

BHARATHIAR UNIVERSITY: COIMBATORE – 641 046

M. Phil. CHEMISTRY

(F.T / P.T)

2008 – 2009 & ONWARDS

**Paper-I : TEACHING TECHNIQUES/PEDAGOGICAL METHODS IN
HIGHER EDUCATION**

Paper-II : RESEARCH METHODOLOGY AND TRENDS IN CHEMISTRY

Paper-III :

1. Organic Chemistry
2. Solid State and Hydrazine Chemistry
3. Organometallic Chemistry of Transition Metals
4. Chemistry of Advanced Materials
5. Photochemistry of – Photophysical Studies
6. Environmental Chemistry
7. Chemistry of Crystalline Solids
8. Physical Organic Chemistry
9. Electro Chemistry
10. Polymer Chemistry
11. Organic Synthetic Methodology and Conformational Analysis

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Paper-I : TEACHING TECHNIQUES/PEDAGOGICAL METHODS IN HIGHER EDUCATION

UNIT – I Higher Education and Learning

Historical Perspectives ... Objectives and Role of Higher Education ... Learning and Learning Hierarchy ... Information Processing ... Learning Events and Outcomes ... Motivation.

UNIT – II Teaching Technology : Designs

Teaching Technology: Meaning, concept and scope ... Instructional Designs: Objective based, Skill based, Competency based, Learning style based and Model based.

UNIT – III Methods and Techniques of Teaching

Large Group Techniques: Lecture, Modified Lecture, Seminar, Symposium, Panel Discussion, Team Teaching, Project Approach and Workshop ... Small Group Techniques: Group Discussion, Simulation, Role Playing, Buzz Technique, Brain Storming, Case Discussion and Assignment ... Systems Approach in Education.

UNIT – IV Measurement and Evaluation in Education

Educational Evaluation: A Conceptual Framework...Methods of Evaluation ... Self Evaluation and Student Evaluation in Higher Education ... Question Banking ... Diagnostic Testing and Remedial Teaching.

UNIT – V Electronic Media in Education

Instructional Media: Concept, Selection, Use and Variety e-Learning V Resources : e-Learning, e-books, e-journals,etc....Web-based Learning: Access and Tteaching Issues.

TEXT BOOKS:

For Units I to IV

Vedanayagam, E.G. (1989) Teaching Technology for College Teachers. New Delhi: Sterling Publishers (P) Ltd.

For Unit V

Rajasekar, S. (2005) Computer Education and Educational Computing, Hyderabad: Neelkamal Publications.

BOOKS FOR REFERENCE:

Kumar,K.L.(1997) Educational Technology, New Delhi:New Age International (P)Ltd.

Sampathkumar, K., Paneerselvam, A and Santhanam, S. (1990) Introduction to Educational Technology, New Delhi: Sterling Publishers (Pvt.) Ltd.

Tony Bates,A.W. (2005) Technology, e-Learning and Distance Education, New York: Routledge.

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PAPER – II: RESEARCH METHODOLOGY AND TRENDS IN CHEMISTRY

UNIT I

U.V - Visible spectroscopy:

Electronic excitation – origin of different bands - intensity of bands – selection rules – laws of photometry – correlation of electronic absorption with molecular structure – chromophoric groups – conjugated systems – systems of extended conjugation – aromatic systems – empirical rules – experimental methods – photometric methods – photometric titrations.

I.R. spectroscopy:

Molecular vibrations – selection rules – force constant – band assignments – applications – organic structures – finger printing – identification of common functional groups – applications.

UNIT II

¹H and ¹³C NMR spectroscopy:

Proton chemical shifts – aromatic ring systems – anisotropic effects – ¹³C chemical shifts – mechanisms of spin - spin coupling – vicinal, geminal and long range proton – proton coupling.

Analysis of NMR spectra:

Accumulation of spectra by the pulsed NMR technique – nuclear relaxation – Fourier transformation – the pulsed FT NMR spectrometer.

Double resonance technique and relaxation mechanisms:

Homonuclear decoupling – heteronuclear decoupling – proton decoupling technique in ¹³C spectrum – INDOR and Nuclear overhauser effect (NOE) – ¹³C relaxation mechanisms – measurement of relaxation times – spin-lattice relaxation (T₁) spin-spin relation (T₂) measurements – assignment technique in ¹³C spectra – chemical shift correlation – quantitative measurement in ¹³C – NMR – relaxation reagents – intensity standards.

UNIT III

ESR Spectroscopy:

Theory – instrumentation – derivative curves ‘g’ values – ‘g’ shift – origin of hyperfine splitting – isotropic systems – anisotropic systems – anisotropic effect zero field splitting – Kramers degeneracy – applications to organic and inorganic systems – identification of free radicals.

X-ray Photoelectron Spectroscopy:

Introduction – Theory of XPS – Instrumentation – Applications of XPS to organic and inorganic systems.

UNIT IV

Mass Spectrometry:

Theory – instrumentation – various types of mass spectrometers – magnetic focusing instruments – sample handling – production and reactions of gaseous ions – isotopic abundance – determination of molecular weights and formulae – metastable peaks – nitrogen rule – ion fragmentation mechanisms – rearrangements – use of mass spectrometry in the structural elucidation of organic compounds – mass spectra of compounds containing different functional groups.

UNIT V

Instrumental Methods

Thermal Methods: Principle and applications of Differential Thermal analysis (DTA), Differential Scanning Calorimetry (DSC), Differential Thermal Gravimetry (DTG) and Thermo Gravimetry (TG). Effects of experimental conditions on the course of thermo analytical curves.

Diffraction Methods: Fundamentals of X-Ray Diffraction- Powder and Rotating crystal methods- use of X-ray powder diffraction data in identifying crystalline solids- details for cubic systems- Comparison of X- ray, neutron and electron diffractions.

Nanoscale Characterization: Principle and applications of SEM and TEM.

REFERENCES:

1. Proton and Carbon ¹³ - NMR Spectroscopy – An Integrated Approach – R.J. Abraham and Loftus.
2. Spectroscopic Identification of Organic Compounds – R.M. Silverstein, G.C. Bassler and Morrill.
3. Physical methods in Inorganic Chemistry- R.S. Drago.
4. Physical methods in Organic Chemistry – Scharz
5. Applications of NMR spectroscopy in Organic Chemistry – Jockmann and Strenhell
6. Applications of absorption spectroscopy of Organic Compounds – J.Dyer
7. Interpretation of Mass Spectra – McLafferty
8. Interpretation of Mass Spectra of Organic Compounds – Budcikowiex, Djerassi and Williams
9. NMR of Organic Chemists –Mathioson
10. Electron Spin Resonance – Elementary theory and Practical Applications – Wertz and Bolton
11. Mass Spectrometry for Organic Chemistry – Raw Johnstone
12. Interpretation of NMR Spectroscopy – R.H Bible
13. High Resolution NMR – Becker
14. Interpretation of Mass Spectra of Organic Compounds – Hamming and Foster
15. Interpretation of ¹³C NMR Spectra – F.W. Wehrli, T.Wirthlin and Heydon.
16. Introduction to X-Ray Diffraction – B.D.Cullity.
17. Solid state Chemistry and its applications – A.R.West.
Scanning Microscopy for Nanotechnology – Weilie Zhou, Zhong Lin Wang.

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PAPER – III ORGANIC CHEMISTRY

UNIT I

Theory of Concerted Reactions:

Definitions – molecular orbitals – frontier orbitals – frontier orbital approach – correlation diagrams – the aromatic transition state concept – general rule for pericyclic reactions.

Electrocyclic Reactions:

Definition – thermal electrocyclic reactions – photochemical electrocyclic reactions – metal catalysed electrocyclic reactions.

Cycloadditions:

Introduction – selection rules for thermal polyene cyclo additions – Diels – Alder reaction – The retro diels – alder reaction – 1,3, - Dipolar cycloadditions – Retro – 1,3 – dipolar cyclo additions.

UNIT II

Cycloadditions involving four electrons:

Concerted –2+2 cycloadditions via intermediates –2+2 cycloadditions of cumulenes – retro 2+2 cycloadditions – chelotropic reactions photochemical 2+2 cycloadditions.

Sigmatropic Rearrangements:

Nomenclature – hydrogen migrations – migrations of atoms other than hydrogen (3,3) sigmatropic changes – the cope and claisen rearrangements – 2,3, - sigmatropic changes – ylide rearrangements – photochemical re-arrangements – the ene reactions – the retro – ene reactions.

UNIT III

Photochemistry:

Light absorption – unimolecular photophysical processes – Jablonski diagrams – radiative transitions – internal conversion – intersystem crossing – energy pooling – excimers and exciplexes.

Photochemical reactions:

Introduction – cis – trans Isomerisation – Norrish type I reaction – Norrish type II reaction – Thermal generation of excited states. Zimmerman rearrangement, photochemical rearrangement of enones. photorearrangement of cyclohex – 2 – enones – rearrangements of 2 – cyclopentenones and related compound.

UNIT IV

Modern reagents in organic synthesis:

Sodium cyanoborohydride – osmium tetroxide – lithium dimethyl copper – thallium trifluoro acetate – sodium hydrogen telluride – silver hexa fluorantimonate – Thiobenzoyl chloride – trichloro-silane – vanadium oxytrifluoro – phosphonitrile chloride – ruthenium tetroxide – barium manganate – benzene selenic acid – benzene selenyl bromide/chloride, aluminium chloride/phosphoryl chloride.

UNIT V

Total synthesis of following compounds:

Cecropia Juvenile Hormone, Marrubin, Epiandrosterone, Buffalin, (+) – Lunacrine, Flindersine, geibalansine, spatheliabis – chromene.

REFERENCES

1. Organic Reactions & Orbital Symmetry – PL. Gilchrist & R.C. Storr
2. Mechanism and Theory in Organic Chemistry, Thomas H Lowry, Kathleen Suhlauer Richarden, Horper and Rao
3. The Conservation of Orbital Symmetry – Woodward and Hofman
4. 1,2 – Cycloaddition Reactions – Muller and J Hamer
5. Pericyclic reactions Vol. I & II AP Merchand and Rt. Lehr.
6. Advances in Photochemistry Vol. IV Wa. Noyes, Cr.S. Hammand J.N. Pilts
7. Organic Photochemistry U L Chapman Vol. I – IV
8. Molecular Photochemistry N J Torro
9. Reagents for Organic Synthesis – Feiser & Feiser Vols. I – XII
10. Chapters 16 & 17 from Rearrangements in Ground and Excited State Vol. 3 edited by Paul de Mayo
11. Natural Products Chemistry Vol. I edited by Koji Nakanishi Tosti Ohto, Sboito, Shinsaku Natori and Shigeo Nozoe
12. M. Ramesh P S Mohan and P Shanmugam, Tetrahedron Vol. 40, p.3431 (1984)
13. M. Ramesh, P.S. Mohan and P Shanmugam, Tetrahedron Vol. 40, p.4041 (1984)
14. P.R.Iyer, S.R.Iyer and K.J. Rajendra Prasad, Indian Journal of Chemistry Vol. 23 B, p.535 (1984)
15. P.Sowmithran and K.J.Rajendra Prasad, Synthesis, 5, 545 (1985)

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PAPER – III SOLID STATE AND HYDRAZINE CHEMISTRY

UNIT I

Crystallography:

Preparation of materials – crystal growth and purification, the crystal systems – lattices and crystal structures – symmetry properties – crystal classes – space groups – X – Rays – crystallography – the powder method – rotating crystal method – crystal structure determination – the structure factor – fourier synthesis of a crystal structure.

Electron and neutron diffraction and structure determination.

UNIT II

The Solid State:

Types of solids – closepacking of spheres – binding in crystals – the bond model – the bond model – non stoichiometry – defects in solids – imperfection and physical properties – electrical, optical, magnetic, thermal and mechanical properties – magnetic materials – mixed oxides – spinels – insulators – semiconductors and super conductors.

UNIT III

Chemistry of Lanthanides and Actinides:

General characteristics – spectral and magnetic properties – structure and bonding in highly coordinated lanthanide and actinide complexes – synthesis, structure and thermal stability of hydrazinium lanthanide and actinide complexes – principles of separation of lanthanide and actinides – use of lanthanide compounds as shift reagents.

UNIT IV

Hydrazine chemistry:

Chemistry of hydrazine – versatility of hydrazine – production of hydrazine and its derivatives – types of hydrazine salts – methods of preparation of simple hydrazinium salts. structure and bonding in hydrazine – configuration of N_2H_5^+ and N_2H_6^+ ions – comparative account of N-N bond length in N_2H_4 , N_2H_5^+ and $\text{N}_2\text{H}_5^{2+}$ species.

Methods of estimation of hydrazine – basicity of hydrazine Applications of Hydrazine and its derivatives.

UNIT V

Metal hydrazine complexes – Hydrazine as a ligand – Reactivity of hydrazine and its salts with metals or metal salts – Synthesis, structure and thermal stability of hydrazine, hydrazinium (1+) and hydrazinium (2+) metal complexes. Infrared spectra of hydrazine, its salts and their metal complexes.

Explosive properties of hydrazinium salts and its complexes. Hydrazines as solvents – Redox reactions.

REFERENCES:

1. Physical Chemistry – W J Moore (1962)
2. Introducing Chemists to X-ray Structure Determination – John Enemark, Journal of Chemical Education, June (1988)
3. Introduction to solids – L V Azarof (1960)
4. Structural Inorganic Chemistry – A F Wells, Fifth edition (1984)
5. Solid State Chemistry – N B Hannay (1976)
6. Inorganic Chemistry – Principles of Structure and Reactivity – James E Huheey 2nd Edition (1978)
7. Comprehensive Inorganic Chemistry – J C Bailar et al, Vol. 4 and 5 (1975)
8. Structure and Bonding (Rare-earths) – J D Dunitz et al, Vol. 25 (1976) p. 23-150
9. Coordination of Trivalent Lanthanide Ions – D G Karraker, Journal of Chemical Education, 47 (1970) p. 424-430
10. Hydrazine and its derivatives – Preparation, properties and Applications – Eckart W Schmidt (1983)
11. Structural and Thermal Studies on Hydrazinium Metal Sulfate and Oxalate Complexes – S Govindarajan (Ph.D. – Thesis).

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PAPER – III ORGANOMETALLIC CHEMISTRY OF TRANSITION METALS

UNIT I

Definition of organometallic compound – 18 electron rule – effective atomic number rule – classification of organometallic compounds – the metal carbon bond types – ionic bond – sigma covalent bond – electron deficient bond – delocalised bond – dative bond – metal carbonyl complexes – synthesis, structure and reactions of metal carbonyls – the nature of M-CO bonding – binding mode of CO and IR spectra of metal carbonyls – metal carbonyls – metal carbonyl anions – metal carbonyl hydrides – metal carbonyl halides – metal carbonyl clusters – Wades rule and isolobal relationship – metal nitrosyls – dinitrogen complexes – dioxygen complexes.

UNIT II

Metal alkyl complexes – stability and structure – synthesis by alkylation of metal halides, by oxidative addition, by nucleophilic attack on coordinated ligands – metal alkyl and 18 electron rule – reactivity of metal alkyls – M-C bond cleavage reactions – insertion of CO to M-C bonds – double carbonylation – insertions of alkenes and alkynes – insertions of metals with C-H bonds – alkylidene and alkylidyne complexes – synthesis of alkylidene complexes in low oxidation states and in high oxidation states – bonding in alkylidene complexes – synthesis and bonding in alkylidyne complexes – reactivity of alkylidene and alkylidyne complexes.

Alkene complexes – synthesis of alkene complexes by ligand substitution, by reduction and by metal atom synthesis – bonding of alkenes to transition metals – bonding in diene complexes – reactivity of alkene complexes – ligand substitution – reactions with nucleophiles – olefin hydrogenation – hydrosilation – Wacker process – C-H activation of alkenes – alkyne complexes – bonding in alkyne complexes – reactivity of alkynes – alkyne complexes in synthesis – cobalt catalysed alkyne cycloaddition.

UNIT III

Cyclopentadienyl complexes – metallocenes – synthesis of metallocenes – bonding in metallocenes – reactions of metallocenes – CpFe/Cp₂Fe⁺ couples in biosensors – bent sandwich complexes – bonding in bent sandwich complexes – metallocene halides and hydrides – metallocene and stereospecific polymerization of 1-alkenes – cyclopentadiene as a non-spectator ligand – monocyclopentadienyl (half-sandwich) complexes – synthesis and structures of allyl complexes – arene complexes – synthesis, structure and reactivity of arene complexes – multidecker complexes.

UNIT IV

Role of organometallic chemistry in catalysis

Coordinative unsaturation – oxidative addition – addition reactions of specific molecules – hydrogen addition – HX addition – addition of X_2 – addition of RX – addition reactions of Si-H, C-C, C-Si and Si-Si bonds – elimination reactions - α and β eliminations – alkane activation – intramolecular and intermolecular C-H activation – activation of sulphur heterocycles – insertion of carbon monoxide – isocyanide insertion – alkene insertion – alkyne insertion.

UNIT V

Homogeneous catalysis by transition metal complexes

Hydrogenation reactions – reversible cis-dihydro catalysts – monohydride catalysts – hydrogenation of alk-1-ene – asymmetric hydrogenation –role of ruthenium complexes in 2001 Nobel Prize for chemistry- transfer hydrogenations – hydrosilation and hydroboration reactions – water gas shift reaction – reduction of carbon monoxide by hydrogen – hydroformylation of alkenes – alcohol carbonylation – decarbonylation reactions – C-C cross coupling and related reactions – alkene oligomerisations and polymerizations – Zeigler-Natta polymerization – alkene dimerisation and oligomerisations – valence isomerisation of strained hydrocarbons – alkene and alkyne metathesis – oxidations of alkanes and alkenes – oxygen transfer reactions – supported homogeneous and phase transfer catalysis.

REFERENCES

1. Organometallics 1, complexes with transition metal-carbon σ -bonds, M.Bockmann, Oxford science publications, Oxford, 1996.
2. Organometallics 2, complexes with transition metal-carbon π -bonds, M.Bockmann, Oxford science publications, Oxford, 1996.
3. Basic organometallic chemistry, I. Haiduc and J. J. Zuckerman, Walter de Gruyter, Berlin, 1985.
4. Inorganic chemistry – Principles of structure and reactivity, J. E. Huheey, Harper International Edition, Harper and Rone, New York, 1978.
5. Inorganic chemistry – Principles of structure and reactivity, J. E. Huheey, E.A.Keiter and R.L. Keiter, Addison-Wesley Publishing Company, New York, 2000.
6. Advanced Inorganic Chemistry, Sixth Edition, F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, John Wiley and sons, Inc, New York, 1999.

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PAPER- III PHOTOCHEMISTRY - PHOTOPHYSICAL STUDIES

UNIT I

Some Current Topics in Photochemistry:

Origin of life- mutagenic effect of radiation- photodynamic therapy– photosynthesis- photoelectrochemistry of excited state redox reactions- solar energy conversion and storage.

UNIT II

Photophysical Process in Electronically Excited Molecules:

Types of photophysical path ways- radiationless transition- internal conversion and intersystem crossing- fluorescence emission- fluorescence and structure- delayed fluorescence.

UNIT III

Photochemistry in Microheterogeneous Systems:

General features of surfactant and lipid- excited state processes and reactions: medium effect- acid-base equilibrium in excited state- depolarization of fluorescence- excited state quenching- excimers and exciplexes- excitation energy transfer- photodimerization and photoredox reactions- structural and dynamic aspects of micellar aggregates.

UNIT IV

Photoprocesses in Molecular Inclusion Complexes:

Introduction- photoprocesses in cyclodextrins- general features of cyclodextrins and inclusion complexes- fluorescence probe analysis- fluorescence depolarization- excimers and exciplex dynamics.

UNIT V

Photoprocesses in Aluminosilicates – Zeolites:

General features of zeolites and their cavities- photochemistry of inorganic ions exchanged into zeolites- photochemistry of organic molecules.

References:

1. G.H. Wald, "Life and light", Scientific American, 201, 1959, 92.
2. A. McLaren and D. Shugar, "Photochemistry of Nucleic Acid and Proteins", Oxford, Pergamon press, 1964.
3. R.F. Reinisch, (ed.), "Photochemistry of Macromolecules", New York, plenum press, 1970.
4. E.I. Robinowitch and Govindjee, "Photosynthesis", New York, Wiley, 1969.
5. G. Stein, "Chemical Storage of Solar Energy and Photochemical Fuel formation", Israel J. Chem. 14, 1975, 213.
6. K.K. Rohatgi-Mukherjee, "Fundamentals of photochemistry", New Delhi, New Age international Publishers, 2002 (Revised edition).
7. N.J. Turro, "Molecular Photochemistry", New York, Benjamin, 1978.
8. J.B. Birks, "Photophysics of Aromatic Molecules", New York, Wiley, 1970.
9. J.R. Lakowicz, "Principles of Fluorescence Spectroscopy", New York, Plenum press, 1984.
10. K. Kalyanasundaram, "Photochemistry in Microheterogeneous Systems", New York, Academic press, 1987.
11. M.L. Bender and M. Komiyama, "Cyclodextrin Chemistry", React. Struct. Concepts, Org. Chem., Vol. 16, Berlin and New York, Springer-Verlag, 1978.
12. J. Szejtli, "Cyclodextrins and their Inclusion Complexes", Budapest, Akadémiai Kiadó, 1982.
13. D.W. Breck, "Zeolite Molecular Sieves", New York, Wiley, 1974.
14. J.A. Rabo, (ed.), "Zeolite Chemistry and Catalysis", Acs Monograph Series, No. 171, Am. Chem. Soc., Washington, D.C. 1976.

PAPER - III ENVIRONMENTAL CHEMISTRY

UNIT I

Chemistry of Water and Waste Water

Basic Principles and their significance with special reference to colour, turbidity alkalinity, acidity, chemical coagulation, hardness, water softening, disinfection, residual chlorine and chlorine demand, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, nitrogen, phosphate, sulphate, gas analysis, enzymes, factors affecting enzymic activity, bio-chemistry of carbohydrates, proteins, fats and oils under aerobic and anaerobic conditions, detergents and their degradation, composition and characteristics of sewage.

UNIT II & III

Chemistry of air Pollutants:

Introduction, definition, classification of air pollutants, effect of air pollutants on man, materials, animals and plants, ambient air quality standards, harmful concentrations, geographical and meteorological factors in air pollution control, measurement of gas flows, volume, quantity and velocity, methods of sampling, particulate collection by liquid scrubbing, centrifugal spray scrubbers, venturi scrubbers, foam scrubbers: field sampling techniques such as deposition, absorption, filtration, condensation, absorption, adhesion, electrostatic precipitation, thermal precipitation; analysis of air pollutants such as particulates sulphur dioxide, carbon monoxide, oxides of nitrogen, hydrogen sulphide, etc, control measures.

Unit IV

Chemistry of Solid Waste:

Chemistry of composting; mechanism involved in the decomposition of organic materials like hemicelluloses, proteins, carbohydrates, food materials, organic insecticides, farm wastes, etc., by aerobic and anaerobic processes.

UNIT V

Chemistry of Incineration and Pyrolysis:

Incineration: definition, incineration of solid waste; combustion characteristics of various inorganic and organic materials, heating values – determination of heating values of combustible liquid and solid wastes, air requirements for combustion, fate of trace constituents such as sulphur during incineration; gaseous pollutants; definition of pyrolysis; chemical changes taking place in organic and inorganic materials during pyrolysis; importance of pyrolysis in the solid waste disposal; chemistry of recycling of solid waste; recycling and reuse of materials such as paper, plastic, glass, etc.

References :

1. Sawyer, C.N. and P.L. McCarty, 'Chemistry for Environmental Engineers', Mc.Graw Hill, 1978.
2. Stumm, W. And J.J. Morgan, 'Aquatic Chemistry', Wiley Interscience 1972.

3. American Public Health Association inc., New York, 'Standard methods for the examination of water and waste water', 1976.
4. Stern, A.C., 'Air Pollution', Vol. 1,2 and 3, Academic Press, New York 1968.
5. Strauss, W.Ed., 'Air Pollution Control', Part 1,2 and 3, Wiley Interscience, New York, 1960.
6. Jacobs,M.B., 'Chemical Analysis of Air Pollutants', Interscience, New York, 1960.
7. Ross. R.D., 'Air Pollution and Industry', V.N. Reinhold Co., New York, 1972.
8. Leithe, W. Translated by R.Kenor, 'The Analysis of Air Pollutants', Ann Arbor, 1971.
9. Hagerty, D.J., J.L.Pavoni and J."E.Heer, Jr., 'Solid Waste Management', Van Nostrand Reinhold Co., New York, 1973.
10. Wilsion,D.G.'Hand book of Solid Waste Management', V.R.Nostrand, Reinhold, New York, 1977.

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PAPER- III CHEMISTRY OF CRYSTALLINE SOLIDS

UNIT I

The crystal systems – lattices and crystal structures – symmetry properties – crystal classes – space groups – experimental methods of X-ray diffraction for powder and single crystal samples – structural analysis and refinement – electron and neutron diffraction in the determination of structures.

UNIT II

Crystal growth phenomena – introduction – nucleation – theories of nucleation – classical theories of nucleation – Gibbs Thomson equation for vapour – modified Thomson's equation for melt – Gibbs Thomson's equation for solution – energy of formation of a nucleus – spherical nucleus – cylindrical nucleus – heterogeneous nucleation – cap shaped nucleus, disc shaped nucleus.

UNIT III

Types of solids – close packing of spheres – binding in crystals – the bond model – non-stoichiometry – defects in solids – imperfection and physical properties – electrical, optical magnetic and mechanical properties – magnetic materials – mixed oxides – spinels, insulators – semiconductors and super conductors.

UNIT IV

Low temperature solution growth- solution, solubility and super solubility – expression of super saturation – methods of crystallization – by slow cooling of solutions – by solvent evaporation – temperature gradient method. crystal growth system – constant temperature bath – crystallizer – filtration assembly – seed, seed mount platform and crystal revolution – unit – gel growth – introduction – principle of gel growth – various types of gel – structure of gel – growth of crystals in gels – importance of gel technique – experimental procedure – single diffusion method – double diffusion method – chemical reduction method – solubility reduction method – growth from the melt – Bridgman technique – Czochralski technique – zone refining.

UNIT V

Phase transitions – definition – Burger's classification – thermodynamic classification – Landau theory of phase transition – first order and second order transitions – structural changes with increasing temperature and pressure – martensitic transformations – order – disorder transitions.

Thermal analysis – basic Principles – instrumentation – applications of thermogravimetry – differential thermal analysis and differential scanning calorimetry.

Reference

1. Crystal Growth Process and Methods – Dr.P.Santhana Raghavan and Dr.P.Ramasamy – K.R.V.Publications.
2. Solid State Chemistry Techniques – Edited by A.K.Cheetham and Peter Day – Oxford Science Publications (1991).
3. Solid State Chemistry and its applications – Anthony R.West – John Wiley and Sons (1987).
4. Crystallography and its applications – L.S.Dent Glasser - ELBS 1982.
5. Solid State Chemistry – D.K.Chakrabarthy – New Age international publishers – 1966.
6. Principles of solid state Physics – Charles Kittel.
7. Physical Chemistry – W.J.Moore (1962).
8. Introducing Chemists to X-ray Structure Determination – John Enemark. Journal of Chemical education, June (1988).
9. Introdication to solids – L.V.Azarof (1960).

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PAPER- III PHYSICAL ORGANIC CHEMISTRY

UNIT I

1.1. Theories of Reaction Rates:

Absolute reaction rate theory – thermodynamic treatment of ARRT – Significance of reaction co-ordinate – application of ARRT to simple unimolecular and bimolecular process – potential energy surfaces – partition functions and activated complexes. Eyring equation – estimation of free energy enthalpy and entropy of activation and their significance – kinetic isotopic effect

1.2. Reaction Mechanisms

Principle of microscopic reversibility – steady state approximation applications.

UNIT II

2.1 Reaction in solution

Introduction – application of ARRT to solution kinetics – the influence of solvent – the ionization of neutral molecules kinetics of ionization – reaction between ions – reaction between ions & molecules – influence of ionic strength – primary salt effect – secondary salt effect.

2.2 Homogenous catalysis

Acid-base catalysis – Hammett's acidity function Bronsted relationship – enzyme catalysis – mechanism of single substrate reactions – Michaelis-Menten law- influence of pH and temperature.

UNIT III

Quantitative structure and Reactivity Relationships

The linear free energy principle – (LFER) linear relationship involving difference reaction – the Hammett correlation. The Hammett equation – steric effects – resonance interaction – normal substituent constants - σ^- , σ^+ constants – inadequacy of dual hypothesis – regularities in the through resonance effect- the Yukawa Tsuno equation – systematic deviation- steric inhibition of resonance – Taft equation – correlation of aliphatic and aromatic reactivities.

UNIT IV

Photochemistry

LAWS OF PHOTO CHEMISTRY- quantum efficiency and its experimental determination – deviation and reasons- excited states and ground state, singlet and triplet states – forbidden transmissions (spin forbidden and symmetry forbidden transition) types of excitation properties of excited states – photolytic cleavage – the fate of excited molecules – physical process – Jablonski – diagram chemical processes – various types. chemiluminescence, bioluminescence, lasers, practical lasers – uses of lasers.

UNIT V

Oxidations with chromium and manganese compounds – oxidations with peracids and other peroxides – oxidation with periodic acid, lead tetra acetate, mercuric acetate - selenium dioxide.

Catalytic hydrogenation and dehydrogenation metal hydride reductions and related reactions dissolving metal reductions and related reactions -reductions and the hydroactive and its derivatives.

Recommended Text Books

1. K.J. Laidler chemical kinetics, 2nd Ed. Tata Mc.Graw Hill 1975 (Unit I, II, IV).
2. W.J. Moore, Physical chemistry 5th Ed. Orient Longman 1982 (Unit I & II).
3. S. Glasstone, Text Book of Physical chemistry Mc Millan (Unit I & II).
4. Harish & Gurdeep. Advanced Physical chemistry, Goel publishing Home, Meerut (Unit I, II & IV)
5. Louis P. Hammett, Physical organic chemistry, Mc.Graw Hill Ltd., Tokyo (Unit III).
6. K.K. Rastoghi & Mukherjee, Fundamentals of Photo Chemistry, Wiley Eastern (1978) (Unit IV).
7. Advanced organic chemistry. Reactions and Mechanism's and structure – Jerry March
8. Organic synthesis – R.O.C. Normal.

References

1. S.W. Benson, "The Foundation of Chemical Kinetics" Mc. Graw Hill, 1960.
2. C.M. Banford and E.F.M. Toiper comprehensive chemical kinetic Vol. I & I Elsevier, 1969.
3. Amdur and Hammes Chemical Kinetics – Mc. Graw Hill.
4. N.H. Turro, Molecular Photochemistry, W.A. Benjamin Reading 1965.
5. R.W. Rft. And I.C. Lowis Tetrahedron 5, 210, 1959.

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PAPER- III ELECTROCHEMISTRY

UNIT I

Introduction and Principles

Definition – cost of corrosion – importance of corrosion studies – classification of corrosion – expressions for corrosion rate. electrochemical principles of corrosion: Faraday's laws – types of electro chemical cells formed in corrosion process. Thermodynamic principles of corrosion: electrochemical series/ standard electrode potentials and thermodynamic corrosion theory – Galvanic series of metals and alloys and limitations.

Forms of corrosion (Definition – cause and effects) : galvanic – crevice – pitting – intergranular - selective leaching - erosion - stress – hydrogen damage.

UNIT II

Kinetics of Corrosion

Importance – graphical presentation of kinetic data - exchange current density – different types of polarization of electrodes. activation polarization and Tafel plots – mixed potential theory – application of electrode kinetics to experimental observations – faradic impedance and corrosion.

UNIT III

Kinetics of Passivity

Introduction – electrochemical behaviour of active/passive metals – Flade potentials – criteria for selecting a metal exhibiting passivity – effects of various factors on electrochemical behaviour and corrosion rate of metal exhibiting passivity – measured versus theoretical anodic polarization behaviour – theories of passivity.

UNIT IV

Monitoring of Corrosion

Determination of corrosion and corrosion inhibition parameters – non-electrochemical methods: Coupon – electrical resistance – gasometric methods. electrochemical methods: polarisation – galvanostatic – potentiostatic– potentiodynamic – AC impedance – hydrogen permeation.

UNIT V

Corrosion Control

Metals and alloys – metal purification – non metallic – cathodic and anodic protection – comparison. Alteration of environment: changing the medium – use of inhibitors - classification of inhibitors – mechanism of inhibition – coating (Elementary ideas only).

References:

1. An introduction to metallic corrosion and its prevention by Raj Narayan, Oxford and IBH Publishing C., New Delhi (1983).
2. Corrosion and Corrosion control (An introduction to corrosion science and engineering) by Herbert H. Uhlig and R.Winston Review, Third Edition, A Wiley – Interscience Publication. New York (1984).
3. Corrosion engineering by Mars G. Fontana, Third Edition, McGraw Hill Book Company, Singapore (1984).
4. Application of inhibitors for acid media by G. Schmitt, Br.Corros. J., 1984. Vol.19, No.4, P.165-172.
5. Test methods for corrosion inhibitors by A.D. Mercer, Br.Corros J., 1985, Vol.20, No.2, P.61-70.
6. Inhibitors – An old remedy for a new challenge (1991 – Whitney Award Lecture) by G. Trabanelli, Corrosion, June 1991. P.410-418.

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PAPER- III POLYMER CHEMISTRY

UNIT I

Step-reaction polymerization (condensation polymerization)

Chemical reactivity and molecular size, theory of reactivity of large molecules, kinetics of condensation polymerization, self catalyzed polymerization, external catalysis of polymerization, cyclization Vs linear polymerization, multi-chain polymerization and their molecular weight determination. Kinetics of degradation of Condensation polymers – hydrolysis of polyimides, hydrolysis of polyesters-interchange reactions in condensation polymers.

UNIT II

Radical Chain (Addition) Polymerization

Kinetics of chain polymerization – dependence of RP on initiator, monomer and temperature. Photo chemical initiation, thermal initiation, redox initiation, initiator efficiency, auto acceleration, kinetics of thermal polymerization. Kinetic chain length and degree of polymerization. Kinetics of chain transfer, chain transfer with monomer, solvents, Non-radical chain polymerization – cationic polymerization – mechanism and kinetics (General), anionic polymerization – kinetics and mechanism (General).

UNIT III

Co-ordination Polymerization

Definition of Ziegler- Natta catalysts, factors determining behaviour of catalysts, importance of physical state of the catalyst, soluble catalyst, colloidal catalyst, heterogeneous catalyst and supported catalysts. Proposed mechanism – monometallic mechanism, bi-metallic mechanism, experimental evidence. Mechanisms for stereochemical control of α -olefins – mode of addition, isotactic propagation, syndiotactic propagation. Industrial uses of co-ordination catalysts.

UNIT IV

Chain Structure and conformation of Polymers

Vibrational spectroscopy and nuclear resonance spectroscopy of polymers – polymethyl methacrylate, polystyrene-propagation statistics. Region regularity and branching in vinyl polymer chains – head-to-tail versus head-to-head; tail-to-tail (special evidence) isomerism – regioregularity – poly vinyl chloride, polyvinyl alcohol - branching in vinyl polymers – polyethylene, polyvinyl chloride - geometrical isomerism in diene polymers –

Polybutadiene and polychloroprene (special evidence) solid state NMR of Polymers (General).

UNIT V

Glass Transition of Polymers

Theories of glass transition. The free-volume theory, the SLF equation, kinetic theory of glass transition, Gibbs and Gi Merzio theory, effect of cross-link density, polymerization, molecular weight, co-polymerization, crystallinity - chemical structure, tacticity and pressure on glass – transition temperature.

References

1. F.W. Bill Mayer, Text Book of Polymer Science' Wiley – Inter Science (1971).
2. H.R. Allcock and F.W. Larube, 'Contemporary Polymer Chemistry' Prentice Hall (1981).
3. L.H. Sperling 'Introduction to Physical Polymer Sciences' John Wiley & Sons (1986).
4. George Odian – 'Principles of Polymerization' McGraw Hill Book Company (1970).
5. P.J. Flory – 'Principles of Polymer Chemistry' Cornell Univ. Press (1953).
6. AD Ketley 'The Stereochemistry of Macromolecules' Decker (1967).
7. Zbinder – 'Infrared spectroscopy of High Polymers' Academic Press (1964).
8. K.J. Saunders 'Organic Polymer Chemistry' – Capman Hall: (1973).
9. Randall – 'Polymer sequence Determination Carbon – 13 NMR Method' Academic Press (1977).
10. Bovey F.A. 'High Resolution NMR of Macromolecules' Academic Press (1972).

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**PAPER- III ORGANIC SYNTHETIC METHODOLOGY AND
CONFORMATIONAL ANALYSIS**

UNIT I

Synthons and synthetic equivalents

Synthon approach- electron donor (nucleophiles)-electron acceptors (electrophiles)-Chiron-umpolung-synthetic equivalents-regioselective and stereoselective alkylation of cyclic ketones, cyclic enones-selective alkylation(mono and di) via enamine reactions.

Functional group interconversions

Modern methods of functional group interconversions involving $>C=O$, $-CHO$, $-OH$, $-SH$, $-COOH$, $>C=C<$, NH_2 , $-COOR$, $CONHR$ functions-reversible protection of reactive sites.

UNIT II

Retrosynthetic Analysis of Simple Organic Compounds

Retrosynthetic analysis of mono & difunctional open chain target molecules and monocyclic target molecules.

Selective reactions and Reagents

Olefination of carbonyl compounds-McMurray's methods-reductions with $LiAlH_4$ and $NaBH_4$ -Mannich reaction-Strecker synthesis-Wolf-Kishner reduction and Grignard reaction.

UNIT III

Stereochemistry and Conformational Analysis

Stereoselective, stereospecific and regiospecific reactions- stereoselectivity in carbonyl addition-Cram's rule- configuration-conformation-torsional strain-Vander Waals strain-gauche interaction-allylic strain- conformational analysis of acyclic molecules.

UNIT IV

Conformational Analysis of cyclic compounds

Conformational analysis of mono and disubstituted cyclohexanes-stability and reactivity-decalins- use of UV,IR & NMR spectroscopy for the conformational analysis of acyclic and cyclic molecules- stereodynamics of fluxional molecules-variable temperature NMR spectra (eg. N,N-dimethylacetamide)

UNIT V

Problem Solving

Solving the structure of simple organic molecules on the basis of UV,IR, NMR & Mass spectral data

References

1. R.K. Mackie and D.M. Smith, "Guide book to Organic Synthesis", ELB, 1982.
2. Jerry March, "Advanced Organic Chemistry: Reaction and Structure" 5th Ed., Wiley 1996.
3. Silverstein and Webster, "Spectrometric Identification of Organic Compounds", 6th Ed., Wiley 1998.
4. W. Kemp, NMR in Chemistry- A Multinuclear Introduction," McMillan, 1986.
5. C.D. Becker, "High Resolution NMR- "Theory and Applications" Academic Press, 2nd Ed., 1980.
6. R.E. Ireland, "Organic Synthesis", Prentice Hall.
7. Eliel, Stereochemistry of carbon compounds.
8. Nasipuri, Stereochemistry of organic compounds.
9. Norman, Principles of Organic Synthesis.
10. Caruthers, Some modern methods of Organic synthesis
11. Waren, Designing Organic Synthesis. A programmed introduction to synthetic approach.

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PAPER – III : CHEMISTRY OF ADVANCED MATERIALS

UNIT – I

General methods of preparation, properties and applications of the following advanced materials:

Liquid crystals , Ceramics (Oxide, carbides and nitrides), Thin films, Dendrimers, Zeolites, Porous membranes (anodic alumina and polycarbonate) - nanocomposites.

UNIT – II

Nanomaterials: Definition, Background- Nature and nanotechnology – Classification -0D, 1D, 2D and 3D. Types of nanomaterials – nanoparticles, nanorods, nanowhiskers – nanotubes – nanofibers.

Synthesis of nanomaterials – Top-down and Bottom-up approaches – Template based synthesis – sol gel method– Physical methods - Physical vapour deposition (Evaporation and sputtering) – Chemical methods – metallorganic chemical vapour deposition (MOCVD) - Thermal decomposition – sonochemical method - chemical reduction (using sodium borohydride, hydrazine and alkali metal solutions) – photochemical reduction –biosynthesis of noble metal nanoparticles..

UNIT – III

Characterization methods in nanoscience and nanotechnology:

Fundamental principles and working of the following techniques: Scanning electron microscopy (SEM) – Atomic force microscopy (AFM) – transmission electron microscopy (TEM) including high resolution transmission electron microscopy and selected area electron diffraction pattern (HRTEM & SAED) – scanning probe microscopy (SPM) – scanning tunneling microscopy (STM) - X-ray photoelectron spectroscopy (XPS)– Energy dispersive X-ray analysis (EDAX) – X-ray diffraction (XRD) –surface plasmon resonance – surface enhanced Raman spectroscopy.

UNIT – IV

Carbon nanotubes : Structure –single walled carbon nanotubes (SWCNT)- multiwalled carbon nanotubes (MWCNT)– synthesis – solid carbon source based techniques (laser

ablation and electric arc methods) - gaseous carbon based techniques (heterogeneous and homogeneous processes) - mechanism of growth of CNT - catalyst free growth and catalytically activated growth using transition metal catalysts (Root based and tip based) - Properties of CNT: Adsorption properties – transport properties – mechanical properties- chemical reactivity- Functionalisation of CNT (oxidation of CNT, reactions of oxidized CNT).

UNIT – V

Applications of Nanomaterials:

Nanoelectro mechanical systems (NEMS)- Data storage devices – diskettes and tapes.

Applications of CNT in catalyst support – gas storage –biosensors – CNT – metal nanocomposites – CNT – polymer composites.

Biological applications of nanomaterials – Drug delivery – nanodevices in medicine. Gold nanoparticles in medicine.

Catalysis using nanomaterials – metal oxide/metal nanoparticles for heterogeneous catalysis.

Nanofibers for biomedical applications as an implant material.

Nanomaterials for environmental applications.

References:

1. Jackie Ying - Nanostructured Materials.
2. G. Timp – Nanotechnology.
3. Robert A. Freitas Jr.- Nanomedicine, Volume I: Basic Capabilities
4. Geoffrey A. Ozin and Andre C. Arsenault, Nanochemistry – A chemical Approach to Nanomaterials, Cambridge.
5. Guozhong Cao – Nanostructures and Nanomaterials: Synthesis, Properties and Applications – Imperial College Press (2004).
6. Douglas Mulhall – Our Molecular Future: How Nanotechnology, Robotics, Genetics and Artificial Intelligence Will Transform Our World.
7. K. Eric Drexler – Nanosystems: Molecular Machinery, Manufacturing and Computation-John Wiley & Sons, Inc.: New York.
8. Reich, S., Thomsen, C. Maultzsch, J., Carbon nanotubes: Basic concepts and Physical properties, Weinheim: Wiley-VCH, 2004.

9. Nalwa, Hari Singh - Nanostructured Materials and Nanotechnology: Concise Edition, Diego: Academic Press, 2002.
10. J.Storrs Hall, Nanofuture: What's Next For Nanotechnology.
11. Norio Taniguchi – Nanotechnology : Oxford University Press.
12. Bharat Bhushan - Springer Hand Book of Nanotechnology.
13. Brown, Hemay and Bursten – Chemistry-The Central Science (6th Edition) -
Published by Prentice – Hall.
14. Jose Rodriguez, Synthesis, properties and applications of oxide Nanomaterials:
Wiley.
15. John Hutchison, Nanocharacterization: Royal Society of Chemistry.

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PAPER III - PHOTOCHEMISTRY - PHOTOPHYSICAL STUDIES

Unit I:

Some Current Topics in Photochemistry:

Origin of life- Mutagenic effect of radiation- Photodynamic therapy– Photosynthesis- Photoelectrochemistry of excited state redox reactions- Solar energy conversion and storage.

Unit II:

Photophysical Process in Electronically Excited Molecules:

Types of photophysical path ways- Radiationless transition- Internal conversion and intersystem crossing- Fluorescence emission- Fluorescence and structure- Delayed fluorescence.

Unit III:

Photochemistry in Microheterogeneous Systems:

General features of surfactant and lipid- Excited state processes and reactions: Medium effect- Acid-Base equilibrium in excited state- Depolarization of fluorescence- Excited state quenching- Excimers and Exciplexes- Excitation energy transfer- Photodimerization and photoredox reactions. Structural and dynamic aspects of micellar aggregates.

Unit IV:

Photoprocesses in Molecular Inclusion Complexes:

Introduction- Photoprocesses in Cyclodextrins- General features of Cyclodextrins and inclusion complexes- Fluorescence probe analysis- Fluorescence depolarization- Excimers and Exciplex dynamics.

Unit V:

Photoprocesses in Aluminosilicates – Zeolites:

General features of Zeolites and their cavities- Photochemistry of Inorganic ions exchanged into Zeolites- Photochemistry of Organic molecules.

References:

1. G.H. Wald, "Life and light", Scientific American, 201, 1959, 92.
2. A. McLaren and D. Shugar, "Photochemistry of Nucleic Acid and Proteins", Oxford, Pergamon press, 1964.
3. R.F. Reinisch, (ed.), "Photochemistry of Macromolecules", New York, plenum press, 1970.
4. E.I. Robinowitch and Govindjee, "Photosynthesis", New York, Wiley, 1969.
5. G. Stein, "Chemical Storage of Solar Energy and Photochemical Fuel formation", Israel J. Chem. 14, 1975, 213.
6. K.K. Rohatgi-Mukherjee, "Fundamentals of photochemistry", New Delhi, New Age international Publishers, 2002 (Revised edition).
7. N.J. Turro, "Molecular Photochemistry", New York, Benjamin, 1978.
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10. K. Kalyanasundaram, "Photochemistry in Microheterogeneous Systems", New York, Academic press, 1987.
11. M.L. Bender and M. Komiyama, "Cyclodextrin Chemistry", React. Struct. Concepts, Org. Chem., Vol. 16, Berlin and New York, Springer-Verlag, 1978.
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