SCHEME FOR ENTRANCE EXAMINATION FOR Ph.D. COURSE IN CHEMISTRY

NOTE: Paper will consist of 100 objective type questions in two parts. The questions should be distributed uniformly throughout the Syllabus.

**Part-I:** 50 objective type questions on Research and Methodology. 100 Marks
**Part-II:** 50 objective type questions on subject. 100 Marks
**Time Allowed:** 2 hours  Max. Marks 200

SYLLABUS FOR PART-I (OBJECTIVE)

**Elementary Knowledge of computers.**
History of development of computers, Mainframe, mini, micro, and super computer systems. General awareness of computer Hardware i.e. CPU and other peripheral devices (Input, Output and auxiliary storage devices). Basic knowledge of computer system software and programming languages.

**Analytical aspects of Chemistry** Statistical analysis and validation: Errors in chemical analysis, Classification of errors: systematic and random, additive and proportional, absolute and relative. Accuracy and precision; Mean, median, average deviation and standard deviation. Correlation coefficient and regression analysis; Certified reference materials (CRMs), Fitting of curve to data point, Least square curve fitting, Significance relationship between dependent and independent variables, F-test t-test and chi square test, understanding analysis of variance (ANOVA).

**Principles of Separation:** Principle and applications of Paper chromatography, Thin Layer chromatography, Column chromatography, Ion exchange. Gas chromatography & High performance liquid chromatography, Solvent extraction.

**Atomic and molecular Spectroscopy:** Principle, instrumentation and applications of Spectrophotometry, Flame Photometry, Atomic absorption spectroscopy

**Electroanalytical techniques:** Conductance studies: Concepts of electrical resistance, conductance, resistivity and conductivity, Specific, Molar and equivalent conductance. Conductometric titration curves.

**EMF studies:** Circuit diagram of simple potentiometer, Indicator electrodes: hydrogen electrode, quinhydrone electrode, antimony electrode and glass electrode, Reference electrodes: Calomel electrode and Ag/AgCl electrode, Nernst equation, standard electrode potential Buffers and Burrer capacity. pH of buffer mixtures based on Henderson-Hasselbalch equation.

**Polarography:** Principle, instrumentation with special reference to dropping mercury electrode, working and applications of Polarography.

**Spectral Studies:** Theoretical treatment of rotational, vibrational and electronic spectroscopy. Principle of spin magnetic resonance, resonance spectroscopy, Mossbauer and photoelectron spectroscopy; group theoretical treatment of Vibrational and Raman spectroscopy.

Applications of the Mass, UV-VIS, IR and NMR, in the elucidation of simple organic compounds.

Characterisation of inorganic compounds by IR, Raman, UV-VIS, NMR, EPR, Mossbauer, electron spectroscopy and microscopic techniques.

Application of PES and ESCA and Auger in study of Surfaces.

Principle and applications TG, DTA and DSC Techniques.

**IUPAC nomenclature of organic and inorganic molecules.**
SYLLABUS FOR PART-II (SUBJECTIVE)

INORGANIC CHEMISTRY

Bonding: Concept of hybridization, Molecular orbitals approach of homo and hetero nuclear diatomic molecules, VSEPR Theory - Shapes of polyatomic molecules. Symmetry elements and point group of simple molecules.

Main group elements and their compounds: Allotropy of carbon, phosphorous and Sulphur, Classification, nomenclature, structure, bonding of main group compounds: boranes, metalloboranes, carboranes, metallacarboranes, silicones, carbides, phosphazenes and sulphur –Nitrogen Compounds.


Organometallic chemistry: Metal carbonyls preparation, structure and bonding. Vibrational spectra of metal carbonyls, important reactions of transition metal carbonyls, Carbonyl clusters.

Organometallic Reactions: Oxidative addition, reductive elimination, insertion reactions; catalytic reactions: Hydrogenation, polymerization, hydroformylation and Wacker Process.

Bioinorganic chemistry: photosystems, porphyrins, metalloenzymes, oxygen transport, electron- transfer reactions; nitrogen fixation.

PHYSICAL CHEMISTRY

Bronsted and Lewis acids and bases, pH and pKa, acid base concept in non aqueous solvent, HSAB concept and Buffer solutions.

Basic principles of quantum mechanics: Postulates; operator algebra; exactly-solvable systems: particle-in-a-box, harmonic oscillator and the hydrogen atom, including shapes of atomic orbitals; Approximate methods of quantum mechanics: Application to the Helium atom.

Thermodynamics: First law of thermodynamics, relationship between C_p and C_v, enthalpies of physical and chemical changes, temperature dependence of enthalpies. Second law of Thermodynamics, entropy Gibbs Helmholtz s equation. Third law of thermodynamics and calculation of entropy

Chemical equilibrium: Free energy and entropy of mixing, partial molar quantities, Gibbs Duhem equation, Equilibrium constant, temperature dependence of equilibrium constant, phase diagram of one and two component systems, Phase rule.

Chemical Kinetics Concepts of order and molecularity of reaction, pseudo-molecular reactions, Rate expressions for first and second order reactions, Temperature dependence of chemical reaction rates. Arrhenius equation, Energy of activation, Collision theory and its limitations, stearic factors, comparison of results with Eyring and Arrhenius equation.
Surface Chemistry Recapitulation of surface tension, Adsorption: freundlich adsorption isotherm, Langmuir theory, Gibbs adsorption isotherm, BET theory and estimation of surface area,

**Macromolecules:** Number –average and weight average molecular weights. Determination of molecular weights, kinetics of polymerization, stereochemistry and mechanism of polymerization.


**Statistical thermodynamics:** Thermodynamic probability and entropy, Maxwell-Boltzman, Bose-Einstein and Fermi-Dirac statistics. Partition function: rotational, vibrational, translational and electronic partition functions for diatomic molecules.

**Dislocation in solids,** Schottky and Frenkel defects, Electrical properties of insulator, semiconductor, superconductors, band theory of solids, Solid state reactions

**ORGANIC CHEMISTRY**

**Nature and Bonding in Organic Molecule:** Hyper-conjugation, Aromaticity in benzenoid and non-benzenoid compounds, alternant and non-alternant hydrocarbon Hückel’s rule,

**Stereochemistry:** Recognition of symmetry elements and chirality, R and S ; and E and Z nomenclature. Diastereoisomerism in acyclic and cyclic systems, Conformational analysis of cycloalkanes, molecules with more than one chiral center, meso compounds, threo and erythro isomers, inter conversion of Fischer and Sawhorse projections.

**Common organic Reactions and Mechanism:**

Generation, structure, stability and chemical reactions involving carbocations, carbanions, free radical carbenes, and nitrenes. Types of mechanism, labelling and Kinetic isotope effects. Hammet equation (sigma-rho) relationship, Types of reactions: Nucleophilic, Electrophilic radical substitution, addition and elimination reactions, thermodynamics and kinetics requirements, non classical carbonium ions neighboring group participation.

**Some important name reactions:** Aldol, Knoevenigel, Claisen, Mannich, Benzoin, Perkin, Stobbe and Dieckmann condensation. Friedel-Crafts reaction, Reimer-Tieman reaction, Gatterman-Koch reaction, Diazonium coupling.

Hofmann, Schmidt, Lossen, Curtius, Beckmann, Fries rearrangement

Pinacol-Pinacolone, Favoriski, Baeyer-Villiger Oxidation, Reformatsky and Diel-alder reactions, Witting reactions, Robinson annulations.

Hydroboration , Oppenaur oxidation, Clemmensen , Wolff Kishner , Meerwein-Pondorf – Verley and Brich Reductions.

**Reactions using Grignard Reagent.**

**Heterocyclic Chemistry:** Synthesis and reactivity of furan, thiophene, Pyrrole pyridine, isoquinoline and indole Skarup synthesis and Fischer Indole synthesis.