UNIVERSITY OF MUMBAI

Syllabus

for the

PET Examination

In

CHEMISTRY

Physical Chemistry

Physical Chemistry

Quantum Chemistry, Chemical Bonding

1) **Max plank theory,** Bohr theory, Debroglies hypothesis, uncertainty principal ,operators and comuttators, postulates of quantum mechanics, Schrodinger equation, application of Schrodinger equation to particle in 1D,2D and 3 D box, concept of degeneracy, Harmonic oscillator, Rigid rotor, Hydrogen atom, radial function and spherical harmonics, shapes and representations of hydrogenic atomic orbitals, variational method, perturbation method, perturbation and variation treatment of the ground state of Helium ,many electron atoms, antisymmetry and Pauli principle, Slater rules and periodicity, R-S coupling, term symbols for He, Li, Be, and B, Valence bond and Molecular orbital theory,H_2 molecule, equivalence of VBT and MOT, VBT treatment to BeH_2 ,H_2O ,NH_3 and CH_4 molecule, Density functional theory, Huckel molecular orbital theory, bond order, charge densities and free valence index, delocalization energy, aromaticity, Application of Huckel theory to ethylene,1,3-butadiene,cyclobutadiene and benzene. VSEPR

2) Molecular Spectroscopy:

Regions of spectrum, width and Intensity of spectral lines, Fourier transform spectroscopy, microwave spectroscopy, classification of molecule, the rigid diatomic molecule, bond distance, non- rigid rotator, intensity profile in microwave spectra, infrared spectra, Morse potential, overtones and combination of hot bands, poly atomic molecule effect of isotopic substitution in microwave and infra red spectra, classical and quantum theory of Raman effect, polarizbility , stokes and antistokes lines, vibrational Raman spectra, rule of mutual exclusion principal Combining IR and Raman data to elucidate structure of molecule, electronic spectra, potential energy curve, Born Oppenheimer Approximation, Frank Condon principle , predissociation, dissociation energies from IR and electronic spectra, principles of magnetic resonance, LASER, ESR, Mossbauer and photoelectron spectroscopy

3) Thermodynamics and Electrochemistry:

First law of thermodynamics, relation between Cp and Cv, Second law of thermodynamics, Maxwell relations and its application ,dependence of enthalpy, entropy and Gibbs fee energy on pressure and temperature, fugacity and its determination ,absolute and residual entropies, Third law of thermodynamics, thermodynamics of mixings(Entropy, Gibbs free energy, Enthalpy and Volume), partial molar quantities, Gbbs-Duhem equation, Gibbs –Dhuem-Margles equation, excess functions, activities and mean ionic activity coefficient. Electrochemical cells, Half-cells reaction, Nernst equation, , liquid junction potential, strong and weak electrolyte, Debye Huckel theory, polarisation ,decomposition-potential and over voltage, batteries, primary and secondary, fuel cells.

4) Surface and Material chemistry

Adsorption, Freundlich, Langmuir and BET adsorption isotherm, surface area determination, surface excess, Gibbs adsorption equation, Micelles and reverse micelles, solubilisation, micro emulsion, basic of polymer chemistry , determination of molecular weight (number and mass average) of polymers ,crystalline and amorphous solids, crystal structure types, Dislocation in solids, Schottky and Frenkl defects, insulators, semiconductors, superconductor and band theory of solids, solid state reaction.

5) Statistical and Non equilibrium Thermodynamics

Thermodynamic probability and entropy, Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics, partition function(translational, rotational , vibrational and electronic), calculation of thermodynamic functions from partition functions, non equilibrium thermodynamics, entropy production, Onsager reciprocal relationships.

6) Reaction kinetics

Molecularity and order of reaction, reaction of fractional order, ,zero, first second and third order reaction, reversible reaction, consecutive reaction, temperature dependence and Arrhenius theory of reaction rates, collision theory of Bimolecular reaction rates, theory of absolute reaction rates, Eyring equation, enthalpy, entropy, and free energy of activation, potential energy surface accompanying simple reaction, dependence of rate constants of ionic reaction on pressure ,dielectric constant, primary and secondary salt effects, enzyme catalysis, Michaelis –Menten mechanism , lineweaver-Burk and Eadie – Hoftsee method, fast reaction, relaxation and flow techniques, oscillatory reaction, unimolecular gaseous reaction and Lindemanns mechanism, Hinselwoods theory, , Kassel,Rice and Ramsperger theory, RRKM theory

7) Group theory and symmetry:

Symmetry elements and symmetry operations, definition of group, multiplication tables, point group, determination of point group, reducible and irreducible representations, character tables, use of charactor tables, Application to chemical bonding and spectroscopy.

8) Nuclear and Radiation Chemistry:

Nuclear dimension, stability of nucleus, isotopes, isotones and isobars, nuclear forces, nuclear models (Shell, liquid drop and Fermi gas model), artificial radioactivity and nuclear reaction (fission and fusion), alpha, beta and gamma decay, measurements of radiation by GM and Scintillation –counters, isotopic dilution analysis, application of radioisotopes, neutron activation analysis

Inorganic Chemistry

Inorganic Chemistry

Main group elements and their compounds: Allotropy, synthesis, structure and bonding, industrial importance of the compounds.

Transition elements and coordination compounds: structure, bonding theories, spectral and magnetic properties, reaction mechanisms.

Inner transition elements: spectral and magnetic properties, redox chemistry, analytical applications.

Organometallic compounds: synthesis, bonding and structure, and reactivity. Organometallics in homogeneous catalysis; electron counting, sixteen electron rule and eighteen electron rule, wade's rule; isolobal analogy; metal-atom clusters.

Bioinorganic chemistry: photosystems, porphyrins, metalloenzymes, oxygen transport, electron-transfer reactions; nitrogen fixation, metal complexes in medicine; bio-mineralization; metallothionein

Inorganic Reaction Mechanisms: Rate of reactions, factors affecting the rate of reactions; Redox reactions: inner and outer sphere mechanisms; complimentary and non-complimentary reactions.

Solid state Chemistry: Structures of compounds of the type: AB, AB_2, A_2B_3, AB_3, ABO_3 (Perovskite), AB_2O_4 (normal and inverse and random spinel)

Liquid Crystals: Introduction and classification of different types of liquid crystals, polymorphism in liquid crystals, properties and applications of liquid crystals, inorganic liquid crystals.

Chemical Toxicology: toxic chemicals in the environment, biochemical effects and speciation of toxic elements like arsenic, lead, mercury and cadmium; antidotes for the toxic elements, biochemical effects of fluoride and pesticides.

Characterization of inorganic compounds by IR, Raman, NMR, EPR, Mossbauer, UV-vis, NQR, MS, electron spectroscopy and microscopic techniques.

X-ray Diffraction: K-shell knockout, Bragg condition, Miller indices, relationship between Miller indices and inter planar spacing, Methods of diffraction, JCPDS format.

Nanomaterials: Introduction to nanotechnology; capping agents, generic challenges in nanomaterial synthesis. Some important properties of nanomaterials: Optical properties of metal and semiconductor nanoparticles, Carbon nanotubes: types, synthesis using various methods, growth mechanism; quantum dots: properties and applications. Aerogels: types of aerogels, properties and applications of aerogels.Applications of nanomaterials in electronics, energy, automobiles, sports and toys, textile, cosmetics, medicine, space and defense.

Inorganic Photochemistry:Transitions between energy states, decay process, photophysical pathways, Jablonski diagram, photochemical pathways, quantum yield, Kasha's rule and Stoke shifts, non-redox processes, photo redox processes;Photosynthesis reactions; light harvesting, solar energy conversion, metal ion sensors, chemo-sensors, artificial photosynthesis.

Magnetic properties of complexes: Classification of substances according to the magnetic properties: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism;Magnetic moment, magnetic susceptibility, Curie equation and Curie temperature, Curie-Weiss law, Neel temperature; Magnetic Properties of solids: ferromagnetic and antiferromagnetic ordering, Hysteresis, Hard and soft magnets, spinels, garnets, ilmenites, perovskite and magneto-plumbites.

Electronic spectra of complexes: Determination of spectral terms for ground state and excited state, energy of terms, Hund's rules, spin orbit (L-S) coupling, selection rules and intensities, crystal field splitting of the terms in ligand field, construction of Orgel diagram and Tanabe Sugano diagram. Calculation of crystal field parameters (10Dq, B', β, β^o) from electronic absorption spectra of octahedral complexes, Charge transfer spectra.

Electrical Properties: Band structures of metals, insulators, semi-conductors and inorganic solids;

Applications of semiconductors; Thomson, Peltier and Seebeck effects, thermocouples and their applications, Hall effect, dielectric, ferroelectric, piezoelectric and pyroelectric materials and their inter-relationship and applications.

Surface Microscopy and Optical studies: Secondary ion mass spectroscopy (SIMS), Auger emission spectroscopy (AES), ESCA, scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM); Circular dichroism (CD) and optical rotatory dispersion (ORD).

Organic Chemistry

ORGANIC CHEMISTRY

Basics of stereochemistry: stereoisomerism,chiralcarbon, enantiomers, distereomers, R/S, D/L, Nomenclature, geometric isomers- E/Z, Syn/anti, configuration. Conformations, conformations of cyclohexane and decalin systems.
Resolution of racemic mixture
Prochiral carbon, Pro-R and Pro-S

Retrosynthesis: synthons/synthetic equivalent, functional group transformation, interconversions, protection and deprotection, umploung, synthesis of simple molecules- bi and tri functional, including aromatic derivatives and six membered rings.

Structural elucidations using IR/PMR/CMR/UV and mass

Reactive intermediates
Generations, structure, stability and reactions
Carbocation, carbanion and enolates, carbenes, carbon radicals, nitrene, benzyns

Name reactions: Pinacol-pinacolone
Benzidine reaction: EAS (Electrophilic aromatic substitutions), Electrophilic addition to olefins, Dundne–phenol reaction, Aldol, Michael, Mannich, Claisen ester, Dieckman,

Nucleophilic aromatic substitutions
Robinson annulations, Favorskii Benzoin, Darzen, Stobbe

Rad: McMurry Coupling, Reactions of NBS, HBr addition to olefin in presence of H_2O_2, Acyloin condensation.
Carbenes: Simmon Smith, Riemann Teimer reaction, insertion reactions.
Nitrenes: Beckman, **Curtius**, Schmidt, Lossen, **Arndt**–**Eistert** synthesis.

Analytical Chemistry

Analytical Chemistry

1. **Language ofAnalytical Chemistry.**
2. **Treatment to analytical data:** Errors (gross errors, systematic errors, random errors), accuracy, validation parameters: Accuracy, precision, mean and standard deviation, calibration, (linear response functions (linear regression-errors in slope and the intercept, error in the estimate of concentration, standard additions), non-linear response functions and weighted regression analysis, internal standards), selectivity and specificity (chromatographic methods), limits of detections (spectrophotometric methods, chromatographic methods and related techniques, receptor binding assay), limit of quantification, sensitivity, ruggedness and robustness, analyte stability in the sample matrix, how to reduce systematic errors, mean and standard deviation, reliability of results, confidence interval, comparison of results, comparison of two means of two samples, experimental design.
3. **Clssical and Instrumental Techniques**
4. **Atomic Absorption Spectrometry:** Principle, interferences, use of electro thermal analyzer, hydride generator and cold vapour for trace metal analysis. Importance of electro thermal analyzer for analysis of biological samples, level of detection; hydride generator for environmental samples and cold vapor technique for mercury analysis
5. **SEPARATION TECHNIQUES :**
   - i. **Solvent Extraction and Solid Phase Extraction:** basic concepts of solvent extraction and solid phase extraction, liquid anion cation, exchangers and crown ethers, mechanism of extraction, extraction equilibria of metal chelates, factors favoring solvent extraction of metal chelates, sorbents. Nature of extracted species. Parameters influencing extraction including e.g. role of diluents, aggregation, third phase formation and counter ion. Applications of liquid-liquid extraction in metallurgy and biotechnology Supercritical Fluid Extraction: Principles, instrumentation and applications. Solid Phase Micro Extraction: Sorbents, methodology, applications and automation.
   - ii. **Chromatography:** General classification of chromatographic methods, concept of plate and rate theories: efficiency, resolution, selectivity and separation capability. Broadening of chromatographic peak and van Deemter equation, optimization of chromatographic conditions. Ion Exchange Chromatography: Synthetic resin based ion exchangers. Type of resin matrices. Breakthrough volume and capacity. Inorganic ion exchangers, chelating ion exchangers, imprinted functional polymers, ligand exchange for separation of organic molecules and enantiomers.
   - iii. **Electrophoretic techniques**
   - iv. Size Exclusion Chromatography: Theory, type of packings, molecular mass determination. Large scale purification of large bio molecules.
   - v. Super Critical Fluid Chromatography: Instrumentation, effect of pressure, mobile phases, comparison with LC and GC. Applications.
   - vi. Membrane based Separations: Principles and applications of microfiltration, ultrafiltration, reverse osmosis, dialysis and electrodialysis. Liquid membranes.
   - vii. **Gas Chromatography:** Principle of GLC and GSC; Instrumentation: carrier gas supply, sample introduction systems, packed & capillary columns; choice of detectors and comparative account of TCD, FID, ECD & thermionic detector.

viii. **High Performance Liquid Chromatography (HPLC):** Types of liquid chromatography, column efficiency in LC; Instrument for LC: mobile phase reservoir and solvent treatment systems, pumping systems, sample introduction systems, columns, Detectors: UV, RI, EC and diode array. Modes of separation: partition, adsorption, ion exchange and size exclusion.

ix. Method development in HPLC: Sselection of stationary phases and mobile phases, gradient elution, polarity index, comparison of detectors, hybrid columns, chiral separations and PLRP-S. Concept of Preparative chromatography and UPLC.

ELECTROANALYTICAL TECHNIQUES

Electroanalytical Chemistry: Ion selective potentiometry: Basic concept, solid state, precipitate and liquid-liquid membrane, enzyme and gas sensing electrodes with applications. Introduction to modern voltammetric techniques viz., Differential pulse polarography, cyclic voltammetry and stripping (cathodic & anodic) voltammetry.

Voltammetry and polarography: Necessity and development of new voltammetric techniques and their comparison with classical DC polarography, Current sampled (TAST) polarography, Pulse (normal, differential and differential double pulse) Polarography, AC and square wave, linear sweep voltammetry and cyclic voltammetry, criteria of reversibility of electrochemical reactions, Quasi reversible and irreversible processes.

Stripping voltammetry, adsorptive stripping voltammetry, voltammetry with ultra micro electrodes chemically modified electrodes. Applications of electrochemical methods in organic synthesis.

Hyphenated Tehniques

Research Methodology

Research Methodology syllabus.

Laboratory Safety, safe practices for storage of chemicals, handling of gases and toxic volatile chemicals, first aids for chemical poisoning (Mercury, lead, carbon monoxide, nitric oxide),
Disposal of chemical waste, materials safety data sheet, fire safety

Types of research,Hypothesis, Null Hypothesis, Data Sources (Primary and secondary);
Defining and Designing a research problem; Project writing; Experimental Design; Role of case studies in research; Statistical methods in research and analysis; methods of interpretation in research;
Role of ICT and computation in research;
Presentation of research; Measure of quality in research; intellectual property affairs; legal provisions and regulatory affairs in research.