

## THIRUVALLUVAR UNIVERSITY

## MASTER OF SCIENCE

## M.Sc. CHEMISTRY

## DEGREE COURSE

## UNDER CBCS

(with effect from 2012-2013)

## The Course of Study and the Scheme of Examinations

S.NO.	Study Components		Ins. hrs /week	Credit	Title of the Paper	Maximum Marks		
						CIA	Uni. Exam	Total
Course Title								
<b>SEMESTER I</b>								
1	MAIN	Paper-1	4	4	Organic Chemistry - I	25	75	100
2	MAIN	Paper-2	4	4	Inorganic Chemistry - I	25	75	100
3	MAIN	Paper-3	4	4	Physical Chemistry - I	25	75	100
4	MAIN PRACTICAL	Paper-1	5	0	Organic Chemistry Practicals - I	-	-	-
5	MAIN PRACTICAL	Paper-2	5	0	Inorganic Chemistry Practicals - I	-	-	-
6	MAIN PRACTICAL	Paper-3	5	0	Physical Chemistry Practicals - I	-	-	-
7	ELECTIVE	Paper-1	3	3	(to choose 1 out of 3) A. Polymer Chemistry B. Heterocyclic Chemistry C. INORGANIC PHOTOCHEMISTRY	25	75	100
			<b>30</b>	<b>15</b>		<b>100</b>	<b>300</b>	<b>400</b>
<b>SEMESTER II</b>								
8	MAIN	Paper-4	3	3	Organic Chemistry - II	25	75	100
9	MAIN	Paper-5	3	3	Inorganic Chemistry - II	25	75	100
10	MAIN	Paper-6	4	4	Physical Chemistry - II	25	75	100
11	MAIN PRACTICAL	Paper-1	5	5	Organic Chemistry Practicals - I	40	60	100
12	MAIN PRACTICAL	Paper-2	5	5	Inorganic Chemistry Practicals - I	40	60	100
13	MAIN PRACTICAL	Paper-3	5	5	Physical Chemistry Practicals - I	40	60	100
14	<b>Compulsory Paper</b>		2	2	<b>Human Rights</b>	25	75	100

## M.Sc. Chemistry : Syllabus (CBCS)

15	ELECTIVE	Paper-2	3	3	(to choose 1 out of 3) A. Green Chemistry B. Material Science C. Applied Electrochemistry	25	75	100
			<b>30</b>	<b>30</b>		<b>245</b>	<b>555</b>	<b>800</b>
<b>SEMESTER III</b>						<b>CIA</b>	<b>Uni. Exam</b>	<b>Total</b>
16	MAIN	Paper-7	4	4	Organic Chemistry - III	25	75	100
17	MAIN	Paper-8	4	4	Inorganic Chemistry - III	25	75	100
18	MAIN	Paper-9	4	4	Physical Chemistry – III	25	75	100
19	MAIN PRACTICAL	Paper-4	5	0	Organic Chemistry Practicals - II	-	-	-
20	MAIN PRACTICAL	Paper-5	5	0	Inorganic Chemistry Practicals - II			
21	MAIN PRACTICAL	Paper-6	5	0	Physical Chemistry Practicals - II	-	-	-
22	ELECTIVE	Paper-3	3	3		25	75	100
			<b>30</b>	<b>15</b>		<b>100</b>	<b>300</b>	<b>400</b>
<b>SEMESTER IV</b>						<b>CIA</b>	<b>Uni. Exam</b>	<b>Total</b>
23	MAIN	Paper-10	4	4	Organic Chemistry- IV	25	75	100
24	MAIN	Paper-11	4	4	Inorganic Chemistry - IV	25	75	100
25	MAIN	Paper-12	4	4	Physical Chemistry - IV	25	75	100
26	MAIN PRACTICAL	Paper-4	5	5	Organic Chemistry Practicals - II	40	60	100
27	MAIN PRACTICAL	Paper-5	5	5	Inorganic Chemistry Practicals - II	40	60	100
28	MAIN PRACTICAL	Paper-6	5	5	Physical Chemistry Practicals - II	40	60	100
29	ELECTIVE	Paper-4	3	3	(to choose 1 out of 3) A. Environmental Chemistry / B. Bioinorganic Chemistry / C. Chemistry OF Natural Products	25	75	100
			<b>30</b>	<b>30</b>		<b>220</b>	<b>480</b>	<b>700</b>

<b>Subject</b>	<b>Papers</b>	<b>Credit</b>	<b>Total Credits</b>	<b>Marks</b>	<b>Total marks</b>
MAIN	12	4-5	58	100	1200
MAIN PRACTICAL	6	4-5	18	400	600
ELECTIVE	4	3	12	100	400
COMPULSORY PAPER	1	2	2	100	100
<b>Total</b>	<b>23</b>	<b>-</b>	<b>90</b>	<b>-</b>	<b>2300</b>

# THIRUVALLUVARUNIVERSITY

## M.Sc. CHEMISTRY

### SYLLABUS

### UNDER CBCS

(with effect from 2012-2013)

## SEMESTER I

### PAPER - 1

## ORGANIC CHEMISTRY I

### OBJECTIVES:

To learn the concepts of stereochemistry, conformational analysis and their Application in the determination of reaction mechanism. To understand the mechanism of nucleophilic and electrophilic substitution reactions.

### UNIT-I: STEREOCHEMISTRY

Optical activity and chirality, Classification of chiral molecules as asymmetric and dissymmetric. A brief Study of dissymmetry of allenes, biphenyls, spiro compounds, trans cyclooctane and cyclononene and molecules with helical structures absolute configuration - R, S notation of biphenyls and allenes. Fischer projection. Inter conversion of Sawhorse, Newmann and Fischer projections. Molecules with more than one asymmetric center (restricted to five carbons). e.g. Erythro and threo compounds. Asymmetric synthesis. Cram's rule.

### UNIT-II: CONFORMATIONAL ANALYSIS

Conformational analysis of disubstituted cyclohexane and their stereochemical features (geometric and optical isomerism (if shown) by these derivatives). Conformation and reactivity of substituted cyclohexanol (oxidation and acylation), cyclohexanone (reduction) and cyclohexane carboxylic acid derivatives (esterification and hydrolysis). Conformation and stereochemistry of cis and trans decalin and 9-methyldecalin.

### UNIT-III: ALIPHATIC NUCLEOPHILIC SUBSTITUTION REACTION

$S_N1$ ,  $S_N2$  and  $S_Ni$  mechanisms - Neighboring group participation - reactivity, structural and solvent effects - substitution in norbornyl and bridgehead systems - substitution at allylic and vinylic carbons - substitution by ambident nucleophiles - substitution at carbon doubly bonded to oxygen and nitrogen - alkylation and acylation of amines, halogen exchange, Von-Braun

reaction, alkylation and acylation of active methylene carbon compounds, hydrolysis of esters, Claisen and Dieckmann condensation.

$S_{E1}$ ,  $S_{E2}$  and  $S_{Ei}$  mechanism, double bond shift - Reactivity. Migration of double bond, keto-enol interconversion, HVZ reaction, Stark-Enamine reaction, halogenation of aldehydes and ketones and decarboxylation of aliphatic acids.

#### **UNIT-IV: ELIMINATION REACTIONS**

E1, E2 and E1cB mechanism - E1, E2 and E1cB spectrum - Orientation of the double bond - Hoffman and Saytzeff rules - Competition between elimination and substitution. Typical eliminations reactions - dehydration, dehydrohalogenation and dehalogenation. Stereochemistry of E2 eliminations in cyclohexane systems. Mechanism of pyrolytic eliminations. Chugaev and Cope eliminations.

#### **UNIT-V: AROMATIC SUBSTITUTION REACTIONS**

Electrophilic substitution-the arenium ion mechanism.Orientation and reactivity (ortho, meta and para directing groups). Typical reactions including Reimer - Tieman reaction, Vilsmeier - Hack, Gattermann, Gattermann - Koch,Kolbe reaction, Synthesis of di and tri substituted benzene (symmetrical tribromo benzene, 2-amino 5-methylphenol, 3 nitro, 4-bromobenzoic acid, 3, 4 dibromonitrobenzene, 1,2,3 - trimethylbenzene) starting from benzene or any monosubstituted benzene.Nucleophilic substitution - methods for the generation of benzyne intermediate and reactions of arylne intermediate. Nucleophilic substitution involving diazonium ions. Aromatic Nucleophilic substitution of activated halides, Ziegler alkylation, Chichibabin reaction.

#### **Recommended Books**

C. Wentrup, Reactive Molecules, John Wiley and Sons, New York (1984).

C.K. Ingold, Structure and mechanism in organic chemistry, Cornell University press.

E.S. Gould, Mechanism and Structures in Organic Chemistry, Holt, New York (1959).

Ernest Eliel, Stereochemistry of carbon compounds, McGraw Hill, New York (1962).

Francis A. Carey and Richard J. Sundberg, Advanced Organic Chemistry, Part A and B, III Edition, Plenum Press (1990).

Graham Solomons, Organic Chemistry

J. March, Advanced organic reaction mechanism and structure, Tata McGraw Hill.

J. Miller, Advanced Organic Chemistry, III Edition

J. Miller, Aromatic Nucleophilic Substitution

Longman, A Guide book to mechanism in organic chemistry

Marc London, Organic Chemistry

Mc Murry, Organic Chemistry, V Edition, Asian Books Pvt Ltd (2000).

Niel Isaacs, Physical Organic Chemistry, ELBS Publications (1987).

P. Ramesh, Basic principles of Organic Stereochemistry, Madurai Kamaraj University.

P.S. Kalsi, Stereochemistry and mechanism through solved problems, Wiley Eastern Ltd., (1994).

P.S. Kalsi, Stereochemistry, Conformation analysis and Mechanism, II Edition, Wiley Eastern Limited, Chennai (1993).

R.K. Bansal, Organic Reaction Mechanism

R.O.C. Norman, Organic Synthesis, Chapman and Hall, NY (1980).

S.M. Mukherji and S.P. Singh, Organic Reaction Mechanism, MacMillan India Ltd., Chennai (1990).

Stanley Pines, Organic Chemistry, IV Edition

T.L. Gilchrist and C.W. Rees, Carbenes, Nitrenes and Arynes, Thomas Nelson and Sons Ltd., London.

Peter Sykes, A Guide book to mechanism in organic chemistry, Pearson Edn., (2006).

## PAPER -2

### INORGANIC CHEMISTRY I

#### Objective

To learn about the inorganic polymers. To study the concept of coordination Chemistry, stability of the complexes and stereochemistry of complexes. To study about structure and bonding.

#### UNIT-I: STRUCTURE AND BONDING I

Polyacids: Isopolyacids and heteropolyacids of vanadium, chromium, molybdenum and Tungsten.

Inorganic Polymers: Silicates, structure - properties - correlation and applications - molecular sieves, polysulphur - nitrogen compounds and poly - organophosphazenes.

#### UNIT-II: STRUCTURE AND BONDING II

Boron hydrides: Polyhedral boranes, hydroboration, carboranes and metallo - carboranes

Metal clusters : Chemistry of low molecularity metal clusters (upto) trinuclear metal Clusters: multiple metal-metals.

#### UNIT-III: COORDINATION CHEMISTRY I

Stability of complexes; thermodynamic aspects of complex formation; factors affecting stability, HSAB approach.

Determination of stability constants by spectrophotometric, polarographic and potentiometric methods.

#### UNIT-IV: COORDINATION CHEMISTRY II

Stereochemical aspects; Stereoisomerism in inorganic complexes; isomerism arising out of ligand distribution and ligand conformation; chirality and nomenclature of chiral complexes; optical rotatory dispersion and circular dichroism.

Macrocyclic ligands; types; porphyrins; corrins, Schiff bases; crown ethers; cryptates.

**UNIT-V: COORDINATION CHEMISTRY III**

Evidence for metal-ligand orbital overlap, molecular orbital theory and energy level diagrams, concept of weak and strong field ligands, Jahn-Teller distortion, charge - transfer spectra.

Term states for “d” - ions, energy diagrams, d-d transitions, Orgel and Sugano - Tanabe diagrams, spin orbit coupling, nephelauxetic effect, spectral and magnetic characteristics of transition metal complexes.

**Text Books**

FA Cotton and G.W. Wilkinson, *Advanced Inorganic Chemistry– A comprehensive Text*, John Wiley and Sons, (1988).

J.E. Huheey, *Inorganic Chemistry*, Harper and Collins, NY, IV Edition, (1993).

K.F. Purcell and J.C. Kotz, *Inorganic Chemistry* WB Saunders Co., USA, (1977).

M.C. Shriver, P.W Atkins, CH. Langford, *Inorganic Chemistry*, OUP, (1990).

N.N. Greenwood and Earnshaw, *Chemistry of the Elements*, Pergamon Press, New York (1984).

NH Ray, *Inorganic Polymers*, Academic Press, (1978)

S.F.A. Kettle, *Coordination Chemistry*, ELBS, (1973).

**Suggested References**

A.B.P. Lever, *Inorganic Electronic Spectroscopy*, II Edn., Elsevier, New York, (1984).

B.E. Douglas DH McDaniel's and Alexander, *Concepts and Models of Inorganic Chemistry*, Oxford IBH, (1983).

B.N. Figgis, *Introduction to Ligand Fields*, Interscience, (1966).

EL. Muttarties, *Polyhedral Boranes*, Academic Press, New York (1975).

M.C. Day and J. Selbin, *Theoretical Inorganic Chemistry*, Van Nostrand Co., NY, (1974).

WU. Mallik, G.D. Tuli, R.D. Madan, *Selected topics in Inorganic Chemistry*, S. Chand and Co., New Delhi, (1992).



## PAPER - 3

### PHYSICAL CHEMISTRY I

#### Objective

To study the partial molar property, fugacity and its significance. Theories and basic concepts of Chemical kinetics - mechanism of acid, base and enzyme Catalysis reaction. To study the ionic conductance, Elements of group theory

#### UNIT-I: THERMODYNAMICS : I

Partial molar properties-Partial molar free energy (Chemical potential) - Partial molar volume and Partial molar heat content - Their significance and determination of these quantities. Variation of chemical potential with temperature and pressure.

Definition of fugacity - determination of fugacity - variation of fugacity with temperature and pressure - the concept of activity and activity coefficients - determination of standard free energies - choice of standard states - determination of activity and activity coefficients for non electrolytes.

#### UNIT-II: CHEMICAL KINETICS: I

ARRT, potential energy surfaces - partition function and activated complex - Eyring equation - estimation of free energy, enthalpy and entropy of activation and their significance.

Reactions in solutions - effect of pressure, dielectric constant and ionic strength on reactions in solutions - kinetic isotope effects - linear free energy relationships - Hammett and Taft equations.

#### UNIT-III: CHEMICAL KINETICS: II

Acid - Base catalysis - mechanism of acid - base catalyzed reactions - Bronsted catalysis law. Catalysis by enzymes - rate of enzyme catalyzed reactions - effect of substrate concentration, pH and temperature on enzyme catalyzed reactions - inhibition of enzyme catalyzed reactions.

#### UNIT-IV: ELECTROCHEMISTRY: I

Mean ionic activity and mean ionic activity coefficient - activity coefficient of strong electrolytes - determination of activity coefficient by electrochemical method.

Debye Huckel limiting law - qualitative and quantitative verification - limitation of Debye Huckel limiting law at appreciable concentrations of electrolytes - Debye - Huckel - Bronsted equation.

**UNIT-V: APPLICATIONS OF GROUP THEORY: I**

Symmetry elements and symmetry operations - group multiplication table - sub groups, similarity transformation and classes, reducible and irreducible representations - direct product representation.

**Text Books**

- S. Glasstone, Thermodynamics for Chemists, Affiliated East West Press, New Delhi (1950).  
J. Rajaram and J.C. Kuriacose, Thermodynamics for Students of Chemistry, Lal Nagin Chand, New Delhi (1986).  
J. Rajaram and J.C. Kuriacose, Kinetics and Mechanism of Chemical Transformations. Mac Millan India Ltd (1993).  
R.J. Laidler, Chemical Kinetics, Harper and Row, New York (1987).  
S. Glasstone, Introduction to Electrochemistry, Affiliated East West Press, New Delhi (1960).  
D.R.Crow, Principles and Applications to Electrochemistry, Chapman and Hall (1991).  
K.V. Ramakrishnan and M.S. Gopinath, Group Theory in Chemistry, Vishal Publications (1998).

**Suggested References**

- W.J. Moore, Physical Chemistry, Orient Longman, London (1972).  
K.G. Denbigh, Thermodynamics of Steady State, Methien and Co. Ltd, London (1951).  
L.K. Nash, Elements of Chemical Thermodynamics, Addison Wesley (1962).  
R.G. Frost and Pearson, Kinetics and Mechanism, Wisely, New York (1961).  
Amdur and G.G. Hammes, Chemical Kinetics, Principles and Selected Topics, McGraw Hill, New York (1968).  
S. Glasstone, Introduction to Electrochemistry, Affiliated East West Press, New Delhi (1960).  
J. Robbins, Ions in Solution - An Introduction of Electrochemistry, Clarendon Press, Oxford (1972).  
D.S. Schonland, Molecular Symmetry, Vannostrand, London (1965).  
N. Thinkham, Group Theory and Quantum Mechanics, McGraw Hill Book Company, New York (1964).

**ELECTIVE**

**PAPER - 1**

**A. POLYMER CHEMISTRY**

**Objective:**

To gain the knowledge in the preparation, properties, characterization and Uses of polymers.

**UNIT- I : Basic Concepts**

Classification – Nomenclature and isomerism – functionality – Molecular forces and chemical bonding in polymers – Molecular weight – Linear, branched and cross linked polymers. Thermoplastic and thermosetting polymers – Elastomers, Fibers and resins. Techniques of polymerization–emulsion, bulk, solution and suspension.

**UNIT– II : Kinetics and Mechanism**

Kinetics and Mechanism of polymerization – free radical, cationic, anionic and co-ordination polymerization (Ziegler - Natta Catalyst). Copolymerisation – Kinetics (Detailed Study). General characterization–Kinetic chain length–degree of polymerization, chain transfer - initiators – inhibitors – retarders.

**UNIT – III**

**A) Structure and Properties**

Structure - property relationship – Mechanical properties, Thermal properties – Glass transition temperature – Factors affecting Glass transition temperature – crystallinity and melting point – related to structure.

**B) Polymer characterization and analysis**

Crystalline nature – X-Ray diffraction – Differential Scanning Calorimetry (DSC) – Thermo Gravimetric Analysis – molecular weight determination – Osmometry (membrane), Viscosity, Ultra centrifuge and Gel Permeation Chromatography.

**UNIT – IV: INDUSTRIAL NATURAL POLYMERS**

Important industrial polymers – preparation and application of polyethylene, poly vinyl chloride, poly urethanes, polytetrafluoro ethylene (TEFLON), Nafion and ion – exchange resins. Importance of natural polymers – application and structures of starch, cellulose and chitosin derivatives.

**UNIT – V : SPECIALITY POLYMERS**

Bio polymers – biodegradable polymers – biomedical polymers – poly electrolytes - conducting polymers – high temperature and fire retardant polymers - polymer blend – polymer composites – polymer nanocomposites – IPN inter penetrating network polymers – Electroluminescent polymers.

**Text Books:**

- F. W. Bill Meyer. Text book of polymer science, III Edition, John Wiley and sons, New York.
- P. J. Flory. Principles of Polymer Chemistry, Cornell Press (recent edition).
- V. R. Gowarikar, B. Viswanathan, J. Sridhar, Polymer Science – Wiley Eastern, 1986.
- G. S. Misra – Introduction to Polymer Chemistry, Wiley Eastern Ltd.,
- P. Bahadur, N. V. Sastry, Principles of Polymer Science, Narosa Publishing House.
- G. Odian, Principles of Polymerization, McGraw Hill Book Company, New York, 1973.

**Suggested References**

- A. Rudin, The Elements of Polymer Science and Engineering. Academic Press, New York, 1973.
- I. C. E. H. Brawn, The Chemistry of High Polymers, Butter worth & Co., London, 1948.
- G. S. Krishenbaum, Polymer Science Study Guide, Gordon Breach Science publishing, New York, 1973.
- E. A. Coolins, J. Bares and E. W. Billmeyer, Experiments in Polymer Science, Wiley Interscience, New York, 1973.

## PAPER – 1

### B. HETEROCYCLIC CHEMISTRY

#### UNIT-I: NOMENCLATURE OF HETEROCYCLES

Replacement and systematic nomenclature (Hantzsch-Widman system) for monocyclic fused and bridged heterocycles. Aromatic Heterocycles  
General chemical behaviour of aromatic heterocycles, classification (structural type), criteria of aromaticity (bond lengths, ring current and chemical shifts in  $^1\text{H}$  NMR-spectra. Empirical resonance energy, delocalization energy and Dewar resonance energy, diamagnetic susceptibility exaltations). Heteroaromatic reactivity and tautomerism in aromatic heterocycles.

#### UNIT-II: NON-AROMATIC HETEROCYCLES

Strain-bond angle and torsional strains and their consequences in small ring heterocycles. Conformation of six-membered heterocycles with reference to molecular geometry, barrier to ring inversion, pyramidal inversion and 1,3-diaxial interaction. Stereo-electronic effects anomeric and related effects, Attractive interactions-hydrogen bonding and intermolecular nucleophilic, electrophilic interactions. Heterocyclic Synthesis. Principles of heterocyclic synthesis involving cyclization reactions and cycloaddition reactions.

#### UNIT-III: SMALL RING HETEROCYCLES

Three-membered and four-membered heterocycles-synthesis and reactions of aziridines, oxiranes, thiranes, azetidines, oxetanes and thietanes. Benzo-Fused Five-Membered Heterocycles Synthesis and reactions including medicinal applications of benzopyrroles, benzofurans and benzothiophenes.

#### UNIT-IV: MESO-IONIC HETEROCYCLES

General classification, chemistry of some important meso-ionic heterocycles of type-A and B and their applications. Six-membered Heterocycles with one Heteroatom. Synthesis and reactions of pyrylium salts and pyrones and their comparison with pyridinium & thiopyrylium salts and phridones. Synthesis and reactions of quionlizinium and benzopyrylium salts, coumarins and chromones.

**UNIT-V: HIGHER HETEROCYCLES**

Six membered Heterocycles with two or more Heteroatoms. Synthesis and reactions of diazoles, triazines, tetrazines and thiazines. Seven- and Large-membered Heterocycles. Synthesis and reactions of azepines, oxepines, thiepinines, diazepines thiazepines, azocines, diazocines, dioxocines and dithiocines.

**Suggested References:**

Heterocyclic Chemistry Vol. 1-3, R.R. Gupta, M. Kumar and V.Gupta, Springer Verlag.  
The Chemistry of Heterocycles, T. Eicher and S. Hauptmann, Thieme.  
Heterocyclic chemistry J.A. Joule, K. Mills and G.F. Smith, Chapman and Hall.  
Heterocyclic Chemistry, T.L. Gilchrist, Longman Scientific Technical.  
Contemporary Heterocyclic Chemistry, G.R. Newkome and W.W. Paudler, Wiley-Interscience.  
An Introduction to the Heterocyclic Compounds, R.M. Acheson, John Wiley.  
Comprehensive Heterocyclic Chemistry, A.R. Katritzky and C.W. Rees, eds. Pergamon Press.

## **PAPER – 1**

### **C. INORGANIC PHOTOCHEMISTRY**

#### **UNIT-I: BASIC OF PHOTOCHEMISTRY**

Absorption, excitation, photochemical laws, quantum yield, electronically excited states, life times-measurements of the times. Flash photolysis, energy dissipation by radiative and non-radiative processes, absorption spectra, Frank-Condon principle, photochemical stages-primary and secondary processes.

#### **UNIT-II: EXCITED STATES OF METAL COMPLEXES**

Excited states of metal complexes: Comparison with organic compounds, electronically excited states of metal complexes, charge transfer spectra, charge transfer excitations.

#### **UNIT-III: LIGAND FIELD PHOTOCHEMISTRY**

Photosubstitution, photooxidation and photoreduction, lability and selectivity, zero vibrational levels of ground state and excited state, energy content of excited state, zero-zero spectroscopic energy, development of the equations for redox potentials of the excited states.

#### **UNIT-IV: REDOX REACTIONS BY EXCITED METAL COMPLEXES**

Energy transfer under conditions of weak interaction and strong interaction-examples formation; condition of the excited states to be useful as redox reactants, excited electron transfer, metal complexes as attractive candidates, (2,2-bipyridine and 1,10-phenanthroline complexes), illustration of reducing and oxidising character of Ruthenium<sup>+2</sup> (bipyridal complex, comparison with Fe (bipy)); role of spin-orbit coupling-life time of these complexes. Application of redox processes of electronically excited states for catalytic purposes, transformation of low energy reactants into high energy products, chemical energy into light.

#### **UNIT-V: METAL COMPLEX SENSITIZERS**

Metal complex sensitizer, electron relay, metal colloid systems, semiconductor supported metal or oxide systems, water photolysis, nitrogen fixation and carbon dioxidereduction.

Book Suggested:

Concepts of Inorganic Photochemistry, A.W. Adamson and P.D. Fleischauer, Wiley.

Inorganic Photochemistry, J.Chem. Educ. vol. 60 No. 10, 1983.

Progress in Inorganic Chemistry, Vol. 30ed. S.J. Lippard. Wiley.

Coordination Chem. Revs. 1981, vol. 39, 121, 1231, 1975, 14, 321,; 1990 97, 313.

Photochemistry of Coordination Compounds, V. Balzari and V. Carassiti, Academic Press.

Elements of Inorganic Photochemistry, G.J. Ferraudi, Wiley.

S.Arunachalam, "Inorganic Photochemistry - An Introduction to Photochemical and Photophysical Aspects of Metal Complexes", Kala Publications, Tiruchirappalli, India, 2002.

D.M. Roundhill, "Photochemistry and photophysics of Metal complexes", Springer;Edition, 1994.



## SEMESTER II

### PAPER - 4

## ORGANIC CHEMISTRY II

### Objective

To learn the various types of reactions, rearrangements and their synthetic utility.

### UNIT-I: ADDITION TO CARBON - CARBON AND CARBON – HETERO MULTIPLE BONDS

Electrophilic, nucleophilic and neighbouring group participation mechanisms - addition of halogen and nitrosyl chloride to olefins. Hydration of olefins and acetylenes. Hydroboration, hydroxylation, Michael addition, 1, 3 - dipolar additions, Carbenes and their additions to double bonds - Simon - Smith reaction. Mannich, Stobbe, Darzen, Wittig, Wittig - Horner and Benzoin reactions. Stereochemical aspects to be studied wherever applicable. Carbenes and nitrenes : Methods of generation , structure, addition reactions with alkenes - insertion reactions.

### UNIT-II OXIDATIONS AND REDUCTIONS

Mechanism - study of the following oxidation reactions - oxidation of alcohols - use of DMSO in combination with DCC or acetic anhydride in oxidising alcohols - oxidation of methylene to carbonyl, oxidation of aryl methenes - allylic oxidation of olefins. Ozonolysis - oxidation of Olefinic double bonds and unsaturated carbonyl compounds-oxidative cleavage of C-C bond. Reduction: Selectivity in reduction of 4-t-butylcyclohexanone using selecterides. Hydridereductions - reduction with  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , tritertiarybutyloxyaluminium hydride, sodium Cyanoborohydride, trialkyltin hydride, hydrazines.

### UNIT-III: MOLECULAR REARRANGEMENTS

A detailed study with suitable examples of the mechanism of the following rearrangements: Pinacol - Pinacolone (examples other than tetramethylethylene glycol) - Wagner - Meerwein, Demjanov, Dienone - phenol, Favorski, Baeyer - Villiger, Wolf, Stevens (in cyclic systems) and Von Richter rearrangements.

### UNIT-IV: MODERN SYNTHETIC METHODS, REACTIONS AND REAGENTS

Synthesis of simple organic molecules using standard reaction like acetylation alkylation of enamines and active methylene compounds, Grignard reactions, Phosphorus and sulphur

ylides Robinson annulation, Diels Alder reactions, protection and deprotection of functional groups (R-OH, R-CHO, RCO-R, R-NH<sub>2</sub> and R-COOH). Uses of the following reagents: DCC, Trimethylsilyliodide, 1, 3-Dithiane (umpolung), diisobutylaluminiumhydride (DIBAL), 9BBN, Trimethylsilylchloride.

#### **UNIT-V: HETEROCYCLES, VITAMINS AND STEROIDS**

Imidazole, oxazole, thiazole, flavones, isoflavones, anthocyanins, pyrimidines (cytoscine and Uaracil only) and purines (adenine, guanine only). Syntheses of parent and simple alkyl or aryl substitution - derivatives are expected. Synthesis of vitamin A1 (Reformatsky and Wittig reaction methods only). Conversion of cholesterol to progesterone, estrone and testosterone.

#### **Recommended Books**

E.S. Gould, Structure and Mechanism,

Francis A. Carey and Richard J. Sundberg, Advanced Organic Chemistry - Part B, 3<sup>rd</sup> Edition (1990).

H.O. House, Modern Synthetic Reactions, The Benjamin Cummings Publishing Company, London (1972).

I.L. Finar, Organic chemistry, Vol. I and II, 5<sup>th</sup> Edition, ELBS Publication.

J. March, Advanced organic reaction mechanism and structure, Tata McGraw Hill.

Mc Murry, Advanced organic chemistry, Thomas Pvt. Ltd.,

Michael B. Smith, Organic Synthesis, McGraw Hill, International Edition (1994).

Michael Smith, Organic synthesis.

Michael Smith, Organic synthesis.

Parmer and Chawla, Organic reaction mechanisms, S. Chand and Co.,

Paul de Mayo, Molecular Rearrangements, Vol. I and II.

R.E. Ireland, Organic synthesis, Prentice Hall of India

R.O.C. Norman, Principles of organic synthesis, Chapman and Hall, London. 1980.

Raymond K. Mackie and David M. Smith, Guide book to Organic synthesis, ELBS Publication.

S.M. Mukherji and S.P. Singh, Organic Reaction Mechanism, MacMillan India Ltd., Chennai (1990).

Stuart Warren, Work book for organic synthesis, The Disconnection Approach, John Wiley & Sons (Asia) Pvt. Ltd.,

W. Carruther, Jain Coldham, Modern Methods of organic synthesis, IV Edition.

W. Carruthers, Some Modern Methods of Organic Synthesis, III Edition, Cambridge University Press, (1993).

## PAPER - 5

### INORGANIC CHEMISTRY II

#### Objectives

To study about the theories of coordination complexes, Chemistry of lanthanides, to learn about Nanotechnology and use of Inorganic Compounds in Biological Chemistry.

#### UNIT-I: THE CHEMISTRY OF SOLID STATE

Structure of Solids; Comparison of X-ray and Neutron Diffraction; structure of Pyrochlore, cadmium iodide and nickel arsenide; spinels; defects in solids, non-stoichiometric compounds. Electrical, Magnetic and optical properties of solids, band theory, Semiconductors, superconductors, Solid state Electrolytes, Types of magnetic Behaviour, Dia, para, ferro, antiferro and ferrimagnetism: Hysteresis.

Solid state lasers, inorganic phosphors, Ferrites.

#### UNIT- II: NUCLEAR CHEMISTRY I

Nuclear properties: Nuclear spin and moments, origin of nuclear forces, salient features of the liquid drop and the shell models of the nucleus.

Models of Radioactive Decay: Orbital electron capture: nuclear isomerism, internal conversion, detection and determination of activity by cloud chamber, nuclear emulsion, bubble chamber, G.M., Scintillation and Cherenkov counters.

Nuclear Reactions: Types, reactions, cross section, Q-value, threshold energy, compound nucleus theory: high energy nuclear reactions, nuclear fission and fusion reactions as energy sources; direct reactions; photonuclear and thermo nuclear reactions.

#### UNIT-III: NUCLEAR CHEMISTRY II

Stellar energy: synthesis of elements, hydrogen burning, carbon burning.

Nuclear Reactors: fast breeder reactors, particle accelerators, linear accelerators, cyclotron and synchrotron.

Radio Analytical Methods: Isotope dilution analysis, Radiometric Titrations, Radio immuno assay, Neutron activation analysis.

**UNIT-IV: THE CHEMISTRY OF LANTHANIDES,ACTINIDES AND NANOTECHNOLOGY**

The Chemistry of solid state, lanthanides and actinides, oxidation state spectral, magnetic characteristics, coordination numbers, stereochemistry, nuclear and non-nuclear applications. Nanotechnology - introduction - preparatory methods, characterization, application as sensors, biomedical applications, application in optics and electronics.

**UNIT-V: BIOINORGANIC CHEMISTRY**

Transport proteins: Oxygen carriers, metalloenzymes, carboxy peptidase, carbonic anhydrase, redox process, iron-sulphur proteins, chlorophyll, salient features of the photo synthetic process, vitamin B<sub>12</sub> role of sodium, potassium, calcium, zinc and copper; fixation of nitrogen, nitrogen cycle.

Anti-cancer drugs and their mechanism of action, Natural and man made radio isotopes and their application.

**Text Books**

A.R. West, Basic solid state chemistry, John Wiley, (1991).

S. Glasstone, Source Book on Atomic Energy, Van Nostrand Co., (1969).

G. Frielander, J.w. Kennedy and J.M. Miller, Nuclear and Radiochemistry, John Wiley and Sons, (1981).

Hari Jeevan Arnikar , Essentials of nuclear chemistry, New Age International (P) Ltd., (2005).

Hari Jeevan Arnikar,Nuclear Chemistry Through Problems, New Age International (P) Ltd., (2007).

G.T. Seaborg, Transuranium elements, Dowden Hitchinson and Ross, (1978).

Nishit Mathur, Nanochemistry, RBSA publishers (2010).

Patric Salomon, A hand book on Nano Chemistry, Dominant publishers and distributors (2008).

G.B. Sergeev ,Nanochemistry ,Elsevier Science and Technology (2007).

U. Saityanarayana, Essentials of Biochemistry, Books and Allied (P) Ltd.,

**Suggested References**

W.E. Addison, Structural principle in inorganic chemistry, Longman (1961).

D.M. Adams, Inorganic solids, John Wiley Sons (1974).

Azaroff, Solid State Chemistry, John Wiley.

B.E. Dogulas DH McDaniel's and Alexander, Concepts and Models of Inorganic Chemistry, Oxford IBH, (1983).

- M.C. Day and J. Selbin, Theoretical Inorganic Chemistry, Van Nostrand Co., New York (1974).
- J.E. Huheey, Inorganic Chemistry - Principles, Structure and Reactivity, Harper Collins, New York, IV Edition (1993).
- N. Greenwood and A. Earnshaw, Chemistry of Elements, Pergamon, NY, (1984).
- F.A. Cotton and G. Wilkinson Advanced Inorganic Chemistry - A Comprehensive Text, John Wiley and Sons, V Edition (1988).
- K.F. Purcell and J.C. Kotz, Inorganic Chemistry - WB Saunders Co., USA (1977)
- WU. Mallik, G.D. Tuli, R.D. Madan, Selected topics in Inorganic Chemistry, S. Chand and Co., New Delhi, (1992).
- M.N. Hughes, The Inorganic Chemistry of Biological processes, Wiley London, II Edition (1982).
- Jonathan W. Stead, David R. Turner and Karl J. Wallace., Core concepts in Supramolecular Chemistry and Nanochemistry, John Wiley sons Ltd (2007).
- Beoffry A.Ozin, Andre Arsenault, Ludovico & Cademartiri. Nano chemistry - A chemical approach to nano materials, Royal Society of chemistry (2009).
- Kenneth J. Klabunde, Nano scale materials in Chemistry A. John Wiley & Sons Publishers (2001).
- L. Stryer, Biochemistry, V Edition, Freeman & Co., New York (2002) .
- D. L. Nelson and M.M. Cox, Lehninger, Principles of Biochemistry, III edition, McMillan North Publication (2002).
- W. Kaim and B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, an Introduction and Guide, Wiley, New York (1995).
- S. J. Lippard and J. M. Berg, Principles of Bioinorganic Chemistry, University Science Books (1994).
- I. Bertini, H. B. Grey, S. J. Lippard and J. S. Valentine, Bioinorganic Chemistry, Viva Books Pvt. Ltd., New Delhi (1998).

## PAPER - 6

### PHYSICAL CHEMISTRY II

#### Objective

To study the different types of molecular spectroscopy, the principles and application of NMR Spectroscopy. To Study enzyme catalysis and kinetics of complex reactions. the applications of Group theory.

#### UNIT-I: SPECTROSCOPY: I

Interaction of matter with radiation - Einstein's theory of transition probability - Rotational spectroscopy of a rigid rotator - non rigid rotator - diatomic and polyatomic molecules.

#### UNIT-II: SPECTROSCOPY: II

Vibrational spectroscopy - harmonic oscillator - unharmonicity - vibrational spectra of polyatomic molecules - vibrational frequencies - group frequencies - vibrational coupling overtones - Fermi resonance. Raman Spectra- Raman effect, rotational and vibrational Raman spectra. Electronic spectra – progressions and Sequences, selection rules, Franck - Condon principle, Solvent effects, Types of electronic transition.

#### UNIT-III: SPECTROSCOPY: III

Resonance spectroscopy - Zeeman effect - equation of motion of spin in magnetic fields - chemical shift – spin-spin coupling - NMR of simple AX and AMX type molecules - calculation of coupling constants -  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  NMR spectra - applications - a brief discussion of Fourier Transformation Resonance Spectroscopy.

#### UNIT-IV: CHEMICAL KINETICS: III

Catalysis by enzymes - rate of enzyme catalyzed reactions - effect of substrate concentration, pH and temperature on enzyme catalyzed reactions - inhibition of enzyme catalyzed reactions. Study of surfaces - Langmuir and BET adsorption isotherms. Kinetics of complex reactions, reversible reactions, consecutive reactions, parallel reactions, chain reactions, general treatment of chain reactions - chain length - Rice Herzfeld mechanism - explosion limits.

Study of fast reactions - relaxation methods - temperature and pressure jump methods-stopped flow and flash photolysis methods.

**UNIT-V: APPLICATIONS OF GROUP THEORY: II**

Orthogonality theorem and its consequences - construction of character table for  $C_{2V}$  and  $C_{3V}$  - hybrid orbitals in non linear molecules ( $CH_4$ ,  $XeF_4$ ,  $BF_3$ ,  $SF_6$  and  $NH_3$ ). Determination of representations of vibrational modes in non linear molecules ( $H_2O$ ,  $PCl_5$ ,  $BF_3$ , and  $NH_3$ ). Symmetry selection rules of infra red and Raman spectra.

**Text books:**

C.N. Banwell and E.M. McCash, Fundamentals of Molecular spectroscopy, IV - Edition, Tata McGraw Hill (2005).

D.N. Sathyanarayana, Vibrational Spectroscopy, New Age International Publishers (2004).

Carrington and Ad. McLachlan, Introduction to Magnetic Resonance, Harper and Row, New York (1967).

J. Rajaram and J.C. Kuriacose, Kinetics and Mechanism of Chemical Transformations. Mac Millan India Ltd (1993).

R.J. Laidler, Chemical Kinetics, Harper and Row, New York (1987).

K.L. Kapoor, A text book of Physical Chemistry, Mac Millan India Ltd., (2001).

K.V. Raman, Group Theory and its Applications to Chemistry, Tata Mc Graw Hill Publishing Co., (1990).

P.K. Bhattacharya, Group Theory and its Applications, Himalaya Publishers.

K.V. Ramakrishnan and M.S. Gopinath, Group Theory in Chemistry, Vishal Publications (1998).

**Suggested References**

Raymond Chang, Basic Principles of Spectroscopy, McGraw Hill Ltd., New York (1971).

G.M. Barrow, Introduction to Molecular Spectroscopy, Mc Graw Hill, New York (1962).

W. Kemp, NMR in Chemistry, Mc Millan Ltd., (1986).

D. McLachlan, Magnetic Resonance, Oxford Chemistry Series, Oxford (1970).

B.P. Staughan and S. Walker, Spectroscopy, Vol. I, II & III, Chapman and Hall (1976).

J.K. Sanders and B.K. Hunter, Modern NMR Spectroscopy, A Guide For Chemists, Oxford University Press, Oxford (1987).

Jk.M. Sanders, E.C. Constable and B.K. Hunter, Modern NMR Spectroscopy - a Work Book of Chemical Problems, Oxford (1989).

C.N. Banwell, Fundamentals of Molecular Spectroscopy, Mc Graw Hill (1966).

R.G. Frost and Pearson, Kinetics and Mechanism, Wisely, New York (1961).

C. Capellos and B.H.J. Bielski, Kinetic Systems, Wisely Interscience, New York (1972).

Amdur and G.G. Hammes, Chemical Kinetics, Principles and Selected Topics, McGraw Hill, New York (1968).

G.M. Harris, Chemical Kinetics, D.C. Health and Co., (1966).

F.A. Cotton, Chemical Applications of Group Theory, John Wiley and Sons inc., New York (1971).

N. Thinkham, Group Theory and Quantum Mechanics, McGraw Hill Book Company, New York (1964).

D.S. Schonland, Molecular Symmetry, Vannostrand, London (1965).

Alan Vincent, Molecular Symmetry and Group Theory-Programme Introduction to Chemical Application, Wiley, New York (1977).



**ELECTIVE**

**PAPER – 2**

**(to choose 1 out of 3)**

**A. GREEN CHEMISTRY**

**Objectives:**

To know eco-friendly methods of synthesis. This helps in planning the synthesis of any type of organic compounds with the revolution of Green Chemistry.

**UNIT I: PRINCIPLES & CONCEPT OF GREEN CHEMISTRY**

Introduction –Concept and Principles-development of Green Chemistry- Atom economy reactions –rearrangement reactions , addition reactions- atom uneconomic-sublimation-elimination-Wittig reactions-toxicity measures- Need of Green Chemistry in our day to day life.

**UNIT II: MEASURING AND CONTROLLING ENVIRONMENTAL PERFORMANCE**

Importance of measurement – lactic acid production-safer Gasoline – introduction to life cycle assessment-four stages of Life Cycle Assessment (LCA) –Carbon foot printing-green process Matrics-eco labels -Integrated Pollution and Prevention and Control(IPPC)-REACH (Registration, Evaluation, Authorization of Chemicals)

**UNIT III:EMERGING GREEN TECHNOLOGY AND ALTERNATIVE ENERGY SOURCES**

Design for Energy efficiency-Photochemical reactions- Advantages-Challenge faced by photochemical process. Microwave technology on Chemistry- Microwave heating –Microwave assisted reactions-Sono chemistry and Green Chemistry –Electrochemical Synthesis-Examples of Electrochemical synthesis.

**UNIT IV: RENEWABLE RESOURCES**

Biomass –Renewable energy – Fossil fuels-Energy from Biomass-Solar Power- Other forms of renewable energy-Fuel Cells-Alternative economics-Syngas economy- hydrogen economy-Bio refinery chemicals from fatty acids-Polymer from Renewable Resources –Some other natural chemical resources.

**UNIT V: INDUSTRIAL CASE STUDIES**

Methyl Methacrylate (MMA)-Greening of Acetic acid manufacture-Vitamin C-Leather manufacture –Types of Leather –Difference between Hide and Skin-Tanning –Reverse tanning – Vegetable tanning –Chrome tanning-Fat liquoring –Dyeing –Application-Polyethylene- Ziegler Natta Catalysis-Metallocene Catalysis-Eco friendly Pesticides-Insecticides.

**References:**

Mike Lancaster , Green Chemistry and Introductory text, II Edition

P.T.Anastas and J.C Warner,Green Chemistry theory and Practice, Oxford University press, Oxford (1988).

P.Tundo *et. al.*, Green Chemistry, Wiley –Blackwell, London (2007).

Protti D.Dondi *et.al.*, Green Chemistry

T.E Graedel, Streamlined Life cycle Assessment, Prentice Hall, New Jersey (1998).

V.K. Ahluwalia, Methods and Reagents of Green Chemistry: An Introduction by Green Chemistry.  
[www.clri.org](http://www.clri.org)

**PAPER – 2**

**B. MATERIALS SCIENCE**

**UNIT- I: Classification of crystals**

Seven crystal systems and fourteen Bravais lattices. Structure and bonding in solids- Cohesive force in crystals, van der waal's interactions, ionic bonding, covalent bonding and hydrogen bonding in solids. Structure aspects of rock salt, rutile, fluorite, antiferite, diamond, zinc blende, wurtzite, Cristobalite, spinels, inverse spinels and silicates.

**UNIT –II: Crystal geometry**

Symmetry elements for solids (including glide planes and screw axis). Introduction to space groups with examples. Techniques of structure determination in solid state – X-ray diffraction, electron and neutron diffractions and electron microscopy – principle, instrumentation and applications; Calculation of structure factor.

**UNIT- III: Theories of metallic state**

Free electron theory, (Brillouin) and Band models. Defects in crystals – Frenkel and Schotky defects, F-centres, effect of defects on the electrical, optical, magnetic, thermal and mechanical properties of crystals. Smart metals- binary and ternary – examples and applications.

**UNIT –IV: Ionic conductors**

Optimised ionic conductors- silver ion, copper ion, alumina and related electrolytes, alkali metal ion, fluoride ion and proton conductors; super conductors – principle and applications. Models of ionic motion- simple hopping motion – cooperative motion models. Photo conducting materials – principle, examples and applications.

**UNIT V: Organic semiconductors**

Organic semiconductors – photo physical processes, thermal and photo generation of carriers; Aromatic hydrocarbons, phthalocynins- anthracene mechanisms; excitons and polarons. Charge transfer complexes – characterization and their electrical properties. Conduction polymers- polyacetylenes, polyanilines and polyvinylidenes- preparation

and Applications. Carbon Nano particles- fullerenes- preparation and potential applications. liquid crystals- classification- thermotropic and lyotropic- nematic, smectic and cholesteric and their applications.

**References:**

Materials science	Raghavan
Materials Science	Vol I and II by Manas Chanda
Structural Inorganic chemistry	A.F . Wells
Introduction to solid state physics	McCreary et al.
Solid state chemistry and applications	Antony West
Solid state chemistry	Hannay
Chemistry of Nanomaterials, Vol. I & II, Wiley VCH Verlag GmbH KGaA, 2002.	C.N.R. Rao, Muller and A. K. Cheetham,

## PAPER – 2

### C. APPLIED ELECTROCHEMISTRY

#### UNIT-I: CONVERSION AND STORAGE OF ELECTROCHEMICAL ENERGY

Pollution problem. History of fuel cells, Direct energy conversion by electrochemical means. Maximum intrinsic efficiency of an electrochemical converter. Physical interpretation of the Carnot efficiency factor in electrochemical energy converters. Power outputs. Electrochemical Generators (Fuel Cells) : Hydrogen oxygen cells, Hydrogen Air cell, Hydrocarbon air cell, Alkaline fuel cell, Phosphoric acid fuel cell, direct NaOH fuel cells, applications of fuel cells.

#### UNIT-II: ELECTROCHEMICAL ENERGY STORAGE

Properties of Electrochemical energy storers: Measure of battery performance, Charging and discharging of a battery, Storage Density, Energy Density. Classical Batteries : (i) Lead Acid (ii) Nickel-Cadmium, (iii) Zinc manganese dioxide. Modern Batteries : (i) Zinc-Air (ii) Nickel-Metal Hydride, (iii) Lithium Battery, Future Electricity storers : Storage in (i) Hydrogen, (ii) Alkali Metals, (iii) Non aqueous solutions.

#### UNIT-III: CORROSION AND STABILITY OF METALS

Civilization and Surface mechanism of the corrosion of the metals; Thermodynamics and the stability of metals, Potential -pH (or Pourbaix) Diagrams; uses and abuses, Corrosion current and corrosion potential -Evans diagrams. Measurement of corrosion rate: (i) Weight Loss method, (ii) Electrochemical Method. Inhibiting Corrosion: Cathodic and Anodic Protection. (i) Inhibition by addition of substrates to the electrolyte environment, (ii) by changing the corroding method from external source, anodic Protection, Organic inhibitors, The fuller Story Green inhibitors. Passivation : Structure of Passivation films, Mechanism of Passivation, Spontaneous Passivation Nature's method for stabilizing surfaces.

#### UNIT-IV: KINETIC OF ELECTRODE PROCESS

Essentials of Electrode reaction. Current Density, Overpotential, Tafel Equation, Butler Volmer equation. Standard rate constant ( $K_0$ ) and Transfer coefficient ( $\alpha$ ), Exchange Current. Irreversible Electrode processes : Criteria of irreversibility, information from irreversible wave. Methods of determining kinetic parameters for quasi-reversible and irreversible waves: Koutecky's methods, Meites Israel Method, Gellings method. Electrocatalysis: Chemical catalysts and

Electrochemical catalysts with special reference to porphyrin oxides of rare earths. Electrocatalysis in simple redox reactions, in reaction involving adsorbed species. Influence of various parameters.

#### **UNIT-V: POTENTIAL SWEEP METHODS**

Linear sweep Voltammetry, Cyclic Voltammetry, theory and applications. Diagnostic criteria of cyclic voltammetry. Controlled current microelectrode techniques: comparison with controlled potentials methods, chronopotentiometry, theory and applications. Bulk Electrolysis Methods : Controlled potential coulometry, Controlled Coulometry, Electroorganic synthesis and its important applications. Stripping analysis: anodic and cathodic modes, Pre electrolysis and Stripping steps, applications of Stripping Analysis. Bioelectrochemistry : bioelectrodics, Membrane Potentials, Simplistic theory, Modern theory, Electrical conductance in biological organism: Electronic, Protonic electrochemical mechanism of nervous systems, enzymes as electrodes.

#### **References :**

Modern Electrochemistry Vol. I, Ila, Vol. IIB, J'OM Bockris and A.K.N. Reddy, Plenum Publication, New York.

Polarographic Techniques by L. Meites, Interscience.

"Fuel Cells : Their electrochemistry". McGraw Hill Book Company, New York.

Modern Polarographic Methods by A.M. Bond, Marcell Dekker.

Polarography and allied techniques by K. Zutshi, New age International publication. New Delhi.

"Electroanalytical Chemistry by Basil H. Vessor & Galen W. ; Wiley Interscience.

Electroanalytical Chemistry by Basil H. Vessor & Galen W. ; Wiley Interscience.

Topics in pure and Applied Chemistry, Ed. S. K. Rangrajan, SAEST Publication, Karaikudi (India).

References:

1. Arthur I. Vogel, "A Textbook of Practical Organic Chemistry", ELBS.
2. N.S. Gnanaprasagam and B. Ramamoorthy, "Organic Chemistry Lab Manual" (2006), S. Visvanathan Printers & Publishers.

**MAIN PRACTICAL**  
**PAPER – 1**  
**ORGANIC CHEMISTRY I**

Identification of components in a two component mixture and preparation of their derivatives.  
Determination of b.p. / m.p. for components and m.p. for the derivatives.

Any Six preparations form the following:

Preparation of o-benzyl benzoic acid

p-Nitrobenzoic acid from p-nitrotoluene

Anthroquinone from anthracene

Benzhydrol from benzophenone

m-Nitroaniline from m-dinitrobenzene

1,2,3,4 - Tetrahydrocarbazole from cyclohexanone

p-Chlorotoluene form p-toluidine

2,3 - Dimethylindole from phenyl hydrazine and 2 - butanone Methyl orange form sulphanilic acid

Diphenyl methane from benzyl chloride

University Examination	Marks
Qualitative organic Analysis	30
Preparation	15
Record	05
<i>Viva voce</i>	10
Total	60

References:

1. Arthur I. Vogel, "A Textbook of Practical Organic Chemistry", ELBS.

2. N.S. Gnanapragasam and B. Ramamoorthy,

"Organic Chemistry Lab Manual" (2006), S. Visvanathan Printers & Publishers.

Internal Assessment	Marks
Two Tests	20
Attendance/ Regularity	10
Results accuracy	10
Total	40

**MAIN PRACTICAL****PAPER – 2****INORGANIC CHEMISTRY PRACTICAL – I**

a) Semimicro qualitative analysis of mixture containing two common and two rare cations. The following are the rare cations to be included. W, Ti, Te, Se, Ce, Th, Zr, V, U, Li, Mo, Be.

Complexometric Titrations (EDTA)- Estimation of Ca, Mg and Zn.

Preparation of the followings:

Potassium tris (oxalate) aluminate (III) trihydrate

Tris (thiourea) copper (I) chloride

Potassium tris (oxalato) chromate (III) trihydrate

Sodium bis(thiosulphato) cuprate (I)

Tris (thiourea) copper (I) sulphate

Sodium hexanitrocobaltate (III)

Chloropentammine cobalt (III) chloride

Bis (acetylacetonato) copper (II)

Hexamminenickel (II) chloride

Bis (thiocyanato) pyridine manganese (II)

Separation of zinc and magnesium on an anion exchange.

University Examination	Marks
Qualitative Inorganic Analysis	20
Preparation	10
EDTA Complexometric Titration	15
Record	05
<i>Viva voce</i>	10
<b>Total</b>	<b>60</b>

Internal Assessment	Marks
Two Tests	20
Attendance / Regularity	10
Results accuracy	10
<b>Total</b>	<b>40</b>



## MAIN PRACTICAL

### PAPER - 3

#### PHYSICAL CHEMISTRY I

Experiments in Thermodynamics, colligative properties, phase rule, chemical equilibrium and chemical kinetics. Typical examples are given and a list of experiments is also provided from which suitable experiments can be selected as convenient.

Heat of solution from Solubility measurements

Determination of molecular weight

Determination of activity and activity coefficient

Phase diagram construction involving two/three component systems

Determination of partial molar quantities

adsorption isotherm

Reaction rate and evaluation of other kinetic parameters using polarimetry, analytical techniques, conductometry, dilatometry

Verification of Beer Lambert law.

Detailed list of Experiments for Physical Chemistry Practical I

Typical list of possible experiments are given. Experiments of similar nature and other experiments may also be given. The list given is only a guideline. Any 15 experiments have to be performed in a year.

Determine the temperature coefficient and energy activation of hydrolysis of ethyl acetate.

Study the kinetics of the reaction between acetone in iodine and - acidic medium by half life method and determine the order with respect to iodine and acetone.

Study the effect of solvent (DSMO-water, acetone-water system).On the rate of acid catalysed hydrolysis of acetal by dilatometry.

Study the Saponification of ethyl acetate by sodium hydroxide conductometrically and determine the order of the reaction.

Determine the order with respect to Silver (I) in the oxidation by spt and rate constant and for uncatalysed reaction.

Study the inversion of cane sugar in the presence of acid using Polari meter.

Determine the rate constant and order of the reaction between potassium persulphate and potassium iodide and determine the temperature coefficient and energy of activation of the reaction.

Study the effect of ionic strength on the rate constant for the saponification of an ester.

Study the salt effect on the reaction between acetone and iodine.

Study the kinetics of the decomposition of sodium thiosulphate by mineral acid(0.5M HCl).

Study the primary salt effect on the kinetics of ionic reactions and test the Bronsted relationship (iodide ion is oxidized by persulphate ion).

Study the kinetics of enzyme catalysed reactions (Activity of tyrosinase upon tyrosine spectrophotometrically).

Study the salt effect, the solvent effect on the rate law of alkaline hydrolysis of crystal violet.

Study the reduction of aqueous solution of ferric chloride by stannous chloride.

Determine the molecular weight of benzoic acid in benzene and find the degree of association.

Determine the activity coefficient of an electrolyte by freezing point depression method.

Study the phase diagram form-toluidine and glycerine system.

Construct the phase diagram for a simple binary system naphthalene - phenantherene and benzophenone-diphenyl amine.

Construct the boiling point composition diagram for a mixture having maximum boiling point and minimum boiling point.

Study the complex formation between copper sulphate and ammonia solution by partition method.

Study the simultaneous equilibria in benzoic acid - benzene water system.

Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride by partition method.

Determine the molecular weight of a polymer by viscosity method.

Determine the viscosities of mixtures of different compositions of liquids and find the composition of a given mixture.

Determine the partial molal volume of glycine/methonal/formic acid/sulphuric acid by graphical method and by determining the densities of the solutions of different compositions.

Study the temperature dependence of the solubility of a compound in two solvents having similar inter molecular interactions (benzoic acid in water and in DMSO water mixture) and calculate the partial molar heat of solution.

Determine the polar molar volume of glycine/methonal/formic acid /sulphuric acid by graphical method and by determining the densities of solutions of different concentrations.

Construct the phase diagram of the three component of partially immiscible liquid system (DMSO-water-benzene; acetone-chloroform -water; chloroform-acetic acid-water)

Construct the phase diagram of a ternary aqueous system of glucose -potassium chloride and water

Study the surface tension - concentration relationship for solutions(Gibb's equation)

Study the absorption of acetic acid by charcoal(Freundlich isotherm)

Study the complex formation and find the formula of silver-ammonia complex by distribution method.

Determine the dissociation constant of picric acid using distribution law.

Construct a chemical actinometry and determine the quantum yield and calibrate the lamp intensity.

UNIVERSITY EXAMINATION	Marks
Procedure	10
Manipulation	15
Result	20
Record	05
<i>Viva voce</i>	10
Total	60

INTERNAL ASSESSMENT	Marks
Two Tests	20
Attendance / Regularity	10
Results accuracy	10
Total	40

## SEMESTER III

### PAPER - 7

## ORGANIC CHEMISTRY III

### Objective:

To understand the concepts of spectral techniques and to apply these techniques for the quantitative and structural analysis of organic compounds. To learn the chemistry of terpenes, alkaloids and free radicals and their importance.

### UNIT-I: UV AND IR SPECTROSCOPY AND THEIR APPLICATIONS

Ultraviolet - Visible spectroscopy - types of electronic transitions - chromophores and auxochromes - factors influencing positions and intensity of absorption bands - absorption spectra of dienes, polyenes and unsaturated carbonyl compounds - Woodward - Fieser rules. IR Spectroscopy - vibrational frequencies and factors affecting them - identification of functional groups - intra and inter molecular hydrogen bonding - finger print region - Far IR region - metal ligand stretching vibrations.

### UNIT-II: NMR SPECTRA AND ITS APPLICATIONS

Nuclear spin - magnetic movement of a nucleus - nuclear energy levels in the presence of magnetic field relative populations of energy levels - macroscopic magnetization - basic principles of NMR experiments - CW and FT NMR -  $^1\text{H}$  NMR - chemical shift and coupling constant - factors influencing proton chemical shift and vicinal proton - proton coupling constant -  $^1\text{H}$  NMR spectra of simple organic molecules such as  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{CHO}$  etc. AX and AB spin system - spin decoupling - nuclear Overhauser effect- chemical exchange.  $^{13}\text{C}$  NMR - proton decoupled and off - resonance  $^{13}\text{C}$  NMR spectra - factors affecting  $^{13}\text{C}$  chemical shift -  $^{13}\text{C}$  NMR spectra of simple organic molecules. Problem solving (for molecules with a maximum number of C10).

### UNIT-III: PHYSICAL METHODS OF STRUCTURAL DETERMINATION

Mass Spectroscopy - Principles - measurement techniques - (EI, CI, FD, FAB, SIMS) - presentation of spectral data - molecular ions - isotope ions - fragment ions of odd and even electron types - rearrangement ions - factors affecting cleavage patterns - simple and

multicentre fragmentation - McLafferty rearrangement. Mass spectra of hydrocarbons, alcohols, phenols, aldehydes and ketones. Octant rule, cotton effect, axial halo ketone rule, ORD and its applications.

#### **UNIT-IV: TERPENES AND ALKALOIDS**

Introduction, classification, isoprene rule, structural determination of terpenoids' Citral, Geraniol, Linalool, Farnesol,  $\alpha$ -pinene and camphor.

Introduction-isolation of alkaloids - total synthesis of quinine, morphine and reserpine.

#### **UNIT-V: FREE RADICALS**

Long and short-lived free radicals, methods of generation of free radicals. Addition of free radicals to olefinic double bonds. The following aromatic radical substitutions are to be studied: decomposition of diazocompounds, phenol - coupling - Sandmeyer reaction, Gomberg reaction, Pschorr reaction, Ulmann reaction, mechanism of Hunsdiecker reaction - Detection of free radicals by ESR.

#### **Recommended Books**

Francis A. Carey and Richard J. Sundberg, Advanced organic chemistry, III Edition (1990).

G.A Swan, Introduction to alkaloids

I.L. Finar, Organic chemistry, Vol. II, 5<sup>th</sup> edition ELBS publication.

J. Dyer, Application of absorption spectroscopy of organic compounds, Prentice and Hall of India, Pvt., New Delhi.

J. March, Advanced organic reaction mechanism and structure, Tata McGraw Hill.

James verghese, Terpene Chemistry.

Neil S. Issac, Physical organic chemistry, ELBS publication 1987.

O.P. Agarwal, Chemistry of organic Natural Products, Goel Publishing House, Meerut.

P.S. Kalsi, Spectroscopy of organic compounds, Wiley Eastern Ltd., Chennai.

Pelletier, Chemistry of alkaloids.

R.M. Silverstein, G.d. Bassler and Monsu, Spectrometric identification of organic compounds, John Wiley and Sons, New York.

S.M. Mukherji and S.P. Singh, Organic Reaction Mechanism, MacMillan India Ltd., Chennai (1990).

Schliemann, Introduction to the spectroscopic methods for the identification organic compounds, 2 volumes, Pergamon Press.

W. Kemp, Spectroscopy, Macmillan Ltd.,

Y.R. Sharma, Structural identification of organic compounds, S. Chand & Co.

## PAPER - 8

### INORGANIC CHEMISTRY III

#### Objective

To study about the Coordination complexes, Substitution in Coordination complexes, to study the Inorganic Photochemistry.

#### UNIT-I: ORGANO METALLIC CHEMISTRY I

Carbon donors: Alkyls and aryls metallation, bonding in carbonyls and nitrosyls, chain and cyclic donors, olefins, acetylene and allyl system, synthesis structure and bonding, metallocenes.

Reactions: Association substitution, addition and elimination reactions, ligand protonation, electrophilic and nucleophilic attack on ligands. Carbonylation, Decarboxylation, oxidative addition and fluxionality.

#### UNIT-II: ORGANO METALLIC CHEMISTRY II

Catalysis: Hydrogenation of olefins (Wilkinson's catalyst), hydroformylation of olefins using cobalt or rhodium catalysts (Oxo process), oxidation of olefins to aldehydes and ketones (Wacker process) polymerization (Zeigler - Natta Catalyst); cyclo oligomerisation of acetylene using nickel catalyst (Reppe's catalyst); polymer-bound catalysts.

#### UNIT-III: COORDINATION CHEMISTRY IV

Electron transfer reactions, outer and inner sphere processes; atom transfer reaction, formation and rearrangement of precursor complexes, the bridging ligand, precursor and successor complexes, Marcus Theory.

Complementary, non-complementary and two electron transfer reactions.

#### UNIT-IV: COORDINATION CHEMISTRY V

Substitution Reactions: Substitution in square planar complexes, reactivity of platinum complexes, influences of entering, leaving and other groups, the trans effect.

**UNIT-V: COORDINATION CHEMISTRY VI**

Substitution of octahedral complexes of cobalt and chromium, replacement of coordinated water, solvolytic (acids and bases) reaction applications in synthesis (platinum and cobalt complexes only).

Inorganic Photochemistry: Photo-substitution, Photoredox and isomerisation process, application of metal complexes in solar energy conversion.

**Text books**

R.C. Mehrotra, A. Singh, *Organo Metallic Chemistry*, Wiley Eastern Co., (1992).

F. Basolo and R.G. Pearson, *Mechanism of Inorganic Reaction*, Wiley NY (1967).

J. Huheey, *Inorganic Chemistry*, Harper and Collins, NY IV Edition, (1993).

K.F. Purcell and J.C. Kotz, *Inorganic Chemistry*, W. Saunders Co., (1977).

S. FA Kettle, *Coordination Chemistry*, ELBS, (1973).

F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley and Sons, V Edition (1988).

D.F. Shriver, Pw. Atkins and C.H. Langford, *Inorganic Chemistry*, OUP (1990).

Guillermo J. Ferraudi, *Elements of inorganic photochemistry*, Wiley (1988).

Arthur W. Adamson, Paul D. Fleischauer, *Concepts of inorganic photochemistry*, Wiley(1975).

**Suggested References**

G. Coates M.I. Green and K. Wade. *Principles of Organometallic chemistry*, Methven Co., London (1988).

P. Powell, *Principles of Organometallic chemistry*, Chappman and Hall. (1998).

G.S. Manku, *Theoretical Principles of Inorganic Chemistry*, McGraw-Hill Education, (1984).

M.C. Day and J. Selbin, *Theoretical Inorganic Chemistry*, Van Nostrand Co., New York (1974).

R.B. Heslop and K. Jones, *Inorganic Chemistry*, Elsevier Scientific Publ., (1976).

F. Basolo and R.G. Pearson, *Mechanism of Inorganic Reaction*, Wiley NY (1967).

M.C. Day and J. Selbin, *Theoretical Inorganic Chemistry*, Van Nostrand Co., New York (1974).

B.E. Dogulas DH McDaniel's and Alexander, *Concepts and Models of Inorganic Chemistry*, Oxford IBH (1983).

WU. Mallik, G.D. Tuli, R.D. Madan, *Selected topics in Inorganic Chemistry*, S. Chand and Co., New Delhi (1992).

## PAPER - 9

### PHYSICAL CHEMISTRY III

#### Objectives

To study the fundamental principles of Quantum Chemistry and its application to Chemical Bonding. Schrödinger wave equation and its applications. To Study the principles of Photochemical reactions. Study of Electrode - Electrolytic interface.

#### UNIT-I: QUANTUM CHEMISTRY: I

The Compton effect - wave particle duality - uncertainty principle - waves - wave equation for electrons - quantum mechanical postulates-the operators - Hermitian property.

#### UNIT-II: QUANTUM CHEMISTRY: II

Schrodinger equation - application of Schrodinger's equation - the particle in a box (one, two and three dimensional cases). Particle in a ring, Schrodinger equation for hydrogen atom (no derivation is required) and the solution.

Approximation methods - Perturbation and Variation methods - application to hydrogen and helium atoms.

#### UNIT-III: QUANTUM CHEMISTRY: III

Born - Oppenheimer approximation - Valence bond theory for hydrogen molecule - LCAO - MO theory for di and polyatomic molecules.

Concept of hybridization - Huckel theory for conjugated molecules (Ethylene, butadiene and benzene) - semi - empirical methods - Slater orbital and HF - SCF methods.

#### UNIT-IV: PHOTOCHEMISTRY: I

Absorption and emission of radiation - Franck - Condon Principle - decay of electronically excited states - Jablonsky diagram - radiative and non radiative processes - fluorescence and phosphorescence - spin forbidden radiative transition -

Internal conversion and intersection crossing - energy transfer process - kinetics of unimolecular and bimolecular photophysical processes-excimers and exciplexes - static and dynamic quenching - Stern-Volmer analysis.



**UNIT-V: ELECTROCHEMISTRY: II**

Electrode - electrolyte interface - adsorption at electrified interface - electrical double layer - electro capillary phenomenon - Lippmann equation - Structure of double layers - Helmholtz - Perrin, Guoy - Chapman and Stern model of electrical double layers.

Diffusion - Fick's law of diffusion - Effect of ionic association on conductance-electro kinetic phenomena -membrane potential.

**Text Books**

R.K. Prasad, Quantum Chemistry, Wiley Eastern, New Delhi (1992).

D.A. Mcquarrie, Quantum Chemistry, University Science Books, Mil Valley, California (1983).

Quantum Chemistry, Allyn and Bacon, Boston (1983).

R. Anantharaman, Fundamentals of Quantum Chemistry, Mac Millan India Limited (2001).

M.W. Hanna, Quantum Mechanics in Chemistry, W.A. Benjamin Inc. London (1965).

N.J.Turro, Modern Molecular Photochemistry, Benjamin, Cumming, Menlo Park, California (1978).

K.K.Rohatgi, Mukherjee, Fundamentals of Photochemistry, Wiley Eastern Ltd., (1978).

S. Glasstone, Introduction to Electrochemistry, Affiliated East West Press, New Delhi (1960).

D.R. Crow, Principles and Applications to Electrochemistry, Chapman and Hall (1991).

**Suggested References**

W.J. Moore, Physical Chemistry, Orient Longman, London (1972).

A.K. Chandra, Introductory Quantum Chemistry, Tata Mc Graw Hill.

J.M. Murrell, S.F.A. Kettle and J.M. Tedder, The Chemical Bond, Wiley (1985).

D.A. Mc Quarrie, Quantum Chemistry, University Science Books, Mill Valley, California (1983).

P.W. Atkins, Molecular Quantum Mechanics, Oxford University Press, Oxford (1983).

J.G.Clavert and J.N.Pitts, Photochemistry, Wiley, London (1966).

R.P.Wayne, Photochemistry, Butterworths, London (1970).

J.O.M. Bokris and A. K. N. Reddy, Electrochemistry, Vol. 1 and 2, Plenum, New York (1977).

P. Dalahay, Electrode Kinetics and Structure of Double Layer, Inter Science, New York (1965).

J.Robbins, Ions in Solution-An Introduction to Electrochemistry, Clarendon Press, Oxford (1993).

H.Reiger, Electrochemistry, Chapman and Hall, New York (1994).

**ELECTIVE**

**PAPER-3**

**(to choose 1 out of 3)**

**A. SCIENTIFIC RESEARCH METHODOLOGY**

**Objectives**

To study about the importance of research, literature survey, error analysis, statistical treatment. To study about the conventions of writing thesis.

**UNIT-I: INTRODUCTION**

Nature and importance of research - aims, objective, principles and problems - selection of research problem - survey of scientific literature - primary and secondary sources - citation index for scientific papers and journals - patents.

**UNIT-II: CONDUCT OF RESEARCH WORK**

Physical properties useful in analysis and methods of separation prior to analysis - Isolation techniques - extraction - Soxhlet extraction, crystallization, sublimation - methods for vacuum sublimation and distillation under reduced pressure.

Chemistry of working with hazardous materials - acid / water sensitive, corrosive, toxic, explosive and radioactive materials.

**UNIT-III: EVALUATION OF ANALYTICAL DATA**

Precision and accuracy - Reliability - determinate and random errors - distribution of random errors - normal distribution curve.

**UNIT-IV: STATISTICAL TREATMENT OF ANALYTICAL DATA**

Statistical treatment of finite samples - the students test and F test - Criteria for rejection of an observation - the Q test, significant figures and computation rules - data plotting - least square analysis.

**UNIT-V: THESIS AND ASSIGNMENT WRITING**

Conventions of writing - the general format - page and chapter format - use of quotations and footnotes - preparation of tables and figures - referencing - appendices - Revising editing and evaluating the final product - proof reading - Meanings and examples of commonly used abbreviations.

**References**

Douglas A. Skoog and Donald, M. West, Fundamental of analytical chemistry, Halt Saundersons International Edition.

J. Anderson, H.M. Durston and M.Poole, Thesis and assignment writing - Wiley Eastern Ltd., (1970).

J. March, Advanced organic chemistry - reactions, Mechanism & Structure. McGraw Hill Student Edition.

Vogel's Textbook of quantitative chemical analysis, ELBS edition.

## PAPER – 3

### B. PHYSICAL ORGANIC CHEMISTRY

#### UNIT-I: PRINCIPLES OF REACTIVITY

Mechanistic significance of entropy, enthalpy and Gibbs free energy. Arrhenius equation. Transition state theory. Uses of activation parameters, Hammond's postulate, Bell-Evans-Polanyi Principle. Potential energy surface model. Marcus theory of electron transfer. Reactivity and selectivity principles. Kinetic Isotope Effect: Theory of isotope effects. Primary and secondary kinetic isotope effects. Heavy atom isotope effects, Tunneling effect, Solvent effects.

#### UNIT-II: STRUCTURAL EFFECTS ON REACTIVITY

Linear free energy relationships (LFER). The Hammett equation, substituent constants, theories of substituent effects. Interpretation of  $\rho$ -values. Reaction constant  $\rho$ . Deviations from Hammett equation. Dual parameter correlations, inductive substituent constant. The Taft model,  $\sigma_1$  and  $\sigma_R$  scales. Solvation and Solvent Effects. Qualitative understanding of solvent-solute effects on reactivity. Thermodynamic measure of solvation. Effects of solvation on reaction rates and equilibria. Various empirical indexes of solvation based on physical properties, solvent-sensitive reaction rates, spectroscopic properties and scales for specific solvation. Use of solvation scales in mechanistic studies. Solvent effects from the curve-crossing model.

#### UNIT-III: ACIDS, BASES, ELECTROPHILES, NUCLEOPHILES AND CATALYSIS

Acid-base dissociation, Electronic and structural effects, acidity and basicity. Acidity functions and their applications. Hard and soft acids and bases. Nucleophilicity scales. Ambivalent nucleophiles. Acid-base catalysis-specific and general catalysis. Brønsted catalysis, Nucleophilic and electrophilic catalysis. Catalysis by noncovalent binding-micellar catalysis. Steric and conformational properties: Various types of steric strain and their influence on reactivity. Steric acceleration. Molecular measurements of steric effects upon rates. Steric LFET, Conformational barrier to bond rotation-spectroscopic detection of individual conformers. Acyclic and monocyclic systems. Rotation around partial double bonds. Winstein-Holness and Curtin-Hammett principle.

#### **UNIT-IV:NUCLEOPHILIC AND ELECTROPHILIC REACTIVITY**

Structural and electronic effects on SN1 and SN2 reactivity. Solvent effect Kinetic isotope effects. Intramolecular assistance. Electron transfer nature of SN2 reaction. Nucleophilicity and SN2 reactivity based on curve-crossing mode. Relationship between polar and electron transfer reactions. Electrophilic reactivity, general mechanism.Kinetic of SE2 Ar reaction.Structural effects on rates and selectivity.Curve-crossing approach to electrophilic reactivity.Radical and Pericyclic Reactivity:Radical stability, polar influences, solvent and steric effects. A curve crossing approach to radical addition, factors effecting barrier heights in addition, regioselectivity in radical reactions.Reactivity, specificity and periselectivity in pericyclic reactions.

#### **UNIT-V:SUPRAMOLECULAR CHEMISTRY**

Properties of covalent bonds-bond length, inter-bond angles, force constant, bond and molecular dipole moments. Molecular and bond polarizability, bond dissociation enthalpy, entropy, intermolecular forces, hydrophobic effects. Electrostatic, induction, dispersion and resonance energy, magnetic interactions, magnitude of interactionenergy, forces between macroscopic bodies, medium effects.

Hydrogen bond.Principles of molecular association and organization as exemplified in biological macromolecules like enzymes, nucleic acids, membranes and model system like micelles and vesicles. Molecular receptors and design principles. Cryptands, cyclophanes, calixeranes, cyclodextrines.Supramolecular reactivity and catalysis. Molecular channels and transport processes, Molecular devices and nanotechnology.

#### **Book Suggested :**

Molecular Mechanics, U. Burket and N.L. Allinger, ACS Monograph 177, 1982.

Organic Chemists, Book of Orbitals: L. Salem and W.L. Jorgensen, Academic Press.

Mechanism and Theory in Organic chemistry, T.H. Lowry and K.C. Richadson, Harper and Row.

Physical Organic Chemistry: N.S. Isaacs, ELBS/Longman.

Supramolecular Chemistry: Concepts and Perspective, J.M. Lehn, VCH.

The Physical Basis of Organic Chemistry: H. Maskill, Oxford University Press.

## PAPER – 3

### C. BIOORGANIC AND MEDICINAL CHEMISTRY

#### UNIT-I:DRUG DESIGN

Development of new drugs, concepts of pro-drugs and soft drugs, Principles of drug design, Quantitative structure activity relationships. History and development of QSAR.- Concepts of drug parameters. High throughput Screening.

#### UNIT-II:MECHANISM OF DRUG ACTION

Antibiotics: Drug action of Penicillin, cephalosporin, tetracycline and macrocyclic antibiotics (no synthesis). Antimalarials: Trimethoprim- NSAIDs: Paracetamol, Meperidine, Aminopyrine-Ibuprofen, Oxyphenylbutazone, Diclophenac sodium, Indomethacin-Antitubercular and antileprotic: Ethambutol, Isoniazide and Daspone - Anaesthetics: Lidocaine, - Antihistamines: Phenobarbital, Diphenylhydramine- Tranquilizers: Diazepam, Trimeprazine, Thiopental - Anti AIDS agents: Acyclovir, Ganciclovir.

#### UNIT-III:NUCLEIC ACIDS

Biological bases, structure and its synthesis - Nucleosides – Nucleotides.DNA and RNA structure- genetic code and its replications.

#### UNIT-IV:INTRODUCTION TO BIO-ORGANIC CHEMISTRY, AMINO ACIDS & PEPTIDES

Basic considerations, proximity effects in organic chemistry, molecular adaptation, molecular recognition and the supra molecular level.Chemistry of living cells, analogy between organic reactions and biochemical transformations, role of enzymes, chemistry of the peptide bond, asymmetric synthesis of amino acids, transition state analogues chemical mutations, proteins, structure, nature and function, synthesis of polypeptides.

#### UNIT-V:BIO MODELS

Host-Guest complexation chemistry, Developments in Crown ether chemistry, membrane chemistry and micelles, cyclodextrin.

**ReferenceBooks**

1. Burger's Medicinal Chemistry & Drug discovery, Vol 1-3, 5<sup>th</sup> Ed, 1995.
2. Wilson, Gisvold & Dorque: Text book of Organic Medical and Pharmaceutical Chemistry, 10<sup>th</sup> Ed, Lippincott publishers, 1998.
3. David A Williams, William O. Foye & Thomas L. Lemke, Foye's Principles of medicinal Chemistry, 6<sup>th</sup> Edition, Lippincott Williams & Wilkins, 2002.
4. Zubay G, Biochemistry, Maxwell Macmillan International Editions, second edition, 1987.
5. R. L. Foster, The Nature of Enzymology, Croom Helm, 1980.
6. D. L. Purich, (Ed), Contemporary Enzyme kinetics and Mechanisms, Academic Press, 1983.
7. Dugas H, Bio-organic Chemistry, A chemical approach to enzyme action, Springer 2003.

## SEMESTER IV

### PAPER - 10

## ORGANIC CHEMISTRY - IV

### OBJECTIVE:

To understand the concepts of Photochemical Reactions, Aromaticity, Antibiotics and proteins. Applications and Techniques of Dyeing.

### UNIT-I: AROMATICITY

Aromaticity of benzenoid, heterocyclic, and non-benzenoid compounds, Huckel's rule - Aromatic systems with pi electron numbers other than six - non-aromatic (cyclo octatetraene etc.) and anti aromatic system (cyclobutadiene etc.) - system with more than 10pi electrons - Annulenes upto C<sub>18</sub> (synthesis of all these compounds is not expected).

### UNIT-II: PHOTOCHEMISTRY

Photochemical excitation - fate of the excited molecules - Joblonski diagram - study of photochemical reactions of ketone - photoreduction - photocyclo addition - Paterno - Buchi reaction - di pi-methane rearrangement - Pericyclic Analysis of electrocyclic, cyclo addition and sigmatropic reactions - correlation diagrams for butadiene - cyclobutene system, hexatriene to cyclohexadiene systems. Structure of bulvalene- a fluxional molecule - Cope and Claisen rearrangement.

### UNIT-III PROTEINS AND NUCLEIC ACIDS

Proteins: Peptides and their synthesis – synthesis of tripeptide. Merrifield synthesis, Determination of tertiary structure of Protein, Bio-Synthesis of Proteins. Nucleic Acids: Types of Nucleic Acids-DNA & RNA polynucleotide chain. Components-biological functions. Structure and role of (genetic Code) DNA and RNA (Nucleotides only) Biosynthesis of Cholesterol.

### UNIT-IV: ANTIBIOTICS

Introduction, structural elucidation and synthesis of penicillin, streptomycin, Chloromycetin and tetracyclines.



**UNIT-V: DYES**

Introduction, various methods of dyeing, classification and preparations of dyes, nitroso dyes, Azodyes, - Fast green, Methyl Orange, Methyl Red, Fast Red, triphenylmethane dyes - Malachite green, Rosaniline, Aniline blue, Crystal violet, Xanthene dyes - Fluorescein, Rhodamine-B, Anthroquinone dyes – Alizarin – Preparation and uses.

**Recommended Books:**

Charles H. Depey and Orville, Molecular Reaction and Photochemistry, L. Chapman, Prentice Hall of India Pvt., Ltd., New Delhi.

Eric E. Conn, Paul. R. Stumpf, George Bruening and Roy H. Dole, Outlines of Biochemistry, V Edition, John Wiley and Sons.

Francis A. Carey and Richard J. Sandburg Advanced Organic Chemistry, Plenum Press, New York.  
I.L. Finar, Organic Chemistry, Vol. II, V Edition ELBS publication.

J. March, Advanced organic reaction mechanism and structure, Tata McGraw Hill.

L. Smith, Robert L. Hill I. Robert Lehman, Robert J. Let Rowitz, Philip Handlar and Abraham white, Principles of Biochemistry General Aspects, VII Edition McGraw Hill Int.,

Lubert Stryer, Biochemistry, Freeman and Co., New York.

O.P. Agarwal, Chemistry of organic Natural Products, Goel Publishing House, Meerut.

## PAPER - 11

### INORGANIC CHEMISTRY - IV

#### Objective

To study about the Inorganic Spectroscopy and Nuclear Chemistry.

#### UNIT-I: INORGANIC SPECTROSCOPY I AND MAGNETIC PROPERTIES

Applications to inorganic systems of the following: ultra violet, visible, infra-red and Raman spectra of metal complexes, organometallic and simple inorganic compounds with special reference to coordination sites, isomerism.

Magnetic Susceptibility and measurements - Guoy method, Faraday method; applications.

#### UNIT-II: INORGANIC SPECTROSCOPY II

Application to Inorganic systems of the followings

NMR, NQR and Mossbauer spectra - NMR of  $^{31}\text{P}$ ,  $^{19}\text{F}$ , NMR shift reagents. NQR - Nitrosyl compounds. Mossbauer spectra of Fe and Sn systems.

#### UNIT-III: INORGANIC SPECTROSCOPY III

ESR Introduction - Zeeman equation, g-value, nuclear hyperfine splitting, interpretations of the spectrum, simple carbon centered free radicals. Anisotropy - g-value and hyperfine splitting constant. McConnell's equation, Kramer's theorem. ESR of transition metal complexes of copper, manganese and vanadyl complex.

Photoelectron spectroscopy (UV and X-ray) - photo electron spectra - Koopman's theorem, time structure in PES, chemical shift and correlation with electronic charges.

#### UNIT-IV: INSTRUMENTAL ANALYSIS

AAS, AES and AFS – Principle, instrumentation and applications, advantages of AAS, interferences; GLC and HPLC – Principle, instrumentation and working, types of detectors; Inductively coupled plasma spectroscopy (ICP)- introduction, instrumentation, interferences and applications.

#### UNIT-V HYPHENATED TECHNIQUES

GC-MS, LC-MS, LC-NMR, Laser Raman spectroscopy - interfaces, advantages and applications.

**Text books**

- A. Earnshaw, Introduction to Magneto Chemistry, Academic Press, London, (1968).  
C.N.R. Rao, I.R. Ferraro, Spectroscopy in Inorganic Chemistry, Vol. I and Vol. II, Academic Press, (1970).  
D. A. Skoog and D.M. West, Principles of Instrumental Methods of analysis, Saunder's College Publ. III Edition, (1985).  
E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock, Structural Methods in Inorganic Chemistry, II Edition, Blackwell Scientific Publications, Oxford, London (1991).  
G.D. Christian and J.E.G. Reily, Instrumental Analysis, Allegen Becon, II Edition, (1986).  
H.A. Strobel, Chemical Instrumentation, Addison - Wesley Pub. Co., (1976).  
R. S. Drago, Physical Methods for Chemists, Saunders College Publishing, Philadelphia (1992).  
Willard Merrit, Dean and Settle, Instrumental methods of analysis, CBS Publ. VI edition, (1986).

**Suggested References**

- AI Vogel, Text book of Qualitative Analysis - IV Edition (1985).  
C. N. Banwell and E.M. Mc Cash, Fundamentals of Molecular Spectroscopy, IV edition, Tata McGraw Hill, New Delhi (1994).  
D.A. Skoog D.M. West, Holt Reinhert and Winston, Fundamental of Analytical Chemistry, Publication, IV Edition (1982).  
D.N. Sathyanarayana, Electronic Absorption Spectroscopy and Related Techniques, Universities Press (India) Ltd., Hyderabad (2001).  
FA Cotton and G Wilkinson, Advanced Inorganic Chemistry, John Wiley and Sons, V Edition (1988).  
G. Aruldas, Molecular Structure and spectroscopy, Prentice Hall of India Pvt. Ltd., New Delhi (2001).  
J. Huheey, Inorganic Chemistry, Harper and Collins, NY, IV Edition, (1993).  
J. M. Hollas, Modern Spectroscopy, IV Edition, John Wiley & Sons, Ltd., Chichester (2004).  
M.C. Shrivvers, P.W Atkins, CH. Langford, Inorganic Chemistry, OUP (1999).  
Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, III Edn., John Wiley and Sons, New York, (1986).  
O. Khan, Molecular Magnetism, New York, VCH (1993).  
R.L. Carlin, Magneto chemistry, Springer-Verlag, New York, (1986).  
S.F.A. Kettle, **Physical Inorganic Chemistry: A Coordination Chemistry Approach**, Oxford University Press, (1998).

**PAPER - 12**

**PHYSICAL CHEMISTRY-IV**

**Objective**

To study the electrochemical kinetics, over potential, corrossions and fuel cells. To study statistical thermodynamics, Quantum statistics and reversible thermodynamics. To study the Experimental methods and kinetics studies of photochemical reactions.

**UNIT-I: ELECTROCHEMISTRY: III**

Mechanism of electrode reactions - polarization and overpotential - the Butler-Volmer equation for one step and multistep electron transfer reactions - significance of electron exchange current density and symmetry factors - transfer coefficient and its significance - mechanism of the hydrogen and oxygen evolution reactions.

Corrosion and passivation of metals - Pourbaix diagram - Evan's diagram - fuell cells - electrodeposition - principle and applications.

**UNIT-II: STATISTICAL THERMODYNAMICS: I**

Objectives of statistical thermodynamics - concept of thermodynamics and mathematical probabilities - distribution of distinguishable and non-distinguishable particles.

Maxwell - Boltzmann distribution law - Partition function - evolution of translational, vibrational and rotational partition functions for mono, diatomic ideal gases –

**UNIT-III: STATISTICAL THERMODYNAMICS: II**

Thermodynamic functions in terms of partition functions-application of partition function to heat capacity of ideal gases - nuclear partition function - contribution to heat capacity of ortho and para hydrogen. Heat capacity of solids – Einstein and Debye models.

**UNIT-IV: STATISTICAL THERMODYNAMICS: III**

Fermi - Dirac and Bose – Einstein statistics - comparison with Maxwell -Boltzmann distribution law and their applications - radiation law - electron gas in metals.

Irreversible Thermodynamics - Forces and fluxes - linear force, flux relation - phenomenological equations.

**UNIT-V: PHOTOCHEMISTRY: II**

Experimental methods - quantum yield and life time measurements - steady state principle - quantum yield and chemical actinometry. Kinetics of photochemical reactions: hydrogen and halogen reactions,

Photoredox, photosubstitution, photoisomerization and photosensitized reactions - photovoltaic and photogalvanic cells, photoelectrochemical cells, photo assisted electrolysis of water, aspects of solar energy conversion.

**Text Books**

S. Glasstone, Introduction to Electrochemistry, Affiliated East West Press, New Delhi (1960).

P.H.Rieger, Electrochemistry, Chapman and Hall, New York (1994).

R.Crow, Principles and Applications to Electrochemistry, Chapman and Hall (1991).

M.C.Gupta, Statistical thermodynamics, Wiley Easter, New Delhi (1990).

R.Hasee, Thermodynamics Of Irreversible Process, Addition Wesley, Reading, Mass (1969).

L.K. Nash, Elements of Chemical Thermodynamics, Addison Wesley (1962).

G.M. Barrow, Physical Chemistry, McGraw Hill (1988).

R.L. De Koch and H.B. Gray, Chemical Structure and Bonding, Benjamin- Cumming, Menlo Park, California.

K.K.Rohatgi, Mukherjee, Fundamentals of Photochemistry, Wiley Eastern Ltd., (1978).

N.J.Turro, Modern Molecular Photochemistry, Benjamin, Cumming, Menlo Park, California (1978).

S.Glasstone, Text Book of Physical Chemistry.

**Suggested References**

C.M.A.Brett and As. Ms O.Brett, Electrochemistry Principles, Methods And Applications, Oup., Oxford(1993).

J. Robbins, Ions in Solution - An Introduction of Electrochemistry, Clarendon Press, Oxford (1972).

J.O.M. Bokris and A.K.N. Reddy, Electrochemistry, Vols. I&II, Plenum, New York, (1977).

B.J.Mc Clenlland, Statistical Thermodynamics, Chapman and Hall, London (1973).

Cleyde, Physical Chemistry, Schaum Series, Mc Graw Hill (1976).

Dole, Thermodynamics, Prentice Hall, New York (1954).

I.Prigogine, Introduction to Thermodynamics of Irreversible Process, Interscience, New York (1961).

N. O. Smith, Elementary Statistical Thermodynamics, A Problem Approach, Plenum Press, New York (1961).

Seans, Salinyar and Tangodie, Statistical Thermodynamics,

J.G.Clavert and J.N.Pitts, Photochemistry, Wiley, London (1966).

P.Dalahay, Electrode Kinetics And Structure Of Double Layer, Inter Science, New York (1965).

R.P.Wayne, Photochemistry, Butterworths, London (1970).

**ELECTIVE**

**PAPER - 4**

**(to choose 1 out of 3)**

**A. ENVIRONMENTAL CHEMISTRY**

**UNIT - I: ATMOSPHERIC CHEMISTRY**

The structure of the earth's atmosphere- chemistry of the lower and upper atmosphere. The chemistry of air pollution- oxides of nitrogen- hydrogen sulphide and oxides of sulphur- Aerosols – ozone depletion and consequences- dioxins burning plastics- other atmospheric chemicals- smog- radio activity and fallout- air pollution abatement. Green house effect- Global warming, oxides of carbon.

**UNIT - II: THE EARTH**

The lithosphere- the chemical composition of earth- the structure and composition of inner earth- the mantle, and the crust. The exploitation of mineral resources and the abuse of earth – earth resources – changing the face of the land- the earth as a dump- recycle- earth resource conservation steps.

The hydrosphere : The fresh water chemistry – the structure and properties of liquid water – lakes, rivers, ponds and stream – river chemistry, pollution and aeration – water additives- isotopes- mercury pollution. The chemical constituents of sea water- organic matter and suspended material- ocean dumping- oil pollution. The role of water in our total environment- the hydrologic cycle- snow and ice – nucleation and precipitation – the chemical composition of rain water- phase changes and isotopic fractionation.

**UNIT - III: THE BIOSPHERE**

The structure of the biosphere, Man's perturbation of the biosphere – Man as a chemical factory – material use and waste – energy use and thermal pollution – ecological disruption – chemical sensation, hormonal imbalance and mutagens- internal pollution. Hydrosphere - lithosphere interaction: The structure of water at an interface – chemical composition of mineral water- weathering and the changing face of the land- the origin of the oceans- sedimentation and the deposition of materials from the hydrosphere – chemical exchange between sediments and the water column.

**UNIT IV: INTERACTIONS**

Lithosphere- biosphere interaction: soil chemistry – the prospects of agriculture- agricultural pollution – pesticides and other persistent pollutants – the deposition of coal and petroleum – theories of origin of petroleum. Atmosphere – biosphere interaction and atmosphere – hydrosphere interaction: history of earth's atmosphere – the nitrogen cycle – the carbon cycle – air – sea interactions.

Biosphere – hydrosphere interaction: The chemistry of water pollution – sewage treatment, primary, secondary- and tertiary – activated sledge – trickling filters- denitrification –biology and energy chain – reactor design theory – anaerobic digestion –eutrophication.

**UNIT - V: POLLUTION CONTROL**

Pollution control in the following: Fertiliser, petroleum, pulp and paper, tanning, sugar, alcohol, electroplating and nuclear reactors.

Analysis of pollutants: Sum, specific and group parameters BOD, COD, specific oxygen demand, DOC, DOCl, DOS, Fe, Cr, Cu, Pb, and Ni- $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_3$  and CO.

**References:**

Chemistry of our environment R.A.Horne

Environmental chemistry A.K.De

Environmental chemical analysis Iain L, Marr and Malcom S. Cresser

Pollution control in process industries S.P.Mahajan.



## PAPER – 4

### B. BIOINORGANIC CHEMISTRY

#### UNIT I: ESSENTIAL AND TRACE METAL IONS

Alkali and alkaline earth and transition metal cations. Crown ethers, Na & K ion transport, Metal ion toxicity in biochemical system. Bio membranes and calcium carriers.

#### UNIT II: RESPIRATORY PROTEINS

Heme-oxygen carrier: Introduction, Models for transports Heme iron proteins, porphyrin system, substituent effects. Oxygen carriers- Haemoglobin, Myoglobin- structural characteristics and Bohr effect. Non-heme oxygen carriers: Hemerythrin and hemocyanin, Model compounds for oxygen carriers- Cobalt Schiff base, Vaska's complexes.

#### UNIT III: METALLOENZYMES (REDOX AND NON REDOX) / METAL ION TRANSPORT AND STORAGE

Hydrolases: Carboxypeptidase, carbonic anhydrase, alkaline phosphatase and other dinuclear phosphatases and hydrolases. Electron Transfer Proteins: Blue copper, Iron-Sulphur proteins – Ferridoxins & Rubredoxin, and cytochromes. Redox enzymes : Cu, Zn SOD and Cytochrome P<sub>450</sub>, Manganese enzyme and xanthine oxidase. Haem enzymes- peroxidase and catalase.

#### UNIT IV: NITROGEN FIXATION AND PHOTOSYNTHESIS

Nitrogenase enzyme : Introduction, Types of nitrogen fixing microorganism, metal clusters in nitrogenase. Nitrogen fixation pathway. Transition metal complexes : Dinitrogen complexes. Biological redox reactions. Photosynthesis and chlorophyll.

#### UNIT V: MEDICINAL BIO-INORGANIC CHEMISTRY/CHELATION THERAPY:

Pt complexes in cancer therapy: Cisplatin and its mode of action, cytotoxic compounds of other metals. Gold containing drugs as antirheumatic agents and their mode of action, Lithium in psychopharmacological drugs. Metal complexes as probes of nucleic acid: Function of metal ions in genetic regulation, Metal DNA and RNA interactions – potential binding sites.

**Reference Books:**

1. Advanced Inorganic Chemistry, F.A. Cotton and G. W. Wilkinson. John Wiley & Sons, 5<sup>th</sup> Ed. 1988.
2. Inorganic Chemistry, Principles of Structure and Reactivity, J. E. Huheey, E.A. Keiter 4th Ed. Harper Collins, 1993.
3. Bioinorganic chemistry, R. W. Hay, Halsted Press, 1984.
4. Principles of Bioinorganic Chemistry, S. J. Lippard and J.M. Berg, Panima Publishing Corporation, 2<sup>nd</sup> Ed., 1995.
5. Inorganic Chemistry of Biological Processes, M.N. Hughes, John Wiley & Sons, 2nd Edition, 1985.

## PAPER – 4

### C. CHEMISTRY OF NATURAL PRODUCTS

#### UNIT-I: TERPENOIDS AND CAROTENOIDS

Classification, nomenclature, occurrence, isolation, general methods of structure determination, isoprene rule. Structure determination, stereochemistry, biosynthesis and synthesis of the following representative molecules : Citral, Geraniol,  $\alpha$ -Terpeneol, Menthol, Farnesol, Zingiberene, Santonin, Phytol, Abietic acid and  $\beta$ -Carotene.

#### UNIT-II: STEROIDS

Occurrence, nomenclature, basic skeleton, Diel's hydrocarbon and stereochemistry, Isolation, structure determination and synthesis of Cholesterol, Bile acids, Androsterone, Testosterone, Estrone, Progesterone, Aldosterone, Biosynthesis of Steroids.

#### UNIT-III: PLANT PIGMENTS

Occurrence, nomenclature and general methods of structure determination. Isolation and synthesis of Apigenin, Luteolin Quercetin, Myrcetin, Quercetin 3-glucoside, Vitexin, Diadzein, Buttein, Aureusin, Cyanidin-7arabinoside, Cyanidin, Hirsutidin, Biosynthesis of flavonoids: Acetate pathway and Shikimic acid pathway.

#### UNIT-IV: PROPHYRINS

Structure and synthesis of Haemoglobin and Chlorophyll.

#### UNIT-V: PROSTAGLANDIS

Occurrence, nomenclature, classification, biogenesis and physiological effects. Synthesis of PGE<sub>2</sub> and PGF<sub>2a</sub>. Pyrethroids and Rotenones; Synthesis and reactions of Pyrethroids and Rotenones. (For structure elucidation, emphasis is to be placed on the use of spectral parameters wherever possible).

**Books Suggested**

Natural Products : Chemistry and Biological Significance, J. Mann, R.S. Davidson, J.B. Hobbs, D.V. Banthrope and J.B. Harbome, Longman, Essex.

Organic Chemistry : Vol. 2, I.L. Finar, ELBS.

Stereoselective Synthesis : A Practical Approach, M. Norgradi, VCH.

Rodd's Chemistry of Carbon Compounds, Ed. S. Coffey, Elsevier.

Chemistry, Biological and Pharmacological Properties of Medicinal Plants from the Americas, Ed. Kurt Hostettmann, M.P. Gupta and A. Marston. Harwood Academic Publishers.

Introduction to Flavonoids, B.A. Bohm. Harwood Academic Publishers.

New Trends in Natural Product chemistry, Ata-ur-Rahman and M.L. Choudhary, Harwood Academic Publishers.

Insecticides of Natural Origin, Sukh Dev, Harwood Academic Publishers.

**MAIN PRACTICAL**

**PAPER-4**

**ORGANIC CHEMISTRY PRACTICAL- II**

**ANY SIX PREPARATIONS FROM THE FOLLOWING INVOLVING TWO STAGES**

sym-Tribromo benzene from aniline.

Benzanilide from benzophenone

m-Nitro benzoic acid from methyl benzoate

2,4.- Dinitrobenzoic acid from p-nitrotoluene

m-Nitro benzoic acid from benzaldehyde

Benzil form benzaldehyde

Anthraquinone from phthalic anhydride

Phthalide from phthalic anhydride

2-Phenyl indole from phenyl hydrazine

2, 4-dinitrophenyl hydrazine from p-nitrochlorobenzene

**ANY TWO EXERCISES IN THE EXTRACTION OF NATURAL PRODUCTS**

Caffeine from tea leaves

Lactose from milk

Citric acid from lemon

Piperine from black pepper

**CHROMATOGRAPHIC SEPARATIONS**

Column chromatography - separation of anthracene and picric acid from anthracene picrate.

Thin layer chromatography separation of green leaf pigments.

Paper chromatography-Identification of amino acid.

**ANY FIVE ESTIMATIONS**

Estimation of aniline  
Estimation of phenol  
Estimation of glucose  
Estimation of amino group  
Estimation of amide group  
Saponification of fat or an oil  
Iodine value of an oil  
Estimation of sulphur in an organic compound  
Estimation of methyl ketone

**SPECIAL INTERPRETATION OF ORGANIC COMPOUNDS UV, IR, PMR AND MASS SPECTRA OF THE FOLLOWING 15 COMPOUNDS**

1,3,5- Trimethyl benzene  
Pinacolane  
n-Propylamine  
p-Methoxy benzyl alcohol  
Benzyl bromide  
Phenylacetone  
2-Methoxyethyl acetate  
Acetone  
Isoopropyl alcohol  
Acetaldehyde diacetate  
2-N,N-Dimethylamino ethanol  
Pyridine  
4-Picoline  
1,3-dibromo - 1, 1- dichloropropene  
Cinnamaldehyde

**Recommended Books**

Arthur I.Vogel, A text book of Practical Organic Chemistry, ELBS  
Raj K. Bansal, Laboratory Manual of Organic Chemistry, Wiley Eastern limited.  
N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Vol.II, Pergamon Press (1997).

UNIVERSITY EXAMINATION	Marks
Preparation	15
Estimation	20
Interpretation of spectra	05
Record	10
<i>Viva voce</i>	10
Total	60

INTERNAL ASSESSMENT	Marks
Two Tests	20
Attendance / Regularity	10
Results accuracy	10
Total	40

## MAIN PRACTICAL

### PAPER - 5

## INORGANIC CHEMISTRY PRACTICAL- II

### QUANTITATIVE ANALYSIS OF COMPLEX MATERIALS

#### ANALYSIS OF ORES

Determination of percentage of calcium and Magnesium in dolomite.

Determination of percentage of  $MnO_2$  in pyrolusite.

Determination of percentage of lead in galena.

#### ANALYSIS OF ALLOYS

Estimation of tin and lead in solder.

Estimation of copper and zinc in brass.

Estimation of chromium and nickel in stainless steel.

#### ANALYSIS OF INORGANIC COMPLEX COMPOUNDS

Preparation of cis and trans potassium bis (oxalato) diaquochromate(III) and analysis of each of these for chromium.

Preparation of potassium tris (oxalato) ferrate (III) and analysis for iron and oxalate.

#### QUANTITATIVE ANALYSIS

Quantitative analysis of mixtures of iron -magnesium; iron - nickel; copper - nickel and copper - zinc.

#### COLORIMETRIC ANALYSIS

(Using) Photoelectric method: Estimation of iron, nickel, manganese and copper.

#### BIAMPEROMETRIC TITRATIONS

(With dead stop endpoint) thiosulphate - iodine system and Iron (II) - cerium (IV) systems.

LIST OF SPECTRA TO BE GIVEN FOR INTERPRETATION.

$^{31}P$  NMR Spectra of methylphosphate

$^{31}P$  NMR Spectra of  $HPF_2$

$^{19}F$  NMR Spectra of  $ClF_3$

$^1H$  NMR Spectra of Tris (ethylthioacetanato) cobalt (III)



Explain high resolution  $^1\text{H}$  NMR spectra of (N-propylisonitrosoacetylacetonato) (acetylacetonato) Nickel (II)

ESR Spectra of the aqueous  $\text{ON}(\text{SO}_3)^{2-}$  ion.

ESR Spectra of the H atoms in  $\text{CaF}_2$ .

ESR Spectra of the  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ .

ESR Spectra of the bis (salicylaldiminato) copper (II)

IR Spectra of the sulphato ligand.

IR Spectra of the dimethylglyoxime ligand and its Nickel (II) complex.

IR Spectra of carbonyls

Mossbauer spectra of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Mossbauer spectra of  $\text{FeCl}_3$ .

Mossbauer spectra of  $[\text{Fe}(\text{CN})_6]^{3-}$

Mossbauer spectra of  $[\text{Fe}(\text{CN})_6]^{4-}$

UNIVERSITY EXAMINATION	Marks	INTERNAL ASSESSMENT	Marks
I. Estimation of Mixture Containing two Metal Ions		Two Tests	20
Volumetric	10	Attendance / Regularity	10
Gravimetric	10	Results accuracy	10
Procedure	03	Total	40
II. Colorimetric estimation / amperometric titration			
Estimation	10		
Procedure	02		
III. Interpretation of Spectra	10		
Record	05		
<i>viva-voce</i>	10		
total	60		

## MAIN PRACTICAL

### PAPER-6

#### PHYSICAL CHEMISTRY PRACTICAL- II

Experiments in electrochemistry: conductometry, potentiometry, pH metry and spectroscopy.

##### CONDUCTIVITY MEASUREMENTS

Determination of equivalent conductance of a strong electrolyte and verification of Debye - Huckel - Onsager Equation

Verification of Debye-Huckel limiting law

Verification of Ostwald's Dilution law for a weak electrolyte. Determination of  $P^K$  values of weak acids and weak bases.

Conductometric titrations between acid (simple and mixture of strong and weak acids) - base, precipitation titrations including mixture of halides.

##### E.M.F MEASUREMENTS

Determination of standard potentials (Copper & Zinc)

Determination of thermodynamic quantities from EMF measurements - potentiometric titrations.

Determination of pH and calculation of  $pK_a$ .

Determination of stability constant of a complex.

Determination of solubility product of a sparingly soluble salt. Redox titrations.

Precipitation titration of mixture of halides by EMF measurements.

##### SPECTROSCOPY

Experiments given only to familiarize the interpretation of spectra provided. Interpretation of simple UV-Visible spectra of simple molecules for the calculation of molecular data and identification of functional groups (5 typical spectra will be provided).

IR and NMR spectral calculations of force constant - identification and interpretation of a spectra (5 each in IR and NMR will be provided).

**LIST OF EXPERIMENTS SUGGESTED FOR PHYSICAL CHEMISTRY PRACTICAL II**

Typical list of possible experiments are given. Experiments of similar nature and other experiments may also be given. The list given is only a guideline. Any 15 experiments have to be performed in a year.

Determination of the equivalent conductance of a weak acid at different concentrations and verify Ostwald's dilution law and calculate the dissociation constant of the acid.

Determination of equivalent conductance of a strong electrolyte at different concentrations and examine the validity of the Onsager's theory as limiting law at high dilutions.

Determination of the activity co-efficient of Zinc ions in the solution of 0.002M Zinc sulphate using Debye-Huckel limiting law.

Determination of the solubility product of silver bromate and calculate its solubility in water and in 0.01 M  $\text{KBrO}_3$  using Debye-Huckel limiting law.

Conductometric titrations of a mixture of HCl,  $\text{CH}_3\text{COOH}$  and  $\text{CuSO}_4$  and NaOH.

Determination of the dissociation constant of an acid at different dilution.

Determination of the solubility of the lead iodide in water, 0.04 M KI and 0.04 M  $\text{Pb}(\text{NO}_3)_2$  at 298 K

Determination of the solubility product of lead iodide at 298 K and 308 K and calculate the molar heat of solution of lead iodide.

Compare the relative strength of acetic acid and mono chloroacetic acid by conductance method.

Determine the basicity of organic acids (oxalic /benzoic).

Determine the electrode potentials of Zn and Ag electrodes in 0.1M and 0.001M solutions at 298 K and find the standard potentials for these electrodes and test the validity of Nernst equation.

Determine the activity co-efficient of an electrolyte at different molalities by EMF measurements.

Determine the dissociation constant of acetic acid titrating it with sodium hydroxide using quinhydrone as an indicator electrode and calomel as a reference electrode.

Study of the electrolytic separation of metals (Ag, Cu, Cd and Zn)

Determine the strength of a given solution of KCl using differential potentiometric titration technique.

Determine the dissociation constant of acetic acid in DMSO, DMF, acetone and dioxane by titrating it with KOH.

Determine the transport number of Ag ions and nitrate ions by Hittorf's method.

Determine the transport number of cadmium ions and sulphate ions by measuring emf of concentration cells with and without transference.

Determine the dissociation constant of monobasic or dibasic acid by all the Alber-Serjeant method.

Determine the pH of the given solution with the help of indicators using buffer solutions and by colorimetric method.

Perform acid-base titration in a non aqueous medium.

Determine the pH of a given solution by EMF method using glass and calomel electrodes and evaluate  $pK_a$  value of an acid.

Determine the pH of a given solution by emf methods using hydrogen electrode and quinhydrone electrode.

Estimate the concentration of cadmium and lead ions by successive reduction in polarography. Verify Illkovic equation.

Determine lead ion by amperometric titrations with potassium dichromate.

Determine ferric ion by amperometric titration.

Determine pH value of an acid-base indicator (methyl red) by colorimetry.

Determine the composition and instability constant of a complex by mole ratio method.

By colorimetry determine simultaneously Mn and Cr.

Study the effect of solvent on the conductivity of  $AgNO_3$ /acetic acid and determine the degree of dissociation and equilibrium constant in different degree of dissociation and mixtures (DMSO, DMF, dioxane, acetone, water) and test the validity of Debye-Huckel Onsager's equation.

Determine the solubility of  $Ca(TiO_3)_2$  in deionised water and in dilute solution of KCl at 298 K. Determine the solubility product graphically.

Determine the equivalent conductivity of a Ca electrolyte and dissociation constant of the electrolyte.

Determine the equivalent dissociation constant of a polybasic acid.

Calculate the thermodynamic parameters for the reaction  $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$  by emf method.

Determine the formation constant of silver-ammonia complex and stoichiometry of the complex potentiometrically.

Determine the stability constant of a complex by polarographic method.

Determine the g value from a given ESR spectrum.

Quantum of marks in respect of Practical Examinations

University Examination	Marks	Internal Assessment	Marks
Procedure	05	Two Tests	20
Manipulation	20	Attendance / Regularity	10
Result	10	Results accuracy	10
Interpretation of spectra	10	Total	40
Record	05		
<i>Viva voce</i>	10		
Total	60		

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