pH electrode, Ion-selective electrodes, Solid-state ISFET electrodes, Direct potentiometry and potentiometric titrations.

Electrogravimetry and Coulometry: Effect of current on cell potential, Ohmic potentials; IR drop, Polarization effects. Electrogravimetric methods - Electrogravimetry without potential control, controlled potential electrogravimetry, Instrumentation and applications. Coulometric methods - Controlled potential coulometry and coulometric titrations, Principles, Instrumentation and applications.

Voltammetry: Excitation signals, linear sweep voltammetry, Voltammetric instruments, Voltammetric electrodes, Voltammograms, Hydrodynamic voltammetry, Voltammetric detectors, Amperometric sensors, Amperometric titrations. Polarography, Pulse polarographic and voltammetric methods, Cyclic voltammetry and stripping methods.

Thermal Methods of Analysis: Thermogravimetry, Differential thermal analysis and differential scanning calorimetry, Thermomechanical analysis, Evolved gas analysis and Thermometric titrations.

UNIT – II

Molecular Fluorescence Spectroscopy: Theory - relaxation processes, Factors affecting fluorescence, Effect of concentration on fluorescence intensity, Fluorescence instruments, Applications of fluorescence methods. Molecular phosphorescence spectroscopy, Chemiluminescence methods.

Atomic Spectrometric Methods: Flame emission spectrometry and Atomic absorption spectrometry.

Analytical Separations: Solvent extraction - Distribution co-efficient, Distribution ratio, Percent extracts, Solvent extraction of metals.

Chromatography: Principles, Classification of chromatographic techniques, Theory of column efficiency in chromatography.

Gas Chromatography: Performing GC separations, GC columns and detectors, temperature selection, Quantitative measurements, Headspace analysis, Thermal desorption, purging and trapping, GC-MS.

Liquid Chromatography: HPLC - Principles, Stationary phases, Equipment for HPLC. HPLC method development, Fast liquid chromatography, LC-MS.

Ion-exchange Chromatography: Cation and anion resins, Ion-chromatography.

Size-exclusion chromatography and Affinity chromatography.

Thin Layer Chromatography: Principles, methodology, instrumentation and applications. Capillary chromatography and Capillary gel electrophoresis.

UNIT – III

Chemical Periodicity: Important periodic properties of the elements, covalent radii, ionic radii, ionization potential, electron affinity and electronegativity.

Structure and Bonding: Properties of ionic compounds, structure of crystal lattices (NaCl, CsCl, ZnS, Wurtzite and rutile), Lattice energy, Born-Haber Cycle, radius ratio rules and their limitations. MO treatment for homo- and heteronuclear molecules. VSEPR model to simple molecules.

Concepts of Acids and Bases: Lux-Flood and solvent system concepts. Hard-soft acids and bases.

Non-aqueous Solvents: Protic solvents (anhydrous H_2SO_4, HF and glacial acetic acid), aprotic solvents (liquid SO_2 and N_2O_4).

d-block and f-block Elements: General properties, comparison of 3d, 4d and 5d elements. Spectral and magnetic properties of compounds of actinides in comparison with those of lanthanides and d-block elements.

UNIT – IV

Coordination Compounds: Preparation of complex compounds, Stability of complex ions in solution, Coordination number and geometry, Bonding in coordination compounds, Electronic spectra and magnetic properties. Reactions of coordination compounds.

Organometallic Compounds: Fundamental concepts, Preparation, structure and bonding in metal carbonyls (nickel, cobalt, iron and manganese), nitrosyls, alkene and ferrocene.

Homogeneous and Heterogeneous Catalysis: Alkene hydrogenation, the Wacker process, Monsanto acetic acid process and water-gas shift reaction and Ziegler-Natta catalysis.

Bio-inorganic Chemistry: Survey of essential and trace elements in biological system, Porphyrin system, Function of haemoglobin and myoglobin, Model compounds for oxygen carriers (cobalt and iridium). Photosystem and nitrogen fixation. Bio-inorganic aspects of cisplatin and auranofin. ***Treatment of toxicity due to inorganics:*** arsenic, lead, iron, cyanide and carbon monoxide.

Electron Transport Proteins and Metalloenzymes: Iron-sulfur proteins and cytochromes, catalase and peroxidase, superoxide dismutase, xanthine oxidase, aldehyde oxidase, carboxy peptidase-A and alcohol dehydrogenase.

UNIT – V

IUPAC nomenclature of organic compounds, **Structure and Reactivity:** Acids and bases, Structural effects on acidity and basicity, Hydrogen bonding, Resonance, Inductive and hyperconjugation effects, Concepts of aromaticity

Reaction Intermediates: Carbocations, Carbanions, Free radicals, Carbenes, Nitrenes, Nitrogen, sulphur and phosphorous ylides

Stereochemistry: Principles, Conformational analysis, Isomerism, Chirality

Reaction Mechanisms: Mechanism of aliphatic and aromatic nucleophilic and electrophilic substitution reactions, Elimination reactions, Addition reactions and mechanisms of reactions of carboxylic acids and their derivatives

Photochemistry and Pericyclic Reactions: Jablonski diagram, Sensitizers, Quenchers, Photochemistry of olefins, conjugated dienes, aromatic compounds, ketones, enones, Paterno-Buchi reaction, Di-pi-methane rearrangement, Electrocyclic, Cycloaddition and Sigmatropic reactions

Heterocyclic Chemistry: Synthesis, typical reactions and applications of 3-, 4-, 5-, 6-membered and fused ring systems

UNIT – VI

Oxidation and Reduction: Oxidation with chromium and manganese compounds, Peroxides, Peracids, Lead tetraacetate, Periodic acid, OsO_4, SeO_2, NBS, Chloramine-T, Sommelet oxidation, Oppenauer oxidation; Catalytic hydrogenations, Wilkinson's catalyst, Bakers yeast, $LiAlH_4$, $NaBH_4$, Birch reduction, Leukart reaction, Hydroboration, Meerwein-Ponndorf-Verley reduction, Wolf-Kishner reduction, Clemenson reduction

Molecular Rearrangements: involving carbon to carbon, carbon to nitrogen and miscellaneous rearrangements

Reagents: Gilmann reagent, DCC, DDQ, trimethyl silyl halides, PTC, Crown ethers, LDA, Tri-butyl tin hydride, Ziegler-Natta catalyst, Diazomethane, Stannous chloride, Sharpless epoxidation, Woodward and Prevost hydroxylation, Peterson reaction, Reformatsky reaction, dithiane, Wittig reaction

Introduction to Disconnection Approach: Basic principles and terminologies used, Synthons and Synthetic equivalents, One group C-X and two group C-X disconnections and applications to simple organic molecules

Named Reactions: Mechanism and synthetic applications of aldol condensation, Claisen-Schmidt, Perkin, Knoevenagel, Stobbe, Darzens glycidic ester condensation, Cannizaro's, Tishchenko, Michael addition and Robinson's annulation reactions

UNIT – VII

Quantum Chemistry: deBroglie equation, Heisenberg Uncertainty principle, operators, Schrodinger wave equation for particles, Application to a particle in 1D & 3D-box systems, H-atom, Rigid rotator and Harmonic oscillator.

Nuclear Chemistry: Radioactive decay, Half life, Liquid drop nuclear model, Definition of curie, Magic number, alpha and beta decay, Binding energy, Oppenheimer-Phillips process, Spallation reactions, Bethe's notation, Nuclear reactions.

Photochemistry: Laws of photochemistry, Quantum yield and its determination, Actinometry, Photosensitization, Photodimerization, Photo catalyst/ZnO, - its application in photo degradation, Photochemical kinetics, Photophysical properties.

Units in radiation chemistry, G-value, Fricke dosimeter, Radioisotopes as tracers, Isotope exchange reactions, Radiometric titration, ^{14}C dating.

Crystallography: X-ray crystallography, Miller indices, Bragg equation, Powder and rotating crystal technique, Fourier series, Electron diffraction, Wierl equation.

Nano particle, nano wires and nano rods, Sol-gel and electrochemical methods.

UNIT – VIII

Electrochemistry: Debye-Huckel theory of strong electrolytes, Debye-Huckel-Onsager equation, Debye-Huckel limiting law, Theories of electrical double layer, Concentration cells, Liquid junction potential, Over voltage, Conductometric and potentiometric titrations, Electrophoresis and zeta potential, True, apparent and abnormal transport numbers, Corrosion inhibition & prevention, Polarography.

Chemical Kinetics: Arrhenius equation, Energy of activation & its determination, Order of reaction, parallel, consecutive & reversible reactions. Simple collision and activated complex theory, Salt effects, Effect of pressure on rates of reactions, Langmuir's theory of surface reactions. Experimental techniques of fast reaction kinetics, Chain reactions, Linear free energy relationship, Hammett & Taft equations, Swain-Scott and Edward equation, Kinetic isotope effect.

Thermodynamics: Concept of entropy & free energy, Helmholtz and Gibbs free energies, Maxwell relations, Third law of thermodynamics, Partial molar properties, Chemical potential, Gibb's Duhem equation, Fugacity, Raoult's law & Henry's law, Heat capacity of solids, Phase rule & its applications, Principle of equipartition of energy, Relation between thermodynamic probability & entropy, Maxwell-Boltzman distribution equation, partition function.

Polymers: Classification and determination of molecular weights, condensation and addition polymers, Polydispersity of polymers, degree of polymerization, co-polymers.

Bio-physical Chemistry: Pharmaco kinetics – Drug-plasma time kinetics, Bio-availability of a drug and first order kinetics.

UNIT – IX

Basic Concepts of Molecular Symmetry and Group Theory: Symmetry elements and symmetry operations, Correlation of Schoenflies and Hermann-Maugin symbols for symmetry elements, Multiplication tables for the symmetry operations of simple molecules, Properties and definition of group theory, Point groups of simple molecules

Basic Principles and Application of Spectroscopy: Electromagnetic radiation, Types of molecular spectra

Microwave Spectroscopy: Rotation spectra of diatomic molecules (rigid and non-rigid rotators), their moment of inertia and bond lengths determination, Classification of polyatomic molecules

Vibration Spectroscopy: Harmonic and anharmonic oscillator, Vibration-rotation of diatomic molecules, Vibration of polyatomic molecules, Fermi resonance, Force constant

Raman Spectroscopy: Stokes and anti-stokes lines, theories of Raman spectra (classical and quantum), Rotation and vibration Raman spectra, Advantages of Raman spectra

Physical characterization of inorganic compounds by NQR, ESR and Mossbauer Spectroscopy

UNIT – X

UV-Vis Spectroscopy: Beer's law, Types of absorption bands (n-π^*, π-π^*, n-σ^*, σ-σ^*), Instrumentation (single and double beam), Qualitative and quantitative applications, Chromophores, Auxochromes, Solvent effect, Effect of polarity on various type of bonds, Predicting λ_{max} using Woodward's empirical rules of simple compounds

IR Spectroscopy: Instrumentation of IR spectrometers (single and double beam), Characteristic group frequencies, Finger print region, Identification of functional groups, Tautomerism, Cis-trans isomerism, Applications

Mass Spectroscopy: Principle, Instrumentation, Molecular ion, Base peak, Meta-stable peak, Nitrogen rule, Mclafferty rearrangement, Mass spectral fragmentation of some simple organic compounds

NMR Spectroscopy: Principle, Relaxation processes, Chemical shift and factors affecting it, Spin-spin coupling, Simplification of complex spectra, Contact shift reagents, Double resonance, NOE; ^{13}C NMR spectroscopy and its comparison with ^{1}H NMR, Multiplicity, Proton decoupling, Application of ^{13}C NMR, NMR of ^{19}F, ^{31}P, ^{11}B and ^{15}N, Two-dimensional NMR spectroscopy, Composite problems involving UV-Vis, IR, NMR and mass for structural elucidation of simple organic compounds

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