UNIVERSITY OF LUCKNOW
LUCKNOW
M.Sc. Chemistry Semester I (Core)
Inorganic Chemistry Syllabus
Paper I CH 101

Unit I

Symmetry and group Theory in chemistry:

Symmetry element and operation, definition of mathematical group, sub group, cyclic group, conjugacy relation and classes, point symmetry group (Schonflies symbols), use of point group symmetry: optical activity, dipole moment, representation of group by matrices, character of representation, the great orthogonality theorem (without proof) and its importance, irreducible representation, character table and their use.

Unit II

Stereochemistry and Bonding: Among main group compounds:

VSEPR, Walsh diagrams (tri-and penta-atomic molecules), $d\pi$-$p\pi$ bonds, Bent rule and energetics of Hybridization, some simple reaction of covalently bonded molecules

Among Transition Metal complexes:

Limitation of crystal field theory, Molecular orbital theory, Octahedral, tetrahedral and square planar complexes, π-bonding and molecular orbital theory.

Unit III

Electronic Spectra of transition metal complexes:

Spectroscopic ground states, correlation, Orgel and Tanabe-Sugano diagram for transition metal complexes (d^1 ï d^9), calculation for Dq, and b parameter, charge transfer spectra, spectroscopic method for assignment of absolute configuration in optically active metal chelates and their stereochemical information.

Unit IV

Magnetic properties of transition metal complexes and Isopoly and Heteropoly acid:

Anomalous magnetic moments, magnetic exchange coupling and spin crossover. Isopoly and Heteropoly acid and salts of V, Mo, W.

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Unit I

Nature of bonding in organic molecules

Delocalized chemical bonding-conjugation, cross conjugation, resonance, hyperconjugation, bonding in fullerenes, tautomerism.

Aromaticity in benzenoid and non-benzenoid compound, alternate and nonalternate hydrocarbon, Huckel rule, energy of p-molecular orbital, annulenes, antiaromaticity,Ɋī aromaticity homoaromaticity, PMO approach.

Bond weaker than covalent-addition compound, crown ether complexes and cryptands, inclusion compound, cyclodextrins, catenanes and rotaxane.

Aliphatic electrophilic substitution

Biomolecular mechanism ï S_E2 and S_E1. The S_E1 mechanism, electrophilic substitution accompanied by doubled bond shifts. Effect of substrates, leaving group and solvent polarity

Unit II

Stereochemistry

Conformational analysis of cycloalkanes, declines, effect of conformation on reactivity, conformation of sugars, steric strain due to unavoidable crowding.

Element of symmetry, chirality, molecules with more than one chiral center, thro and erythro isomer, methods of resolution, optical purity, enantiotopic and diastereotopic atoms, group of faces, stereospesific and stereoselective synthesis, asymmetric synthesis, optical activity in absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape.

Stereochemistry of compound containing nitrogen, sulphur and phosphorous.

Aliphatic nucleophilic substitution

The SN_2, SN_1 and SET mechanism.

The neighboring group mechanism, neighboring group participation by ´ and bond, anchimeric assistance.

Classical and nonclassical carbocations, phenonium ions, norboryl system, common carbocation rearrangement. Application of NMR spectroscopy in detection of carbocations.

The S_N1 mechanism

Nucleophilic substitution at an allylic, aliphatic trigonal and vinylic carbon.

Reactivity effect of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound, ambident nucleophile, regioselectivity.

Unit III

Reaction Mechanism: structure and reactivity

Types of mechanism, types of mechanism, thermodynamics and kinetic requirements, kinetic thermodynamic control, Hammonds postulate, Curtin-hammett principle.

Potential energy diagram, transition state and intermediates, methods of determining mechanism, isotope effect. Hard and soft acids and bases.

Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes

Effect of structure on reactivity ï resonance and field effect, steric effect, quantitative treatment. The Hammett equation and linear free energy relationship, substituent and reaction constants, Taft equation.

Unit IV

Pericyclic Reactions

Molecular orbital Symmetry, Frontier orbital of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyclic reactions. Woodward Halfmann correlation diagram, FMO and PMO approach, electrocyclic reaction ï conrotatory and disrotatory motion, 4n, 4n+2 and allyl systems. Cycloaddition ï antarafacial and suprafacial addition, 4n and 4n+2 systems, 2+2 addition of ketenes, 1,3 dipolar cycloaddition and chelotropic reactions.

Sigmatropic rearrangement ï Suprafacial and antarafacial shift of H, sigmatropic shift involving corban moieties, 3,3 and 5,5-sigmatropic rearrangement. Claisen, cope and aza-cope rearrangements. Fluxional tautomerism. Ene reaction

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Unit I

Chemical Dynamics

Theory of reaction rate: collision, activated complex and unimolecular reaction i.e. Lindemann and preliminary ideas (Hinshelwood, Rice Ramopereger and RKKM theories), thermodynamics of reaction rate.

The ideas of reaction kinetics in solution with special reference to kinetic salt effects.

The fast reaction kinetics, fundamental aspects of NMR, Relactation methods, flow and flesh photolysis. Preliminary ideas of molecular reaction dynamics.

Simple ideas of Oscillatory chemical reaction, belosov- Zhabotinsky reaction.

Photochemical reaction: Chain reaction involving Hydrogen Chlorine, Hydrogen- bromine reaction and pyrolysis if acetaldehyde. Kinetics of enzyme reaction.

Unit II

Surface chemistry

A. Adsorption

Surface tension, capillary action , pressure difference across curved surface (Laplace equation), vapor pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, estimation surface area (BET equation), surface film of liquids (electro ï kinetic phenomenon), catalytic activity at surface.

B. Micelles

Surface active agent, classification of surface active agent, micellization, hydrophobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactant, counter ion binding to micelles, thermodynamics of micellization ï phase separation and moss action models , solubilization, micro emulation, reverse micelles.

C. Macromolecules:

Polymer ï definition, classification of polymer, electrically conducting , five resistant, liquid crystal polymer, kinetics and mechanism of polymerization (Chain reaction and step growth), molecular mass, number and mass average molecular mass, molecular mass determination (Osmometry, diffusion and light scattering methods),sedimentation, chain configuration of macromolecules, calculation of average dimensions of various chain structures.

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Unit III

Electrochemistry

Activity, activity coefficient, Debye-Huckel theory for electrolytic solution, determination of activity and activity coefficient, ionic strength.

Electrochemistry of solution, Debye-Huckel ï Onsager treatment and its extension, ion solvent interaction, Debye Huckel, B Jerum mode.

Thermodynamics of electrified interface equation, deviation of electro-capillarity, Lippmann equation (surface excess), methods of determination, structure of electrified interfaces. Guoy Chapman, Stern, Bockris, Devanathan method.

Over potential, exchange current density, deviation of Butler- Volmer, Tafel plot.

Electrocatalysis ï Influence of various parameters, Hydrogen electrode.

Nernst-Planck equation, electrocardiography.

Polarography theory, likovic equation, half wave potential and its significant.

Introduction to corrosion, homogenous theory, form of corrosion, corrosion monitoring and prevention Methodism.

Unit IV

X-ray and electron diffraction

Bragg condition, miller indices, Laue method Bragg method, Debye-Scherrer method of X-ray structural analysis of crystals, index reflection, identification of unit cell from systematic absences in diffraction pattern. Structure of simple lattices and X-ray intensities, structure factor and its relation to intensity and electron density, phase problem. Description of the procedure for an X-ray structure analysis, absolute configuration of molecules, Ramchandran diagram.

Scattering intensity vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecule. Low energy electron diffraction and structure of surfaces.