



DRAVIDIAN UNIVERSITY
Centre for Off-Campus Education & Research
Syllabus for M.Phil/Ph.D Chemistry
Paper II: Broad Field

UNIT – I:

Crystal Field Theory, Salient Features, Splitting of d-orbitals in Octahedral and Tetrahedral fields, 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. Stoichiometric reactions in catalysis, homogeneous catalytic hydrogenation, hydroformylation, (oxo reaction), isomerisation, Zeigler-Natta polymerization of olefins, oxopalladation reactions, Activation of small molecules by coordination

UNIT – II:

(A) Oxidations

(a) 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 tetroxide, 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.

(B) Reductions

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

UNIT – III:

Methods of determining Rate laws, Collision theory of reaction rates, Steric factor, Activated complex theory, Arrhenius Equation, Treatment of unimolecular reactions, Lindemann, Lindemann – Hinshelwood. Effect of dilution on equivalent conductance-Inter ionic attraction, Debye-Huckel-Onsager treatment, derivation of Debye-Huckel-Onsager equation, Verification and limitation of Onsager equation, Bjerrum treatment of electrolytes, Debye-Falkenhagen and Wien effects.

UNIT – IV:

Instrumentation and sample handling, Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols and amines. Detailed study of vibrational frequencies of carbonyl compounds (ketones, aldehydes, esters, amides, acids, anhydrides, lactones, lactams and conjugated carbonyl compounds). Effect of hydrogen bonding and solvent effect on vibrational frequencies, overtones, combination bands and Fermi resonance, FT-IR.

UNIT – V:

Applications of H¹ NMR

Shielding mechanism, mechanism of measurement, chemical shift values and correlation for protons bonded to carbon (aliphatic, olefinic, aldehydic and aromatic) and other nuclei (alcohols, phenols, enols, carboxylic acids, amines and amides), chemical exchange, effect of deuteration, complex spin-spin interaction between two, three, four and five nuclei (First order spectra), virtual coupling. Stereochemistry, hindered rotation, Karplus curve variation of coupling constant with dihedral angle. Simplification of complex spectra: nuclear magnetic double resonance, contact shift reagents, Nuclear overhauser effect (NOE).

Mass Spectrometry

Introduction, ion production, types of ionization, EI, CI, FD, and FAB, factors affecting fragmentation, ion analysis, ion abundance, Mass spectral fragmentation of organic compounds, common functional groups, molecular-ion peak, metastable peak, Mc. Lafferty rearrangement. Nitrogen rule, isotope labeling, High resolution mass spectrometry, Examples of mass spectral fragmentation of organic compounds with respect to their structure determination.
