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**Semester - II**

**MCH-201: Inorganic Chemistry II**

**Unit - 1**

**Electronic Spectral Studies of Transition Metal Complexes :**

Spectroscopic ground states, correlation Orgel and Tanabe – Sugano diagrams for transition metal complexes ( d1- d9 states ), Selection rules for electronic spectroscopy. Intensity of various type electronic transition. Calculation of  $Dq$ ,  $B$  and  $C$  parameters, charge transfer spectra.

**Unit - 2**

**Magnetic Properties of Transition metal Complexes :**

Type of magnetic bodies, two sources of paramagnetism, orbital and spin effect, Curie equation and Curie – Weiss law, Determination of magnetic exchange coupling.

**Unit- 3**

**Metal II complexes :**

Metal carbonyl, structure and bonding, vibrational spectra of metal carbonyls and structure elucidation, important reaction of carbonyls, preparation bonding, structure of transition metal nitrosyl, dinitrogen and dioxygen complexes, tertiary phosphine as ligand.

**Unit - 4**

**Metal Clusters :**

Higher boranes, carboranes, metallocboranes and metallocarboranes compounds, dinuclear, trinuclear, tetranuclear, hexanuclear clusters with metal metal multiple bonds.

**Unit - 5**

**Optical Rotatory Dispersion and Circular Dichroism :**

$\frac{d[\alpha]_D}{d\lambda}$   $\frac{d[\theta]_D}{d\lambda}$   $\frac{d[\epsilon]_D}{d\lambda}$   $\frac{d[\sigma]_D}{d\lambda}$   $\frac{d[\rho]_D}{d\lambda}$

Linearly and circularly polarized lights optical rotator power and circular birefringence, Ellipticity and circular dichroism, ORD and Cotton effect, Faraday and Kerr effects, Assignment of electronic transitions, application of ORD and CD for the determination (i) absolute configuration of complexes and (ii) isomerism due to non planarity of chelate rings.

### Book Suggested

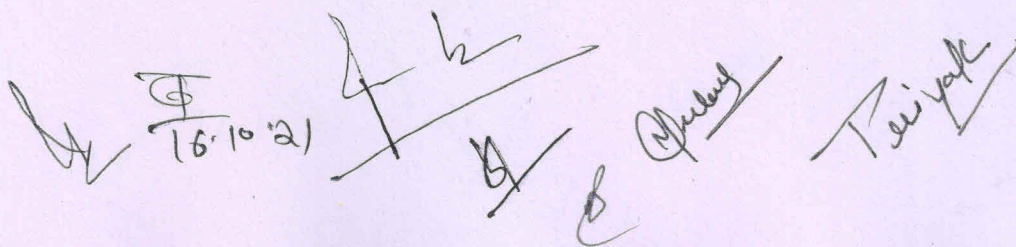
1. Advanced Inorganic Chemistry, F. A. Cotton and Wilkinson. John Wiley.
2. Inorganic Chemistry, J. E. Huey, Harps and Row.
3. Chemistry of the element, N. N. Greenwood and A. Ernshow. Pergamon.
4. Inorganic Electronic Spectroscopy, A. B. P. LEVER, Elsevier.
5. Magnetochemistry, R. I. Carlin, Springer verlag.
6. Comprehensive Coordination Chemistry eds. G. Wilkinson, R. D. Gillars and J. A. Mc Cleverty, pergamon.
7. Element of magnetochemistry. A. Shyamal & R.L. Dutta.

## MCH – 202 : ORGANIC CHEMISTRY II

### Unit – I

#### Aromatic Electrophilic Substitution :

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The ortho/para ratio, ipso attack, orientation in other ring systems. Quantitative



treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vilsmeier reaction, Gatterman - Koch reaction.

### **Aromatic Nucleophilic Substitution :**

The S<sub>N</sub>Ar SN1, benzyne and SN1, mechanism, Reactivity effect of substrate structure, leaving group and attacking nucleophile. The Von Richter-Sommelet - Hauser, and Smiles rearrangements.

## **Unit - II**

### **Free Radical Reactions :**

Types of free radical reactions, free radical substitution mechanism, mechanism at an aromatic substrate, neighbouring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. Reactivity in the attacking radicals. The effect of solvents on reactivity. Allylic halogenations (NBS), oxidation of aldehydes to carboxylic acids. Auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmeyer reaction. Free radical rearrangement. Hunsdiecker reaction.

## **Unit - III**

### **Addition Reactions :**

Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, region - and chemoselectivity, orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Hydroboration, Michael reaction, Sharpless asymmetric epoxidation.

## **Unit - IV**

### **Addition to Carbon - Hetero Multiple bonds :**

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acid esters and nitriles. Addition of Grignard reagents, organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds. Wittig reaction. Mechanism of condensation reactions involving enolates - Aldol,

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Knoevenagel, Claisen, Mannich, Benzoin, perking and Stobbe reaction. Hydrolysis of esters and amides, ammonolysis of esters.

### Elimination Reactions :

The E2, E1 and E1cB mechanisms and their Spectrum. Orientation of the double bond. Reactivity- effects of substrate structures, attacking base, the leaving group and the medium. Mechanism and orientation in pyrolytic elimination.

### Unit - V

### Pericyclic Reactions :

Molecular orbital symmetry, frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyclic reaction. Woodward-Hoffmann correlation diagrams. FMO and PMO approach. Electrocyclic reactions-conrotatory and disrotatory motions,  $4n$  and  $4n+2$  diagrams. FMO and PMO approach. Electrocyclic reactions-conrotatory and disrotatory motions,  $4n$  and  $4n+2$  and allyl systems. Cycloadditions-antarafacial and suprafacial additions,  $4n$  and  $4n+2$  systems,  $2+2$  addition of ketenes, 1,3 dipolar cycloadditions and cheletropic reactions. Sigmatropic rearrangements-suprafacial and antarafacial shifts of H, sigmatropic involving carbon moieties, 3,3- and 5,5 sigmatropic rearrangements. Claisen, Cope and aza-Cope rearrangements. Fluxional tautomerism. Ene reaction.

### Book Suggested :

12. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March, John Wiley.
13. Advanced Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum.
14. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
15. Structure and Mechanism in Organic Chemistry, C.K. Ingold, Cornell University Press.
16. Organic Chemistry, R.T. Morrison and R.N. Boyd, Prentice-Hall.
17. Modern Organic Reactions, H.O. House, Benjamin.

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18. Principles of Organic Synthesis, R.O.C. Norman and J.M. Coxon, Blackie Academic &\* Professionsl.
19. Reaction Machanism in Organic Chemistry, S.M. Mukherji and S.P. Singh, Macmillan.
20. Pericyclic Reactions, S.M. Mukherji, Macmillan, India
21. Stereochemistry of Organic Compound, D.Nasipuri, New Age Internationl.
22. Stereochemistry of Organic Compounds, P.S. Kalsi, Age Internationl.

## MCH – 203 : PHYSICAL CHEMISTRY II

### Unit – I

#### Chemical Dynamics :

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Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius equation and activated complex theory: ionic reactions, kinetic salt effects, steady state kinetics, kinetic and thermodynamic control of reaction, treatment of unimolecular reactions. Dynamic chain (hydrogen-bromine reaction pyrolysis of acetaldehyde, decomposition of ethane), photochemical (hydrogen-bromine and hydrogen-chlorine reactions) and homogenous catalysis, kinetics of enzymereactions, general features fo fast reactions, study of fast reactions by flow method, relaxation method flash photolysis ad the nuclear magnetic resonance method dynamics of unimolecular reaction (Lindemann Hinshelwood and Rice-Ramsperger-Kassel-Marcus (RRKM) throries for unimolecular reactions).

## Unit – II

### Surface Chemistry :

#### Adsorption

Surface tension, capillary action, pressure difference across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibbs adsorption isothobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization-phase separation and mass action modeld, solublization, micro emulsion, reverse micelles.

## Unit – III

### Macromolecules :

Polymer-definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization, mechanism of polymerization molecular mass, number and mass average molecular mass, molecular mass determination (Osmometry, viscometry, diffusion and light scattering methods), sedimentation chain configuration of macromolecules, calculation of average dimension of various chain structures.

## Unit – IV

### Non Equilibrium Theromodynamics :

Theromodynamics criteria for non- Equilibrium state, entropy production and entropy flow, entropy balance equation for different irreversible processes (e.g.,

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heat flow chemical reaction etc.) transformations of the generalized fluxes and forces, non Equilibrium stationary states, phenomenological equations, microscopic reversibility and Onsager's reciprocity relation, electrokinetic phenomena, diffusion, electric conduction.

### Unit - V

#### Electrochemistry :

Electrochemistry of solutions. Debye-Huckel- Onsager treatment and its extension, ion solvent interactions. Debye-Huckel-Jerum mode. Thermodynamics of electrified interface equation. Derivation of electro capllarity, Lippmann equations (surfaceexcess). Methods of determination. Structure of electrified interfaces.

Overpotentials, exchange current density, derivation of Butler Volmer equation, Tafelplot. Quantum aspects of charge transfer at electrodes-solution interfaces, quantization of charge transfer, tunneling. Semiconductor interfaces-theory of double layer atsemiconductor electrolyte solution interfaces, structure of double layer interfaces.effect of light at semiconductor solution interface. Polarography theory, Ilkovic equation, half wave potential and its significance.

#### Books Suggested :

11. Physical Chemistry, P.W. Atkins, ELBS.
12. Introduction to Quantum Chemistry, A.K.Chandra, Tata M Graw Hill.
13. Quantum Chemistry, Ira N. Levine, Prentice Hall.
14. Coulson's Valence, R. Mc Ween y, ELBS.
15. Chemical Kineties. K. J. Laidler, Mc Graw- Hill.
16. Kineties ans Mechanism of Chemical Transformation J. Rajaraman and J. Kuriacose, Mc Millan.
17. Micelles. Theoretical and Applied Aspects, V. M.Oraoi, Plenum.
18. Modern Electrochemistry Vol I and II J.O.M. Bockris and A.K.N. Reddy, Planum.

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19. Introduction to Polymer Science, V.R. Gowarikar, N. V. Vishwanathan and J. Sridhar, Wiley Eastern.

## MCH – 204 : Spectroscopy II and Diffraction

### Methods

#### Unit – I

#### Nuclear Magnetic Resonance Spectroscopy :

Nuclear spin Nuclear resonance, saturation, shielding og magnetic nuclei chemical shift and its measurements, factors, influencing chemical shift, deshielding spin-spin interactions. Factors influencine coupling constant “j” Clessification (AXB, AMX, ABC, A2B2 etc ) spin decoupling; basic ideas about instrument, NMR studies of nuclei other then protin-13C, 19F and 31P FT NMR, advantages of FT NMR.

#### Unit – II

#### Nuclear Quadrupole Resonance Spectroscopy :

Quadrupole nuclei, quadrupole moments, electric field gradient. Copliong constant. Splitting. Applications.

#### Unit – III

#### Electron Spin Resonance Spectroscopy :

Basic principles, zero field splitting and Kramer’s degeneracy, factors affecting the ‘g’ value Isotropic and anisotropic hyperfine coupline constants, spin Hamiltonian. Spin densitles and Mc Connell relationship, measurement techniques, applications.

#### Unit – IV

#### X-ray Diffraction :

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A signature on the far right: *Ramya*



Bragg condition, miller indices, Laue Method, Bragg method, Debye Scherrer method of X-ray structural analysis of crystals, index reflections, identification of unit cells 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.

## Unit – V

### Electron Diffraction :

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

### Neutron Diffraction :

Scattering of neutrons by solids measurement techniques, Elucidation of structure of magnetically ordered unit cells.

### Books suggested

11. Modern Spectroscopy, J.M. Hollas, John Wiley.
12. Applied Electron Spectroscopy for chemical analysis D. H. Windawi and F.L.Ho, Wiley Interscience.
13. NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry, R. V. Parish, Ellis Harwood.
14. Physical Methods in Chemistry, R. S. Drago, Saunders College.
15. Chemical Applications of Group theory, F. A. Cotton.
16. Introduction to Molecular Spectroscopy, G. M. Barrow, Mc Graw Hill.
17. Basic Principles of Spectroscopy, R. Chang, Mc Graw Hill.
18. Theory and Application of UV Spectroscopy, H. H Jaffe and M. Orchin, IBH Oxford.
19. Introduction to Photoelectron Spectroscopy, P. K. Ghosh, John Wiley.

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