Babasaheb Bhimrao Ambedkar Bihar University, Muzaffarpur
Directorate of Distance Education

CHEMISTRY

Syllabus for M.Phil (chemistry) 1st and 2nd Semester Session 2014-2015

Semester I	Title of the Course	Marks			Credits
		IA	UE	Total	
Paper I	Research Methodology	**20**	**80**	**100**	4
Paper II	Physical Methods in Chemistry	**20**	**80**	**100**	4
Paper III	Analytical Chemistry	**20**	**80**	**100**	4

Semester II	Title of the Course	Marks			Credits
Paper IV	**Special Papers** **(Choose Any One)** 1. Organic Chemistry 2. Solid State and Hydrazine Chemistry 3. Organometallic Chemistry of Transition Metals 4. Photochemistry of Photophysical Studies 5. Environmental Chemistry	**20**	**80**	**100**	4
Paper V	**Special Papers** **(Choose Any One)** 1. Chemistry of Crystalline Solids 2. Physical Organic Chemistry 3. Electro Chemistry 4. Polymer Chemistry 5. Organic Synthetic Methodology and Conformational Analysis	**20**	**80**	**100**	4
Paper VI	Dissertation and VivaVoce Viva Voce 50 marks Dissertation 150 marks			200	8

Paper I - Research Methodology

UNIT – I Methods in Research

Problem identification – Designing hypothesis – Literature Survey – Planning and execution of actual investigation – Interpretation of Data – Drawing statistical conclusions.

UNIT – II Literature Survey

Sources of Information – Primary, Secondary and Tertiary sources - Journals – Abstracts – Reviews – Books – Article databases – Journal Impact Factor – Review of literature of the identified problem

UNIT – III Investigation and Paper Writing

General principles of research – Scientific originality of research – Experimentation – Observation – Hypothesis testing – Result Interpretation – Paper writing – Background – Importance of the research – Methodology – Tables and Figures - Results and Discussion – Conclusion – References – Publication of the paper in journals.

UNIT – IV Data Analysis

Errors and types – Sampling size – Knowing the kind of data – Mean, Standard deviation, Standard error - Selection of appropriate Statistical test - Significance testing – F distribution – *t* distribution – Normal distribution – Paired and Unpaired *t* tests – ANOVA – Correlation and Regression

UNIT – V Safety and Ethics in Chemical Handling

General Laboratory Practice (GLP) – Safe working and Protective environment – First aid – Safe storage, Use and Disposal of chemicals – Handling radioactive chemicals – Disposal procedures for difference chemicals

References:

1. Research Methodology, C.R.Kothari, New Age International Publishers, 2004.
2. Maeve O"Connor, „Writing successfully in science" Chapman and Hall, London, 1995.
3. Chemical safety matters-IUPAC –IPCS, Cambridge Univ. Press, 1992.
4. S. C. Gupta, „Fundamentals of Statistics", Sixth Edn., Himalaya publ. House", Delhi, 2006

Paper II - Physical Methods in Chemistry

Unit I

UV Visible spectroscopy – Instrumentation – Microstates – Term symbols and energylevels for d^1 – d^9 ions in cubic and square fields – intensity of bands – group theoretical approach to selection rules – effect of distortion and spin –orbit coupling on spectra – Evaluation of 10 Dq and βvalues for octahedral complexes of cobalt and nickel – applications to simple coordination compounds – applications to organic compounds and calculation of λ_{max} – charge transfer spectra.

IR and Raman spectroscopy – Instrumentation – preparation of samples and pellet making– applications of IR and Raman spectroscopy – combined uses of IR and Raman spectroscopy in structural elucidation of simple molecules like N2O, ClF3, NO_3^- ClO_4^- -Predicting IR bands for simple organic molecules – effect of coordination on ligand vibrations – uses of group vibrations in the structural elucidation of metal complexes of urea, thiourea, cyanide, thiocyanate, nitrate, sulphate and dimethyl sulfoxide – effect of isotopic substitution on the vibrational spectra of metal carbonyls with reference to the nature of bonding, geometry and number of C-O stretching vibrations (group theoretical treatment) – Applications of Raman Spectroscopy. Photo electron spectroscopy - Principle – Auger electron spectroscopy – electron spectra in chemical analysis.

Unit II

NMR spectroscopy – Bloch equations, the quantum mechanical description of the NMR experiment, transition probabilities, Relaxation effects, Fourier transform NMR –measurements of T1 and T2. Effect of quadrupolar nuclei evaluation of thermodynamics and kinetic data using NMR techniques, second order spectra –Quantum mechanical treatment of coupling, effect of relative magnitudes of J on the spectrum of an AB and ABX molecules, double resonance experiment. Spectral simplification and determination of signs of coupling constants. Examples for different spin systems – chemical shifts and coupling constants (spin – spin coupling) involving different nuclei (^1H, ^{19}F, ^{31}P, ^{13}C) – elementary aspects of Solid State NMR. NMR of paramagnetic molecules – isotropic shifts contact and pseudo contact interactions – lanthanide shift reagent. Characteristics of quadrupolar nucleus – effect of field gradient and magnetic field upon quadrupolar energy levels – NMR transitions applications – Basic principles and applications of NQR. Sampling techniques, factors influencing group frequencies both internal and external quantitative studies, hydrogen bonding (intermolecular and intramolecular) conformational aspects in cyclic 1,2 –diols and 1,3 –diols, 1H NMR spectroscopy – coupling constant – first order and second order splitting spin – spin splitting – dependence of J on dihedral angle – vicinal and geminal coupling constants – Karplus equation – long range, coupling constants, influence of stereo chemical factors on chemical shift of protons, simplification of complex spectra – double resonce techniques, shift reagents, chemical spin decoupling of rapidly exchangeable protons (OH, SH, COOH, NH, NH_2) – an elementary treatment of NOE phenomenon – 2D technique (COSY, NOESY and ROSY) ^{13}C NMR spectroscopy. Basic theory of FT – NMR – Relaxation – broad band decoupling. Off resonance decoupling and chemical shift correlations (CH, CH_2, CH_3, $=CH_2$, =C, aromatic). NQR – Basic Principles.

Unit III

EPR spectroscopy - Factors affecting the magnitudes of g and A tensors in metal species – Zero field spitting and Kramer's degeneracy – spectra of V(II) , Mn(II), Fe(II), Co(II), Ni(II) and Cu (II) complexes- applications of EPR to a few biological molecules containing Cu(II), Fe(II) and Fe(III) ions – spin densities and McConnel relationship – Applications of EPR to some simple systems such as CH_3, p-benzosemiquinone. Xe^{2+} **Moss Bauer spectroscopy** - Isomer shifts – magnetic interactions – Mossbauer emission spectroscopy – application to iron and tin compounds. Mass spectrometry - Instrumentation – resolution, EI and CI methods – base peak, isotopic peaks, metastable peak, parent peak, determination and use of molecular formula, recognition of molecular ion peak – FAB Fragmentation – general rules – pattern of fragmentation for various classes of compounds, McLafferty rearrangement, Importance of metastable peaks.

Unit IV

Diffraction Methods - Crystal symmetry – combination of symmetry elements – crystal classes – screw axis and glide planes – space group – crystal axes – crystal systems, unit cell, Bravais lattices, asymmetric unit – space group – Equivalent positions- relationship between molecular symmetry and crystallographic symmetry – basic concepts and examples.

X – Ray diffraction - The concept of reciprocal lattice and its applications – X-ray diffraction by single crystals – structure factor – determination of space group by symmetric phase problem in structure analysis – heavy atom method – Fourier synthesis – refinement of structure. Neutron diffraction - Magnetic scattering – applications and comparison with X-ray diffraction. Electron diffraction - Basic principles and application to simple molecules – XeF_6, $Be(BH_4)_2$, ferrocene, Cr(II)acetate.

Unit V

Quantum Chemistry - The variation method and perturbation theory. Application to the helium atom; anti symmetry and exclusion principle, Slater determination, wave functions. Term symbols and spectroscopic states. Born-Oppenheimer approximation Hydrogen molecular ion. LCAO – MO and VB treatments of the hydrogen molecule, electron density, forces and their role in chemical bonding, Hybridization and valence MO's of water, ammonia and methane. Huckel pi-electron theory and its applications to ethylene, butadiene and benzene, idea of self consistent fields. Group theoretical representations and quantum mechanics. Vanishing of integrals. Spectroscopic selection rules for vibrational electronic, vibronic Raman spectroscopy, MO treatment of large molecules with symmetry. Instrumentation and applications of Electro analytical techniques Electro organic synthesis.

Text Books

1. Huheey JE, Keiter EA and Keiter RA, 2000, Inorganic Chemistry, Principles of Structure and Reactivity, 4th edition, New Delhi, Pearson Education (Asia).
2. Silverstein RM and Webster FX, 2003, Spectrometric Identification of Organic Compounds, 6th edition, New York, John-Wiley and Sons Inc.
3. Kalsi PS, 1990, Stereochemistry Conformation and Mechanism, 4th edition, New Delhi, New Age International Publishers.
4. Straughan BP and Walker S, 1976, Spectroscopy vol: 1-3, London, Chapmann and Hall.
5. Drago RS, 1980, Physical Methods in Chemistry, New Delhi, W. B. Saunders.

Reference Books

1. Rifi MR and Covitz FH, 1974, Introduction to Organic Electrochemistry, New York, Marcel Dekker.
2. Kemp W, 1993, Organic Spectroscopy, 3rd edition, London, ELBS with Macmillan.
3. Cotton FA, Wilkinson G, Murillo CA and Bochman M, 2003, Advance Inorganic Chemistry, 6th edition, New York, John-Wiley and Sons Inc.
4. Kalsi PS, 1999, Stereochemistry and Mechanism Through Solved Problems, 3rd edition, New Delhi, New Age International Publishers.
5. Sutton D, 2000, Electronic Spectra of Transition Metal Complexes, New Delhi, Narosa Publishing House.
6. Nasipuri D, 2000, Stereochemistry of Organic Compounds, New Delhi, Narosa Publishing House.
7. Bancroft M, 1973, Mossbauer Spectroscopy, New Delhi, Tata McGraw-Hill Publishing Company.
8. Wheatly PJ, 1959, The Determination of Molecular Structure, London, Oxford at the Clarendon Press.
9. Ebsworth EAV, 1987, Structural Methods in Inorganic Chemistry, 3rd ed, London, ELBS.

Paper III - Analytical Chemistry

UNIT – I Microscopy Techniques

Electron Microscopy – Transmission Electron Microscopy (TEM) – Scanning Electron Microscopy (SEM) – Atomic and Molecular force Microscopes - Fluorescence Microscopy – FRET – Confocal Microscopy

UNIT – II Spectroscopy

UV-Visible Spectroscopy – Atomic Absorption Scpectroscopy – H^1 NMR – ^{13}C NMR – 2D NMR – ESR spectroscopy – Applications

UNIT – III Chromatographic Techniques

Thin Layer Chromatography (TLC) - High Performance Liquid Chromatography (HPLC) – Gas Chromatography (GC) – Infra red Spectroscopy (IR) - Electrophoresis

UNIT – IV Mass Spectrometry

Basic Instrumentation – Ionization techniques – EI, CI, FD, MALDI – Analysis of Mass Spectrum - Applications – LCMS – GCMS – Molecular weight determination – Protein identification – Nucleic acid identification

UNIT – V Electro Analytical Techniques

Potentiometric sensors – Electrodes – Electrogravimetry –Chrono amperometry - Cyclic voltammetry – Stripping analysis

Reference:

1. T. Pradeep, Nano: The Essentials, Mc Graw-Hill Edn, New Delhi, 2007.
2. Spectrometric Identification Organic Compounds, Silverstein and Webster, Wiley, 1998.
3. Instrumental Methods of Analysis, H.H. Willard, L.L. Merritt, and J.A. Dean, East-West Press, NewDelhi, 1988.
4. H. Gunther, NMR spectroscopy, basic principles, concepts and application in chemistry, John Wiley & Sons, 2nd Ed., 1995.

5. A.J. Bard L.F. Faulkner, Electrochemical methods – Fundamentals and Applications, Second Edn., Wiley-VCH, 1998.
6. Bioanalytical Chemistry, S. K. Mikkelsen and Eduardo Corton, Publisher: Wiley-Interscience - John Wiley & Sons, Inc., 2004

PAPER – IV 1.ORGANIC CHEMISTRY

UNIT I

Theory of Concerted Reactions: Definitions – molecular orbitals – frontier orbita ls – frontier orbital approach – correlation diagrams – the aromatic transition state concept – general rule for pericycle reactions. Electrocyclic Reactions: Definition – thermal electrocyclic reactions – photochemical electrocyclic reactions – metal catalysed electrocyclic reactions. Cycloadditions: Introduction – selection rules for thermal polyenecyclo 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 proc
esses – Jablonski diagrams – radiative transitions – internal conversion – inter
system 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 o0rganic synthesis: Sodium cyanoborohydride – osmium tetraoxide – lithium dimethyl copper – thallium trifluoro acetate – sodium hydrogen telluride – silver hexa fluorantimonate – Thiobenzoyl chloride – trichloro-silane – vanadium oxytrifluro – phosphonitrile chloride – ruthenium tetraoxide – barium magnaganate – 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 HLowry, Kathleen
Suhueller 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. Piltts
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, India Journal of Chemistry Vol. 23 B, p.535 (1984)
15.P.Sowmithran and K.J.Rajendra Prasad, Synthesis, 5,545 (1985)

PAPER – IV 2. SOLID STATE AND HYDRAZINE CHEMISTRY

UNIT I

Crystallography: Preparation of materials – crystal growth and puri fication, the crystal systems – lattices and crystal structures –symmetry properties – crystal classes – space groups – X – Rays – crystallography – the powder method – ro
tating crystal method – crystal structure determination – the structure factor – fo
urier 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 – insul
ators – 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 $N_2H_5^{2+}$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 2ndEdition (1978)
7.Comprehensive Inorganic Chemistry – J C Bailar et a
l, Vol. 4 and 5 (1975)
8.Structure and Bonding (Rare-earths) – J D Dunitz etal, Vol. 25 (1976) p. 23-150
9.Coordination of Trivalent Lanthanide Ions – D G Kar
raker, 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).

PAPER – IV 3. 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 alkylidynecomplexes. 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 X2– addition of RX – addition reactions of Si-H, C-C, C-Si and Si-Si bonds – elimination reactions – α and βeliminations – alkane activation – intramolecular and intermolecular C-H activation – activation of sulphur heterocycles – insertion ofcarbon 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, Brelin, 1985.

4.Inorganic chemistry – Principles of structure and reactivity, J. E. Huheey, Harpe 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.

PAPER- IV 4. 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 reations- 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 Microheterog
eneous Systems”, New York, Academic press, 1987.
11.M.L. Bender and M. Komiyama, “Cyclodextrin Chemistr
y”, React. Struct. Concepts, Org. Chem., Vol. 16, Berlin and New York,
Springer-Verlag, 1978.
12.J. Szejtli, ”Cyclodextrins and their Inclusion Complexes”, Budapest,
Académiai Kaidò, 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 – IV 5. 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, disingection, 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 degradat
ion, 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, form 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 PL. 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

PAPER- V 1. 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.Introducation to solids – L.V.Azarof (1960).

PAPER- V 2. PHYSICAL ORGANIC CHEMISTRY

UNIT I

1.1.Theories of Reaction Rates: Absolute reaction rate theory – thermodyn
amic 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 – Hammet's acidity function Br
onsted relationship – enzyme catalysis – mechanism of single substrate reactions – Michalis -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 cettler correlation. The Hammett equation – steric effects – resonance interaction – normal substitutent constants - σ-, σ+ constants – inadequancy of dual
hypothesis – regularities in the through resonance effect- the Yukawa Tsuno equation – systematic deviation-steric inhabitation of resonance – Taft equation – correlation of aliphatic and aromatic relativities.

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, 2ndEd. Tata Mc.Graw Hill 1975 (Unit I, II, IV).
2.W.J. Moore, Physical chemistry 5thEd. 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.

PAPER- V 3. ELECTRO CHEMISTRY

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. act
ivation 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 metal
lic – 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 tocorrosion 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.

PAPER- V 4. 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 degrad
ation 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' Cormell 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).

PAPER- V 5. ORGANIC SYNTHETIC METHODOLOGY AND CONFORMATIONAL ANALYSIS

UNIT I

Synthons and synthetic equivalents Synthon approach- electron donor (nuecleophiles)-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 interconversionsinvolving >C=O, -CHO, -OH, -SH, -COOH, >C=C<, NH2,
-COOR, CONHR functions-reversible protection of reactive sites.

UNIT II

Retrosynthetic Analysis of Simple Organic Compounds Retrosynthetic analysis of mono & difunctional openchain target molecules and monocyclic target molecules. Selective reactions and Reagents Olefination ofcarbonylcompounds-McMurray's methods-reductions with LiAlH4 and NaBH4-Mannich reaction-Strecker synthesis-Wolf-Kishner reduction and Grignard reaction.

UNIT III

Stereochemistry and Conformational Analysis Stereoselctive, 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 acylic 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 acylic and cyclic molecules- stereodynamics of fluxional molecules-variable temperature NMR spectra (eg. N,N-dimethylacetamide)

UNIT V

Problem 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" 5thEd., Wiley 1996.
3.Silverstein and Webster, "Spectrometric Identification of Organic Compounds", 6thEd., 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, 2ndEd., 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.