Scheme for Entrance Examination for Ph.D. Course in Chemistry

Paper No.	Nomenclature of the paper	Max. Marks	Time Allowed
I	Objective type	100	1hr.
II	Chemistry (Descriptive)	100	2 hrs.

Paper I will consist of objective type questions (50 questions) with major emphasis on research methodologies, aptitude of scientific and quantitative reasoning, elementary knowledge of computer science and general awareness of chemical sciences.

SYLLABUS FOR PAPER -I

1. COMMON ELEMENTRY KNOWLEDGE OF COMPUTER

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 systems software and programming language.

2. CHEMICAL SCIENCES

Structure and Bonding: Concept of hybridization. Molecular orbitals and electronic configuration of homonuclear and heteronuclear diatomic molecules. Shapes of polyatomic molecules; VSEPR, theory. Symmetry elements and point groups for simple molecules. Bond lengths, bond angles, bond order and bond energies. Types of Chemical Bond (weak and strong) intermolecular forces, structure of simple ionic and covalent solids, lattice energy.

Acids and Bases: Bronsted and Lewis acids and bases, pH and pKa, acid-based concept in non-aqueous media; HSAB concept. Buffer solution.

Redox Reactions: Oxidation numbers. Redox potential. Electrochemical series. Redox indicators.

Energetics and Dynamics of Chemical Reactions: Law of conservation of energy. Energy and enthalpy of reactions. Entropy, free-energy, relationship between free energy change and equilibrium. Rates of chemical reactions (first-and second -order reactions). Arrhenius

equation and concept of transition state. Mechanisms, including SN1 and SN2 reactions, electron transfer reactions, catalysis. Colligative properties of solutions.

Aspects of s.p.d.f. Block Elements: General characteristics of each block. Chemical principles involved in extractions and purification of iron, copper, lead, zinc and aluminium. Coordination chemistry: structural aspects, isomerism, octahedral and tetrahedral crystal - field splitting of d-orbitals. CFSE, magnetism and colour of transition metal ions. Sandwich compounds, metal carbonyls and metal clusters. Rare gas compounds, non-stoichiometric oxides. Radio activity and transmutation of elements. Isotopes and their applications.

IUPAC Nomenclature of Simple Organic and Inorganic Compounds.

Concept of Chirality: Recognition of symmetry elements and chiral structures; R-S nomenclature, diastereoisomerism in acyclic and cyclic systems; E-Z isomerisms. Conformational analysis of simple cyclic (chair and boat cyclohexanes) and acyclic systems. Interconversion of Fischer, Newman and Sawhorse projections.

Common Organic Reactions and Mechanisms: Reactive intermediates. Formation and stability of carbonium ions, carbanians, carbenes, nitrenes, radicals and arynes. Nucleophilic, electrophilic, radical substitution, addition and elimination reactions. Familiar name reactions: Aldol, Perkin, Stobbe, Dieckmann condensations; Hofmann, Schmidt, Lossen, Curtius, Beckmann and Fries rearrangements; Reimer -Tiemann, Reformatsky and Grignard reactions. Diels -Alder reactions; Clasien rearrangements; Friedel -Crafts reactions; Wittig reactions; and Robinson annulation. Routine functional group transformations and interconversions of simple functionalities. Hydroboration, Oppenaur oxidations; Clemmensen, Wolff- Kishner, Meerwein-Ponndorf-Verley and Birch reductions.

Spectral Techniques: Elementary principles and applications of electronic, vibrational, NMR, EPR and Mass Spectral techniques to simple structural problems.

SYLLABUS FOR PAPER-II

Twenty five (25) questions will be set in all. Question no. 1 of 20 marks relating to research methodology is compulsory. From the remaining 24 questions of general nature of the subject carrying 10 marks each, the candidates are required to attempt any 8 questions.

Chemistry of Non-transition Elements: General discussion on the properties of the nontransition elements; special features of individual elements; synthesis, properties and structure of their halides and oxides, polymorphism of carbon, phosphorus and sulphur. Synthesis, properties and structure of boranes, carboranes, borazines, silicates carbides, silicones, phosphazenes, sulphur -nitrogen compounds: peroxo compounds of boron, carbon and sulphur; oxy acids of nitrogen, phosphorus, sulphur and halogens, interhalogens pseudohalides and noble gas compounds.

Chemistry of Transition Elements: Coordination chemistry of transition metal ions; Stability constants of complexes and their determination; stabilization of unusual oxidation states. Stereochemistry of coordination lcompounds. Ligandfield theory, splitting of d-orbitals in low-symmetry environments. Jahn- Teller effect; interpretation , of electronic spectra including charge transfer spectra; spectrochemical series, nephelauxetic series Magnetism: Dia-, para-, ferro- and antiferromagnetism, quenching of orbital angular moment, spinorbit coupling, inorganic reaction mechanisms; substitution reactions, trans effect and electron transfer reactions, photochemical reaction of chromium and ruthenium complexes. Fluxional molecules iso-and heteropolyacids; metal clusters. Spin crossover in coordination compounds.

Chemistry of Lanthanides and Actinides: Spectral and magnetic properties; Use of lanthanide compounds as shift reagents.

Organometallic Chemistry of Transition Elements: Synthesis, structure and bonding, organometallic reagents in organic synthesis and in homogeneous catalytic reactions (hydrogenation, hydroformaylation, isomerisation , and polymerization); pi-acid metal complexes, activation of small molecules by coordination.

Topics in Analytical Chemistry: Adsorption partition, exclusion electrochromatography, Solvent extraction and ion exchange methods. Application of

atomic and molecular absorption and emission spectroscopy in quantitative analysis Light scattering techniques including nephelometry and Raman spectroscopy. Electronalytical techniques: voltammetry, cyclic, voltammetry, polarography, amperometry, coulometry and conductometry ion-elective electrodes. Annodic stripping voltammetry; TGA, DTA, DSC.

Bioinorganic Chemistry: Metal ions in Biology, Molecular mechanism of ion transport across membranes; ionophores. Photosynthesis, PSL, PSH; nitrogen fixation, oxygen uptake proteins, cytochromes and ferrodoxins.

Solids: Dislocation in solids, Schottky and Frenkel defects, Electrical properties; Insulators and semiconductors; superconductors; band theory of solids, Solid-state reactions.

Quantum Chemistry: Planck's quantum theory, wave-particle duality. Uncertainty-Principle,. operators and commutation relations: postulates of quantum mechanics and Schrodinger equation: free particle, particle in a box, degeneracy, harmonic oscillator, rigid rotator and the hydrogen atom. Angular momentum, including spin; coupling of angular momenta including spin-orbit coupling.

The variation method and perturbation theory. Application to the helium atom; antisymmetry and Exclusion Principle, Slater determinantal wave functions. Terms symbols and spectroscopic states.

Born-Oppenheimer approximation. Hydrogen molecule ion. LCAO-MO and VB treatments of the hydrogen molecule; electron density, forces and their role in chemical binding. Hybridization and valence MOs of H_2O, NH_3 and CH_4. Huckel pi-electron theory and its applications to ethylene, butadiene and benzene. Idea of self-consistent fields.

Spectroscopy: Theoretical treatment of rotational, vibrational and electronic spectroscopy. Principles of spin magnetic resonance spectroscopy, Mossbauer and photoelectron spectroscopy, group theoretical treatment for vibrational and Raman spectroscop

Thermodynamics: First law of thermodynamics, relation between C_p and C_V; enthalpies of physical and chemical changes; temperature dependence of enthalpies. Second law of thermodynamics, entropy, Gibbs-Helmoholtz 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.

Ideal and Non-ideal solutions. Excess functions, activities, concept of hydration number: activities in electrolytic solutions; mean ionic activity coefficient; Debye-Huckel treatment of dilute electrolyte solutions.

Electrochemistry: Electrochemical cell reactions, Nernst equation, Electrode Kinetics, electrical double layer, electode/electrolyte interface, Batteries, primary & secondary Fuel Cells, corrosion and corrosion prevention.

Surface Phenomena: Surface tension, adsorption on solids, electrical phenomena at interfaces, including electrokinetic, micelles and reverse micelles: solubilization, micro-emulsions. Application of photoelectron spectroscopy. ESCA and Auger spectroscopy to the study of surfaces.

Statistical Thermodynamics: Thermodynamic probability and entropy; Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Partition function: rotational, translational, vibrational and electronic partition functions for diatomic molecules; calculations of thermodynamic functions and equilibrium constants.

Non-equilibrium Thermodynamics: Postulates and methodologies, linear laws, Gibbs equation, Onsager reciprocal theory.

Reaction Kinetics: Methods of determining rate laws. Mechanisms of photochemical, chain and oscillatory reactions. Collision theory of reaction rates; steric factor, treatment of unimolecular reactions. Theory of absolute reaction rates, comparison of results with Eyring and Arrhenius equations. Ionic reactions: salt effect. Homogeneous catalysis and Michaelis-Menten kinetics; heterogeneous catalysis.

Fast Reaction: Luminescence and Energy transfer processes. Study of kinetics by flow techniques, relaxation methods, flash photolysis technique.

Macromolecules: Number-average and weight average molecular weights; Determination of molecular weights. Kinetics of polymerization. Stereochemistry and mechanism of polymerization.

Aromaticity: Huckel's rule and concept of aromaticty (n) annulenes and heteroannulenes, fullerenes (C60)

Stereochemistry and conformational Analysis: Asymmetric synthesis: enantio and diastereo selective synthesis, Cram's rule and Prelog generalization. Effects of conformation on reactivity in acyclic compounds and cyclohexanes. Stereochemistry of Biphenyls, allenes and spiranes.

Selective Organic Name Reactions: Favorskii reaction; Stork enamine reaction; Michael addition, Mannich Reaction; Sharpless asymmetric epoxidation; Ene reaction, Barton reaction, Shapiro reaction, Bacyer-Villiger reaction.

Mechanisms of Organic Reactions: Labelling and Kinetic isotope effects, Hammett equation, (sigma-rho) relationship, non-classical carbonium ions, neighbouring group participation.

Pericyclic Reactions: Selection rules and stereochemistry of electrocyclic reactions, cycloaddition and sigmatropic shifts, Sommelet, Hauser, Cope and Claisen rearrangements.

Heterocyclic Chemistry: Synthesis and reactivity of furan, thiophene, pyrrole, pyridine, quinoline, isoquinoline and indole; Skraup synthesis, Fischer indole synthesis.

Reagents in Organic Synthesis: Use of the following reagents in organic synthesis and functional group transformations; Complex metal hydrides, lithium dimethylcuprate, lithium disopropylamide (LDA) dicyclohexylcarbodimide. 1,3-Dithiane (reactivity umpolung), trimethylsilyl iodide, tri-n-butyltin hybride, Woodward and prevost hydroxylation, osmium tetroxide, DDQ, selenium dioxide, Wilkinson's catalyst, Baker yeast.

Bioorganic Chemistry: Elementary structure and function of biopolymers such as proteins and nucleic acids.

Photochemistry: Cis-trans isomerisation, Paterno-Buchi reaction, Norrish Type I and II reactions, photoreduction of ketones, di-pimethane rearrangement, photochemistry of areanes.

Spectroscopy: Applications of mass, UV-VIS, IR and NMR spectroscopy for structural elucidation of organic compounds.

Drug Design: Prodrugs, Hard & Soft drugs, Structure-Activity Relationship (SAR), Bioisosterism, Theories of drug activity, QSAR-Development of QSAR, Drug Receptor interactions, Physio-Chemical parameters.

Capsules: Processing of capsules; Hard & Soft gelatin capsules, Microencapsulation; its importance & applications in pharmaceutical formulations, techniques and equipments used.

Tablets: Processing of tablets, Various additives included in formulation of tablets, coating of tablets; Principle, equipments & importance, Evaluation of coated tablets, Defects of films.

Principles of Pharmaceutical Processing: Mixing, Filtration, Drying, Compression, Humidification, Miling.

Model Test Paper for Ph.D. entrance Test 2012

Paper-I

Each question will has four alternate responses. You have to Fill (O) THE CORRECT RESPONSE IN THE BOX PROVIDED AGAINST EACH QUESTION IN THE RESPONSE SHEET

Q. 1 In $POCl_3$, the P atom shows multiple bonding of the type
(a) pπ-pπ (b) dπ- dπ (c) pπ-dπ (d) none of these

Q. 2 The compound which does not show paramaganetism is
(a) NO (b) ClO_2 (c) $[Cu(NH_3)_4]Br_2$ (d) $[Ag(NH_{3)2}]Cl$

Q. 3 Which of the following enthalpies is always negative?
(a) Enthalpy of formation
(b) Enthalpy of Solution
(c) Enthalpy of combustion
(d) Enthalpy of melting

Q. 4 What is the hybridization of Xe in the molecule $XeOF_2$
(a) sp (b) sp^3d (c)sp^3d^2 (d) sp^2

Q. 5 Bromination of aniline produces
(a) 2-bromoaniline
(b) 4-bromoaniline
(c) 2,4,6-tribromoaniline
(d) 2,6-dibromoaniline

Q. 6 Phenol gives salicyldehyde on heating with chloroform and sodium hydroxide. It is known as:
(a) Cannizaro reaction
(b) Reimer-Tiemann reaction
(c) Claisen reaction
(d) Hell-Volhard-Zelinsky reaction

Paper-II

Q. 1 (a) Sketch the metal and ligand orbitals involved in
(i)Metal –carbenes
(ii) Metal-alkynes **(2)**

(b) Discuss the stepwise replacement of water by another ligand L in $[Fe(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ based upon the above discussion, determine the metal ions in the spectrochemical series. **(4)**

(c) What structures have been assigned to the following interhalogen compounds: IF_5, IF_7 and ICl. **(3)**

(d) What happens when Molten ICl_3 is electrolysed (give reaction). **(1)**