

DURCET-2015

CHEMISTRY SYLLABUS

INORGANIC CHEMISTRY

Bonding in Metal Complexes

Transition metal π - complexes with unsaturated organic molecules such as alkenes, alkynes, ally, diene, dienyl, arene and trienyl complexes, General methods of preparation, properties, nature of bonding and structural features, Important reactions relating to nucleophilic and electrophilic attack on ligands and to organic synthesis.

Reaction Mechanisms in Complexes

Reactivity of metal complexes, Inert and labile complexes, Kinetics and mechanisms of substitution reactions, Kinetics of substitution reactions in octahedral complexes, Acid hydrolysis, Factors affecting acid hydrolysis, Base hydrolysis, Conjugate base mechanism, Anation reactions, Substitution reactions in square planar complexes, Trans effect, theories and applications of trans effect, Electron transfer reactions, Inner sphere and outer sphere mechanisms, Marcus theory.

Metal Ligand Equilibria in Solutions

Stepwise and overall formation constants and their interrelationship, Trends in stepwise formation constants, Factors affecting the stability of metal complexes, Chelate effect and its thermodynamic origin, Determination of binary formation constants by pHometry and spectrophotometric methods.

Metal Carbonyls

Preparation of metal carbonyls of Mn, Fe, Co and Ni, Bonding in Carbonyls, EAN in carbonyls, π bonding in carbonyls, Terminal and bridging carbonyls, Measurement of π bond strength in carbonyls, Structures of mononuclear, binuclear, trinuclear and tetranuclear carbonyls.

Metal Nitrosyls:

Metal Nitrosyls and chemistry of linear and bent nitrosyl, Nitrosyls as NO^+ and NO^- donors, Analytical uses of nitrosyl complexes.

Bio Inorganic Chemistry

Photo systems, Nitrogen Fixation, electron-transfer reactions metalloenzymes, porphyrins, oxygen transport, metal complexes in medicine.

Electronic Spectra of Complexes

Frank-Condon principle, Russell-Saunders coupling, Spectroscopic term symbol, Multiple terms of excited states (microstates), selection rules, Break down of selection rules, spin orbit coupling, Band Intensities, Orgel Diagrams for d1 to d9 configurations. Tanabe-Sugano Diagrams, Spectra of octahedral complexes of metal ions in aqueous media like Ti^{3+} , Cu^{2+} ,

V³⁺, Ni²⁺, Cr³⁺, Co²⁺, Cr²⁺, Fe²⁺, and Mn²⁺ , Spectra of spin paired configurations of Mn³⁺, Mn²⁺, Fe³⁺, Fe²⁺ and Co²⁺ , Spectra of Tetrahedral complexes of Mn²⁺, Co²⁺, Cu²⁺ and Ni²⁺, Calculation of Dq and B parameters, Charge transfer spectra.

Spectral Techniques of Inorganic Complexes

Mossbauer spectroscopy, NQR spectroscopy, Electron spin resonance spectroscopy.
Separation techniques

ORGANIC CHEMISTRY

Aromaticity

Delocalized chemical bonding, conjugation, cross conjugation, resonance, hyper conjugation, and tautomerism. Huckle's rule and the concept of Aromaticity, Aromaticity in benzenoid and non-benzenoid compounds, alternant and non-alternant hydrocarbons, Anti-Aromaticity, Pseudo-Aromaticity and Homo-Aromaticity, metallocenes- ferrocene, azulenes, fulvenes and annulenes.

Elimination Reactions

Types of β -elimination reactions-E2, E1 and E1CB mechanisms. Orientation of double bonds in elimination reactions- Saytzeff and Hofmann rules, Stereochemistry- Syn and anti eliminations. Dehydration, dehydrogenation, dehalogenation, decarboxylative eliminations, pyrolytic eliminations, molecular rearrangement during elimination.

Rearrangements

General mechanistic considerations, nature of migration, migratory aptitude, a detailed study to the following rearrangements: Pinacol-pinacolone, Wagner-Meerwein, Demjanov, Benzil-Benzilic acid, Favorskii, Arndt-Eistert synthesis, Neber, Beckmann, Hofmann, Curtius, Lossen, Schmidt, Fries, Shapiro reaction.

Methods of organic synthesis

Oxidations

Alcohols to carbonyls: Chromium (iv) oxidants-Dimethyl sulfoxide oxidation, periodate oxidation, Oppenauer oxidation, oxidation with manganese dioxide, DDQ, oxidation with silver carbonate (b) Alkenes to epoxide: peroxide induced epoxidations (c) Alkenes to diols: oxidation with potassium permanganate, osmium tetra oxide, Prevost reaction (d) Ketones to esters: Baeyer-villiger oxidation (e) Oxidative bond cleavage-cleavage of alkenes by transition metals (f) Oxidation of alkyl or alkenyl fragments: selenium dioxide and chromium trioxide oxidations.

Reductions

Reduction with lithium aluminum hydride, sodium boro hydride, alkoxides, bis-methoxy ethoxy aluminum hydride, Boron aluminum hydride and derivatives-catalytic hydrogenation-dissolving metal reductions, Non-Metallic reducing agents including enzymatic and microbial reductions

Chemistry of Organo Boron, Phosphorus and Sulfur reagents

Electronic structure and bonding in Boron, Phosphorus and Sulphur compounds – Their reactivity and applications in Organic Synthesis.

Boron Reagents

Hydroboration, Organo boranes in the formation of C-C bonds, alcohols, amines, halogen and carbonyl compounds, Free radical reactions of Organo boranes.

Phosphorus Reagents

Formation of carbon, Carbon double bonds, Functional group transformations, Deoxygenation reactions Reactivity as electrophiles and nucleophiles, Reactions of quaternary phosphonium compounds.

Sulphur Reagents

Sulphur yields, stabilized and non-stabilized, Preparation and reactivity, sulphonyl carbanions.

Organic spectroscopy

Structure determination of organic compounds by IR, UV- Vis, ^1H & ^{13}C NMR and Mass spectroscopic techniques

Polymer Chemistry

Basic concepts in polymer Chemistry

Polymer Characterization

Synthetic polymers

PHYSICAL CHEMISTRY

Quantum Chemistry

Introduction to Exact Quantum Mechanical Results

Angular momentum

Electronic Structure of Atoms

Molecular Orbital Theory

Chemical Dynamics

Methods of determining Rate laws, Collision theory of reaction rates, Steric factor, Activated complex theory, Arrhenius Equation, Treatment of unimolecular reactions, Lindemann, Lindemann – Hinshelwood. Dynamic chain, hydrogen-bromine reaction, pyrolysis of acetaldehyde, decomposition of ethane, photochemical reactions-hydrogen-bromine, hydrogen- chlorine reactions, Autocatalysis, hydrogen-oxygen reaction, explosion limits.

Thermodynamics

Classical Thermodynamics Basic concepts of laws of thermodynamics, free energy, chemical potential and entropy, partial molar properties: their significance and determination of partial molar volume, fugacity and its determination.

Statistical Thermodynamics

Concept of distribution, thermodynamic probability and most probable Distribution, Ensemble averaging, Postulates of ensemble averaging, canonical, grandcanonical and micro-canonical ensembles, partition functions, translational, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in terms of partition functions, Heat capacity, chemical equilibria and equilibrium constant in terms of partition functions, Entropy of monatomic gases (Sackur-Tetrad equation)

Electrochemistry

Strong Electrolytes

Activity and Activity Coefficients

Reversible Electrochemical Cells

Irreversible Electrode Phenomenon

Polarography

Chemical Kinetics

Effect of substituent on the rate of reaction-Hammett's and Taft's equation, use of ρ and σ constants and extended Hammett equation.

Acid-Base catalysis: Homogenous acid-base catalysis-mechanism of acid base catalysis, protolytic and prototropic mechanism.

Enzyme catalysis: Specification and classification of enzymes, Kinetics and mechanism of single substrate reaction, Michael-Menten kinetics, production, detection and estimation of free radicals.

Symmetry and Group Theory

Symmetry Elements and Symmetry operation, Definitions of a group, sub-group, Relation between orders of a finite group and its sub-group, Conjugacy Relation and classes-point symmetry group, Schonflies symbols, Representation of groups by matrices (representation for C_n , C_{nv} , D_{nh} etc. groups to be worked out explicitly), character of a representation. The great orthogonality theorem (without proof), Character tables.

DRAVIDIAN UNIVERSITY
DURCET – 2015 ENTRANCE EXAMINATION

Time: 2 Hours
Mark : 120

Maximum

SECTION - A
(General Aptitude)
Each Question carries One Mark

Marks: 30 x 1 = 30

1 - 30

SECTION – B
(Subject: Chemistry)
(Multiple Choice Questions)
90

Marks: 90 x 1 =

31 - 120