BHARATHIDASAN UNIVERSITY TIRUCHIRAPPALLI- 620 024

M.Sc. Chemistry

(For the candidates admitted from the academic year 2015 -16 onwards offered through Centre for Distance Education)

Course Duration: 2 Years – (Non-Semester System)

Eligibility: B.Sc. Chemistry

Year	Paper	Title of the Paper	Exam Hours	Marks
I YEAR	Major Paper I	Organic Chemistry	3	100
	Major Paper II	Inorganic Chemistry	3	100
	Major Paper III	Physical Chemistry	3	100
	Major Paper IV	**Practical I** Organic Chemistry	6	100
	Major Paper V	**Practical II** Inorganic Chemistry	6	100
				500
II YEAR	Major Paper VI	Physical Methods in Chemistry	3	100
	Major Paper VII	Analytical Chemistry	3	100
	Major Paper VIII	Green Chemistry & Nano Science	3	100
	Major Paper IX	**Practical III** Physical Chemistry	6	100
	Major Paper X	**Practical IV** Analytical Chemistry	6	100
		TOTAL		**1000**

(Passing Minimum 50% both theory and practical)

Note: Compulsory Record should be submitted at the time of practical examination

MAJOR PAPER I - ORGANIC CHEMISTRY

UNIT – I

Nomenclature, Reactive intermediates, Methods of Determining reaction Methods.

1.1. Nomenclature of alicyclic, bicyclic and tricyclic compounds. Nomenclature of heterocycles having not more than two hetero atoms such as oxygen, nitrogen and sulphur.

1.2 Aromatic character: six-, Five-, seven-, and eight-membered rings - Other systems with aromatic sextets – Huckel's theory of aromaticity, Concept of homoaromaticity and antiaromaticity, systems with 2,4,8 and 10 electrons, systems of more than 10 electrons, alternant and non-alternant hydrocarbons (azulene type). Bonding properties of systems with $(4n + 2)\pi$ electrons and $4n\pi$ electrons, Heteraromatic molecules. Annulenes and sydnones and fullerenes.

1.3 Thermodynamic and kinetic aspects, Hammond's postulate, isotope effects. Energy profile diagrams – Intermediate versus transition state, Product analysis and its importance, Crossover experiments, Kinetic methods, Stereochemical studies, Isotopic and substitutent effects.

UNIT – II

Stereochemistry

2.1 Fundamentals of Organic Stereochemistry: Principles of symmetry – Stereoisomerism – Optical isomerism - Definitions – Conventions used in stereochemistry: Newman, Sawhorse and Fischer notations and interconversions and epresentations. Nomenclature, correlation of configuration. Cahn – Ingold – Prelog rules for simple molecules. Optical activity and chirality – Types of molecules exhibiting optical activity – Fischer projection – Absolute configuration. Molecules with more than one chiral centre – Molecular chirality – Atropisomerism – Biphenyls, allenes and spiranes.Methods of determining configuration. Enantiomerism of compounds containing chiral heteroatoms

2.2 Geometrical Isomerism E & Z Nomenclature, Determination of configuration of geometrical isomers, Stereospecific and stereoselective synthesis – [Elementary examples].

2.3 Basic concepts of conformational analysis – cyclohexane and decalins.

UNIT- III

Substitution Reactions

3.1 Aliphatic Nucleophilic substitution – Mechanisms – Effect of structure - Stereochemical factors – Neighbouring group participation, substitutions at allylic and vinylic carbons. Correlation of structure with reactivity – Solvent effects.

3.2 Aliphatic Electrophilic Substitution: SE^2,SE^i and SE^1mechanisms ,Diazonium coupling reactions.

3.3 Aromatic Nucleophilic substitution – SN1 SNAr ,Benzyne mechanism – reactivity orientation.

3.4 Aromatic electrophilic substitution reaction - Orientation, reactivity and mechanisms based on transition state theory with suitable reactions, – Origins of Hammett equation – Principles of Hammett correlation – Effect of structure on reaction mechanisms Hammett parameters; σand ρ, modified forms of Hammett equation. Taft Equation.

UNIT – IV

Addition and Elimination Reactions

4.1 Addition to carbon – carbon multiple bonds: Electrophilic, nucleophilic and free radical additions – Orientation of the addition – Stereochemical factors influencing the addition of bromine and hydrogen bromide, hydroxylation, hydroboration leading to formation of alcohols. Addition to carbonyl and conjugated carbonyl systems - Mechanism – Grignard reagents – 1,2 and 1,4-additions (dimethyllithiumcuprate),Benzoin , Knovenagel, Stobbe and Darzen'sglycidic ester condensation and Reformatsky reactions.

4.2 Elimination Reactions: Mechanisms; E1,E2, E1cB – Stereochemistry of elimination, Hofmann and Saytzeff rules – Competition between elimination and substitution - Pyrolyticcis elimination, Chugaev reaction – Examples such as dehydration, dehydrohalogenatio, Hofmann degradation, Cope elimination – Bredt's rule with examples.

UNIT V

Organic Photochemistry &Pericyclic Reactions

5.1 Organic Photochemistry – Fundamental concepts – Jablonski diagram – Energy transfer, characteristics of photoreactions, photoreduction and photoxidation, photoreactions of ketones and enones, Norrish Type I and II reactions. Photochemistry of alkenes, dienes and aromatic compounds, Photoadditions – Barton reaction – ParternoBuchi reaction.

5.2 Concerted reactions – stereochemistry-orbital symmetry and concerted symmetry and correlation diagram – Frontier molecular orbital approach – Woodward and Hoffmann rules – Electrocylcic reactions – cycloaddition reactions – sigmatropic rearrangements – selection rules and examples with simple molecules – 1,3 and 1,5 hydrogen shifts –Cope and Claisen rearrangements. Other molecular rearrangements

References

1. J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 5th ed.,Wiley, 2000.
2. D. Nasipuri, Stereochemistry of organic compounds-Principles and applications,
3. New Age International, 2nd Edition,2002.
4. I.L. Finar, Organic Chemistry, Vol.II, 5th ed., ELBS 1975.
5. J.M. Coxon, B. Halton, Organic Photochemistry, Camb. Uni. Press, 2nd edition, 1987.
6. G.R. Chatwal ,OrganicPhtochemistry, Himalaya Publications house, 1st edition, 1998.
7. P.S. Kalsi, Stereochemistry , Wiley eastern limited, New Delhi, 1990.
8. S.H. Pine, J.B. Hendrickson, D.J. Cram and G.S. Hammond, Organic chemistry, McGraw Hill, 4th ed., 1980.
9. T.H. Lowry and K.S. Richardson, Mechanism and Theory in Organic Chemistry,Harper and Row, 1976.
10. F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry, Parts A & B, Plenum, 2002.

MAJOR PAPER II- INORGANIC CHEMISTRY

UNIT I

1.1 Coordination Chemistry: Principles

Studies of coordination compounds in solution – detection of complex formation in solution – Stability constants – stepwise and over-all formation constants – simple methods (Potentiometric, pH metric and photometric methods) of determining the formation constants - Factors affecting stability – statistical and chelate effects – Forced configurations.

1.2 Theories of Metal - Ligand bond

VB theory and its limitations – Crystal field theory - splitting of d-orbitals under various geometries – Factors affecting splitting – CFSE and evidences for CFSE (Structural and thermodynamic effects) – Spectrochemical series – Jahn-Teller distortion – Spectral and magnetic properties of complexes – Site preferences - Limitations of CFT – Ligand field theory – MO theory – sigma – and pi-bonding in complexes – Nephelauxetic effect – The angular overlap model.

UNIT II

2.1 Coordination Chemistry – Reaction Mechanism

Kinetics and mechanism of reactions in solution – labile and inert complexes – Ligand displacement reactions in octahedral and square planar complexes – acid hydrolysis, base hydrolysis and anation reactions – trans effect – theory and applications. Electron transfer reactions – electron exchange reactions – complementary and non-complementary types – inner sphere and outer sphere processes .

2.2 **Inorganic Photochemistry** Electronic transitions in metal complexes, metal-centered and charge-transfer transitions – Various photophysical and photochemical processes of coordination compounds – Unimolecular charge-transfer photochemistry of cobalt(III) complexes. Mechanism of CTTM photoreduction. Ligand-field photochemistry of chromium(III) complexes, Adamson's rules, photoactive excited states, V-C model – photophysics and photochemistry of ruthenium-polypyridine complexes, emission and redox properties – photochemistry of organometallic compounds, metal carbonyl compounds, compounds with metal-metal bonding Reinecke's salt chemical actinometer.

UNIT III

3.1 General Principles of Bioinorganic Chemistry and Biomineralisation

Occurrence and availability of Inorganic elements in biological systems. Biomineralisation Control and assembly of advanced materials in Biology - Nucleation and crystal growth – various biominerals – calcium phosphate – calcium carbonate – Amorphous silica, Iron biominerals – strontium and barium sulphate.

3.2 **Function and Transport of Alkali and Alkaline Earth Metal Ions**

Characterization of K^+ , Na^+ , Ca^{2+} and Mg^{2+} - complexes of alkali and alkaline earth metal ions with macrocycles - Ion channels – ion pumps. Catalysis and regulation of bioenergetic processes by the Alkaline Earth Metal ions Mg^{2+} and Ca^{2+}.

Metals at the Center of Photosynthesis Primary Processes in Photosynthesis – Photosystems I and II - Light Absorption (Energy Acquisition) – Exciton transport (Direct Energy Transfer) – Charge separation and electron transport – Manganese catalyzed oxidation of water to O_2.

UNIT – IV

4.1 Cobalamines, Heme and Non Proteins Hemoglobin

Reactions of the alkyl cobalamins– One-electron Reduction and Oxidation – Co-C Bond Cleavage – coenzyme B_{12} – Alkylation reactions of methylcobalamin. Hemoglobin and Myoglobin – Oxygen transport and storage – Electron transfer and Oxygen activation. Cytochromes, Ferredoxins and Rubredoxins – Model systems, mononuclear non-heme iron enzymes.

4.2 **Copper Containing Proteins and Nickel containing Enzyme**

Classification and examples - Electron transfer – Oxygen transport - Oxygenation – oxidases and reductases – Cytochrome c oxidase – Superoxide dismutase (Cu, Zn) and Urease.

UNIT – V

5.1 **Medicinal Bioinorganic Chemistry and Chemotherapy**

Bioinorganic Chemistry of quint essentially toxic metals. Lead, Cadmium, Mercury, Aluminium, Chromium, Iron, Copper, Plutonium. Detoxification by metal chelation. Drugs that act by binding at the metal sites of Metalloenzymes. Chemotherapy with compounds of certain non-essential elements. Platinum complexes in Cancer therapy – Cisplatin and its mode of action – Cytotoxic compounds of other metals – Gold containing drugs as anti-rheumatic agents and their mode of action - Lithium in Pschycopharmocological drugs. Radiopharmaceuticals – Technetium.

5.2 **Reactions and Catalysis by Organomatallics**

Organometallic reactions – Ligand association and dissociation – oxidative addition and reductive elimination – Insertion reactions – Reactions of coordinated ligands in organometallics - Hydrogenation, hydroformylation, epoxidation, metathesis, polymerization of olefins, olefin oxidation (Wacker process) and carbonylation of methanol.

Text Books and Reference Books

1. J. E. Huheey, Inorganic Chemistry, 3rd ed., Harper & Row Publishers, Singapore.
2. Purcell and Kotz, Inorganic Chemistry, Saunders Golden Sunburst Series, W. B. Saunders Company, Philadelphia.
3. S. J. Lippard and J. M. Berg, Principles of Bioinorganic ChePanima Publishing Company, New Delhi, 1997.
4. W. Kaim and B. Schewederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life , John Wiley & Sons, New York, USA.
5. Cotton and Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley Interscience Publication, John Wiley & Sons, New York, USA.
6. Chem. Education, 62, No. 11, 1985, Bioinorganic Chemistry , State of the Art.
7. G. L. Eichorn, Inorganic Biochemistry, Volumes 1 & 2, 2nd ed., Elsevier Scientific Publishing Company, New York, 1973.
8. R. H. Crabtree, The Organometallic Chemistry of the Transition Metals, John Wiley & Sons, New York.
9. S. E. Kegley and A. R. Pinhas, Problems and Solutions in Organometallic Chemistry, University Science Books, Oxford University Press.
10. A. J. Pearson, Metalloorganic Chemistry,
11. A. W. Parkins and R. C. Poller, An Introduction to Organometallic Chemistry
12. I. Haiduc and J. J. Zuckerman, Basic Organometallic Chemistry
13. P. Powell, Principles of Organometallic Chemistry, 2nd ed., Chapman and Hall, London.
14. B. Douglas, D. H. McDaniel and J. J. Alexander, Concepts and Models of Inorganic Chemistry, 2nd ed, John Wiley & sons, New York.
15. Oxford Chemistry Primers Series, No. 12, M. Bochmann Organometallics 1: Complexes with transition metal-carbon σ bonds and No. 13 M. Bochmann Organometallics 2: Complexes with transition metal-carbon π-bonds
16. J. P. Collman, L. S. Hegedus, J. R. Nortan and R. G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books. Mill Valley, CaliforniaR. Hoffmann, Angew. Chem. Int. Ed., Engl. 21, 711-800 1982.
17. M. C. Day and J. Selbin, Theoretical Inorganic Chemistry, Affiliated East West Press Pvt. Ltd. 2nd ed.,1985.
18. A.W.Adamson, Inorganic Photochemistry, John Wiley & Sons, New York.
19. S.F.A. Kettle, Physical Inorganic Chemistry – A Coordination Chemistry Approach, Spectrum Academic Publishers, Oxford University Press, 1996.
20. A. W. Adamson and P. D. Fleischauer, Concepts of Inorganic Photochemistry, Wiley, New York, 1975.
21. J. Ferraudi, Elements of Inorganic Photochemistry, Wiley, New York, 1988

MAJOR PAPER III - PHYSICAL CHEMISTRY

UNIT – I

Group theory - Concepts

1. 1 Elements of group theory – definition – group multiplication tables – conjugate classes, conjugate and normal subgroups – symmetry elements and operations – point groups – assignment of point groups to molecules, - Matrix representation of geometric transformation and point groups – reducible and irreducible representations– properties of irreducible representation – construction of character tables – bases for irreducible representation – direct product – symmetry adapted linear combinations – projection operators.

Chemical Kinetics

1.2 .Theories of reaction rate – Absolute reaction rate theory (ARRT) - Significance of reaction co-ordinate – Potential energy surfaces – Kinetic isotope effect – Molecular dynamics – Principle of microscopic reversibility - Explosions and hydrogen – oxygen reactions. Application of ARRT to solution kinetics - Effect of solvent and ionic strength, influence of pressure on rates in solution - Enzyme catalysis- Mechanism of single substrate reactions – MichaelisMenton law – Kinetics of processes in micellar and reverse micellar systems.

UNIT – II

Quantum Chemistry

2.1 Bohr's theory of hydrogen atom : Hydrogen spectra, Photoelectric effect, Wave-particle dualism, Uncertainty principle. Schrödinger equation, Postulatory basis of quantum mechanics. Operator algebra: operator, linear and hermitian, eigen functions and eigen values, angular momentum operator, commutation relations, related theorems.

2.2. Applications of wave mechanics to simple systems – particle in a box, one and three-dimensional, rigid rotator, harmonic oscillator – Hydrogen atom solution –Pauli principle – derminental form of wave function, Helium atom and effective nuclear charge-Approximation methods – Variation methods, application to Hydrogen and Helium atoms– Perturbation method for nondegenerate systems.Angular momentum in many electron systems – Spin orbit interaction, L-S and j-j coupling schemes

UNIT – III

Photochemistry and Radiation Chemistry:

3.1 Photophysical processes electronically excited molecules Jablonski diagram – Stern-Volmer equation and its applications – experimental techniques in photochemistry – chemical actinometers –lasers and their applications.

Radiation Chemistry

3.2 Differences between radiation chemistry and photochemistry – sources of high energy radiation and interaction with matter – radiolysis of water, solvated electrons – Definition of G value – Curie –Linear energy transfer LET and Rad – Scavenging techniques- use of dosimetry and dosimeters in radiation chemistry- application of radiation chemistry.

3.3. **Fast reaction techniques:** Introduction, flow methods (continuous and stopped flow methods)- Relaxation methods (T and P jump methods) – Pulse techniques (pulse radiolysis, flash photolysis, Shock tube method)- molecular beam method – lifetime method.

UNIT – IV

Molecular Thermodynamics

4.1 Thermodynamics of systems of variable composition – partial molar properties – chemical potential – relationship between partial molar quantities – Gibbs Duhem equation and its applications (the experimental determination of partial molar properties not included).

4.2 Thermodynamic properties of real gases – fugacity concept – calculation of fugacity of real gas – Activity and activity coefficient – concept – definition – standard states and experimental determinations of activity and activity coefficient of electrolytes.

4.2 Calculation of Thermodynamic probability of a system – Difference between thermodynamic probability and statistical probability – Ergodic hypothesis –Derivation of Boltzman distribution equation – physical significance of partition function- translational, rotational, vibrational and electronic partition functions – Quantum statistics – Bose – Einstein and Fermi – Dirac distribution equations – comparison of B.E and F.D statistics with Boltzman statistics – Concept of Negative Kelvin Temperature. Relationships between partition function and thermodynamic properties such as E, H, Cp, Cv, P. Derivation of PV=RT, Molecular interpretation of entropy- Derivation of S=klnW - Calculation of S, A, G etc., from partition functions.

UNIT – V

Electrochemistry

5.1 Electrolytic conductance Debye-Huckel-Onsager theory – Debye Falkenhagen and Wien effect. Electrode – electrolyte equilibrium, electrode potential – concentration cells – liquid

junction potentials. Processes at Electrodes- The rate of charge transfer - current density – Butler – Volmer Equation – Tafel equation – Electrical double layer potential – Theory of multiple layers at electrode – electrolyte interfaces – Double layer capacity – Electrokinetic phenomena, Applications: Fuel cells and power storage.

Surface Phenomena

5.2 Surface Phenomena: Gibbs adsorption isotherm – solid- liquid interfaces – contact angle and wetting – solid-gas interface – physisorption and chemisorption – Langmuir, BET isotherms – surface area determination. Kinetics of surface reactions involving adsorbed species – Langmuir-Hinshelwood mechanism, Langmuir – Rideal mechanism – Rideal –Eley mechanism. Some interfacial aspects on Micelles, Reverse micelles, Micro emulsions and Membranes.

References:

1. F. Albert Cotton, Chemical Applications of Group Theory, Third Edition John Wiley & Sons, Singapore 2003
2. Robert L. Carter, Molecular Symmetry and Group Theory John Wiley and Sons, Inc.,New York, 1998.
3. A.K. Chandra, Introductory Quantum Chemistry, 4th ed,. Tata McGraw Hill 1994.
4. I.N. Levine, Quantum Chemistry, 5th edn, Prentice Hall, 2000.
5. P.W. Atkins, Molecular Quantum mechanics, Clarendon Press New York, 1973.
6. R.K. Prasad, Quantum Chemistry,New Age International Publishers, New Delhi, 1997.
7. K.J. Laidler, Chemical Kinetics, 2nd ed., Tata McGraw Hill, 1975.
8. D. A. McQuarrie and J. D. Simon, Physical chemistry, A Molecular Approach, Viva Books
9. J. N. Gurtu& A. Gurthu, Advanced Physical Chemistry, PragathiPrakashan, Meerut , 2006.
10. P.W. Atkins,Physical Chemistry, 7th edn, Oxford University press, 2002.
11. D. A. McQuarrie and D. Simon, Physical chemistry, A Molecular Approach ,Viva Books Pvt. Ltd,
12. J. Rajaram and J.C. Kuriacose, Thermodynamics for Students of Chemistry – Classical, Statistical and Irreversible, ShobhanLalNagin, New Delhi, 1981.
13. R.P.Wayne, Photochemistry, Butterworths,London(1970).
14. K.K.Rohatgi-Mukerjee, Fundamentals of Photochemistry , Wiley Eastern Ltd.,(1986)
15. G.Hughes, Radiation Chemistry, Oxford University Press (1973)
16. S.Glasstone, Introduction to Electrochemistry, Affiliated East-West Press, 1968.
17. J.Albery, Electrode Kinetics, Clarendon Press, Oxford Chemical Series, 1979.
18. G.W.Castellan, Physical Chemistry, Narosa, New Delhi, 1986.
19. I. M. Klotz and P.M.Rosenberg, Chemical Thermodynamics: Basic Theory and Methods, 3 edn. W.A. Benjamin, New York, 1974.
20. J.I. Steinfeld, J.S.Francisco and W.L. Hase, Chemical Kinetics and Dynamics, 2nd edn, Prentice Hall, New Jersey, 1999.
21. R.K.Dave, Chemical Kinetics, Campus Books, 2000.

MAJOR PAPER IV

Practical I Organic Chemistry

I Qualitative Analysis of an organic mixture containing two components. Pilot separation , bulk separation , analysis , derivation.

II Preparation of Organic compounds.(Single stage). (a) methyl –m- nitrobenzoate from methylbenzoate (nitration) (b) glucose pentaacetate from glucose (acetylation) (c) resorcetophenone from resorcinol (acetylation) (d) benzophenone oxime from benzophenone (addition) (e) Phenyl-azo-2-napthol from aniline (diazotization)

MAJOR PAPER V –

Inorganic Chemistry Practical II

1. Semi-micro qualitative analysis of a mixture containing two common and two rare cations.
2. Estimation of Copper, Ferric, Nickel, Chromium and Manganese using photoelectric colorimeter

MAJOR PAPER VI - PHYSICAL METHODS IN CHEMISTRY

UNIT – I

Theoretical principles of Molecular Spectroscopy:

1.1.Microwave spectroscopy – rotational spectra of diatomic molecules, rigid and nonrigid rotors, - Intensity of spectral lines, - Effects of isotopic substitution – Microwave spectra of polyatomic molecules – Linear and symmetric top molecules,

1.2.Infrared spectra – diatomic molecules, simple harmonic and anharmonic oscillators, - diatomic vibrating rotator, rotation-vibration spectrum of carbon monoxide, water - Instrumentation, Sampling techniques, factors influencing group frequencies – Both internal and external – quantitative studies. Hydrogen bonding – (intermolecular and intramolecular).

1.3 Raman spectra – Rotational Raman spectra of linear and symmetric top molecules – Vibrational Raman spectra, Rotational fine structure.

1.4 Electronic spectra of diatomic molecules, - Vibrational coarse structure – Intensity of vibrational lines in electronic spectra – Fortratdigram.

UNIT – II

Advanced Spectroscopy :**NMR**

2.1. ^{1}H NMR Spectroscopy – Multiplicity – Coupling constant – First order and second order proton, Spin - spin splitting – Dependence of J on dihedral angle – Vicinal and geminal coupling constants – Karplus equation – long range coupling constants, Influence of stereochemical factors on chemical shift of protons. Simplification of complex spectra – Double resonance techniques, shifts reagents. Chemical spin decoupling of rapidly exchangable protons (OH, SH, COOCH, NH, NH_2), an elementary treatment of NOE phenomenon.^{13}C NMR Spectroscopy – Basic theory of FT – NMR, Relaxation – Broad band decoupling. Off resonance decoupling and chemical shifts of common functional groups, DEPT spectra. Identification of small compounds based on NMR data. 2D Techniques: ^{1}H – ^{1}H COSY, ^{1}H – ^{13}C COSY – HMBC and NOESY.

2.2. Applications to inorganic compounds – Spin spin coupling involving different nuclei (^{1}H, ^{19}F, ^{31}P, ^{13}C) Effect of quadrupolar nuclei (^{2}H, ^{10}B, ^{11}B) on the ^{1}H NMR spectra, Satellite spectra. Systems with chemical exchange - evaluation of thermodynamic parameters in simple systems – study of fluxional behavior of molecules – an elementary treatment of second order spectra – examples – NMR of paramagnetic molecules – isotropic shifts contact and pseudo-contact interactions – Lanthanide shift reagents.

UNIT – III

Advanced Spectroscopy: UV –Vis

3.1 UV-Visible Spectroscopy : Introduction - Instrumentation, Sampling techniques - Woodward–Fieser and Scott rules for conjucateddienes and polymers, ketones, aldehydes, ∝,β-unsaturated acids, esters, nitriles, and amides. Differentiation of geometrical isomers and positional isomers – Disubstituted benzene derivatives - Study of steric effect in aromaticity.

Electronic Spectroscopy

3.2 Microstates, terms and energy levels 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 10Dq and β for octahedral complexes of cobalt and nickel – applications to simple coordination compounds – charge transfer spectra – electronic spectra of $[Ru(bipy)_3]^{2+}$.

UNIT – IV

Electron spin resonance spectroscopy:

4.1 Basic principles – comparison between esr and nmr spectra – hyperfine splitting – factors affecting the magnitude of g – values – calculation of unpaired electron density on an atom in a delocalized system – applications to organic free radicals. Spin densities and McConnell relationship – Factors affecting the magnitude of g and A tensors in metal species - Zero-field splitting and Kramers degeneracy – Spectra of VO(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes – Applications of EPR to a few biological molecules containing Cu(II) and Fe(III) ions.

Optical rotatory dispersion and circular dichroism :

4.2 Introduction to theory and terminology – cotton effect – ORD curves – axial haloketone rule and its applications – octant rule – its applications – applications of ORD to determine absolute configuration of monocyclic ketones – comparision between ORD and CD – their inter relationships.

UNIT – V

Mass Spectrometry

5.1 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.

Mossbauer Spectroscopy

5.2 Isomer shifts – Magnetic interactions – Mossbauer emission spectroscopy – applications to iron and tin compounds.

NQR spectroscopy

5.3 Characteristics of quadrupolar nucleus – effects of field gradient and magnetic field upon quadrupolar energy levels – NQR transitions – applications of NQR spectroscopy.

5.4 X-ray diffraction and Neutron diffraction : X-ray diffraction by single crystal – Space groups –Systematic absences in X-ray data and identification of lattice types , glide planes and screw axes.X-ray intensities, structure factor and its relation to intensity and electron density , phase problem. Structure solution by Heavy atom method and direct method.Determination of absolute configuration of molecules.Scattering intensity vs Scattering angle, wierl equation, measurement technique, elucidation of structure of simple gas phase molecules.magnetic scattering, measurement techniques. Elucidation of structure of magnetically ordered unit cell.

References:

1. C.N. Banwell, Fundamentals of molecular Spectroscopy, 3rd ed., TMH, New Delhi, 1983.
2. B.P. Straughan and S.WalkerSpectroscopy Vol.3, Chapman Hall London, 1976.
3. G.M. Barrow, Introduction to Molecular Spectroscopy, McGraw Hill, New York, 1964.
4. P.M. Silverstein, F. X. Wester, Spectroscopic Identification of Organic Compounds, 6th ed., Wiley 1998.
5. W. Kemp, Organic Spectroscopy, 3rd Ed., MacMillon, 1994.
6. J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall, 1965.
7. Y.R. Sharma , Elementary Organic Spectroscopy – Principles and Chemical applications, S.Chand,1992.
8. P.S.Kalsi, Spectroscopy of Organic Compounds.
9. Clegg,W., Crystal structure determination, Oxford University press , New York,1998.
10. Stout,G.H., Jensen , L.H. X-ray structure determination : A practical guide , John wiley& sons Publication: New York,1989
11. Glusker, J.P., Trueblood,K.N. Crystal structure analysis: A primer., Oxford university press, New York, 1972.
12. R.S. Drago, Physical Methods in Inorganic Chemistry, 3rd Ed., Wiley Eastern Company .
13. R.S.Drago, Physical Methods in Chemistry, W.B. Saunders Company, Philadelphia, London.
14. F.A. Cotton and G.Wilkinson,Advanced Inorganic Chemistry, 3rd ed., Wiley-Eastern Company, New Delhi 1990.
15. P.J. Wheatley, The Determination of Molecular Structure, .
16. Lewis and Wilkins, Modern Coordination Chemistry,.
17. E.A.V.Ebsworth, Structural Methods in Inorganic Chemistry, 3rd ed., ELBS, Great Britain, 1987.

MAJOR PAPER VII - ANALYTICAL CHEMISTRY

UNIT 1

Instrumental methods of Analysis:

1.1 Principles and Applications of Extended X-ray absorption fine structure (EXAFS) – Surface extended X-ray absorption (SEXAFS) – Atomic Absorption Spectroscopy (AAS) - Flame Emission Spectroscopy (FES).Turbidimetry – Theory and Applications.

UNIT II

Data and Error Analysis :

2.1 Various types of Error – Accuracy, precision, significant figures – Frequency distributions, the binomial distribution, the Poisson distribution and normal distribution – Describing data, population and sample, mean, variance, standard deviation, way of quoting uncertainty, robust estimators, repeatability and reproducibility of measurements – Hypothesis testing, levels of confidence and significance, test for an outlier, testing variances, means t-Test, Paired t-Test –

2.2 Analysis of variance (ANOVA) – Correlation and Regression – Curve fitting , Fitting of linear equations, simple linear cases, weighted linear case, analysis of residuals – General polynomial equation fitting , linearizing transformations, exponential function fit – r and its abuse – multiple linear regression analysis, elementary aspects.

UNIT III

Chromatography:

3.1 Solvent extraction – principles of ion exchange, paper, thin layer and column Chromatography techniques – Columns, adsorbents, methods, Rf values, McReynold's constants and their uses – HPTLC, HPLC techniques – Adsorbents, columns, detection methods, estimations, preparative column – GC-MS techniques: methods, principles and uses.

UNIT IV

Thermo analytical methods:

4.1 Principles and applications of Thermogravimetry Analysis (TGA) – Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC). Thermometric titrations.

UNIT V

Electroanalytical techniques and Fluorescence spectroscopy:

5.1 Electrochemical sensors, ion sensitive electrodes, glass – membrane electrodes, solid liquid membrane electrodes – ion-selective field effect transistors (ISFETs) – Sensors for the analysis of gases in solution – Amperometric gas sensors – Principles- Apparatus – techniques – applications.Introduction, linears sweep voltammetry and cyclic voltammetry, Experimental setup, simple electrotransfer reaction, electron transfer reaction followed by chemical reaction and solutions, limiting experimental factors – potential step and current step method, chronoamperometry, chronocoulometry, chronopotentiometry – polarography – methods for determination of number of electrons.

5.2 Basic aspects of synchronous fluorescence spectroscopy – Spectral hole burning – flow cytometry – Instrumentation on fluorescence ratio – Fluorimeters (quantization).

References:

1. D.B.Hibbert and J.J. Gooding, Data Analysis for chemistry, Oxford University Press, 2006
2. J.Topping , Errors of Observation and their treatment, Fourth Edn., Chapman Hall, London, 1984
3. R. Stock and C. B. F. Rice, Chromatographic Methods, Chapman and Hall, New York.
4. V.K.Srivastava& K.K. Srivastava, Introduction to Chromatography, S. Chand & Co., New Delhi, 2nd ed,1981.
5. Willard, Merrit, Dean and Settle, Instrumental methods of Analysis CBS Publishers and Distributors, 6th ed., 1986.
6. Skoog, D. A., West, D. M., Holler, F. J., Fundamentals of Analytical Chemistry, 7th edition, Harcourt College Publishers, Singapore. (Pages 523 - 665).
7. A.Sharma, S.G. Schulman, Introduction to Fluoresceence Spectroscopy, Wiley-Interscience. New York,1999
8. C.N.Banwell and E.M.McCash, Fundamentals of Molecular spectroscopy, 4thed., Tata McGraw-Hill, New Delhi, 1994.
9. Vogel, A. I., Text book of Quantitative Inorganic Analysis, ELBS.
10. Daniel C Harris, Quantitative Chemical Analysis, 4th ed., W. H. Freeman and Company, New York, 1995.
11. S.C.Gupta, Fundamentals of Statistics,6th ed., Himalaya Publ. House, Delhi, 2006.
12. Organic electro chemistry by Henning Lund &Ole Hammerich, 4thedition,Publisher: Marcel Dekker, Inc, New York.

MAJOR PAER VIII

GREEN CHEMISTRY and NANO SCIENCE

UNIT-I **Introduction to green chemistry**: Green chemistry-relevance and goals, Anastas' twelve principles of green chemistry - Tools of green chemistry: alternative starting materials, reagents, catalysts, solvents and processes with suitable examples.

UNIT-II **Microwave mediated organic synthesis (MAOS), Ionic liquids**

2.1 Microwave activation – advantage of microwave exposure – specific effects of microwave – solid supports reactions _ Functional group transformations – condensations reactions – oxidations – reductions reactions – multi-component reactions.

2.2 Ionic liquids and PTC Introduction – synthesis of ionic liquids – physical properties – applications in alkylation – hydroformylations – expoxidations – synthesis of ethers – Friedel-craft reactions – Diels-Alder reactions – Knoevengal condensations – Wittig reactions – Phase transfer catalyst - Synthesis – applications.

UNIT III **Supported catalysts and bio-catalysts for Green chemistry Tools of Green Chemistry**

3.1 Introduction – the concept of atom ecomomy – supported metal catalysts — the use of Biocatalysts for green chemistry -— fine chemicals by microbial fermentations — Baker's yeast mediated biotransformations – Bio-catalyst mediated Baeyer-Villiger reactions.

3.2 Tools of Green Chemistry Alternative synthesis, reagents and reaction conditions: A photochemical alternative to Friedel-crafts reactions - Dimethyl carbonate as a methylating agent – the design and applications of green oxidants – super critical carbon dioxide for synthetic chemistry.

UNIT IV: **Nanomaterials – An Introduction & Synthetic** methods Definition of nanodimensional materials - Historical milestones - unique properties due to nanosize,Quantum dots, Classification of Nanomaterials .General methods of synthesis of nanomaterials – Hydrothermal synthesis,Solvothermal synthesis,Microwave irradiation, sol – gel and Precipitation technologies, Combustion Flame-Chemical Vapor Condensation Process, gas Phase Condensation Synthesis,Reverse Micelle Synthesis, Polymer – Mediated Synthesis, Protein Microtube – Mediated SynthesisSynthesis of Nanomaterials using microorganisms and other biological agents, Sonochemical Synthesis, Hydrodynamic Cavitation. Inorganic nanomaterials – Typical examples –nano TiO2 / ZnO/CdO/CdS. Reactions in Nanospace / Nanoconfinement / Nanocapsules- Cavitands, Cucurbiturils, Zeolites, M.O.Fs, Porous silicon, Nanocatalysis.

UNIT –V **Carbon Clusters and Nanostructures** Nature of carbon bond − New carbon structures − Carbon clusters: Discovery of C60 − Alkali doped C60 − Superconductivity in C60 − Larger and smaller fullerenes. Carbon nanotubes: Synthesis − Single walled carbon nanotubes − Structure and characterization − Mechanism of formation − Chemically modified carbon nanotubes − Doping − Functionalizing nanotubes −Application of carbon nanotubes. Nanowires

Nanotechnology and nanodevices: DNA as a nanomaterial, DNA – knots and junctions, DNA – nanomechanical device designed by Seeman. Force measurements in simple protein molecules and polymerase – DNA complexes. Molecular recognition and DNA based sensor. Protein nano array, nanopipettes, molecular diodes, self assembled nano transistors, nanoparticle mediated transfection.

References: 1. Green Chemistry – Environmentally benign reactions – V. K. Ahluwalia. Ane Books India (Publisher). (2006).

2. Green Chemistry – Designing Chemistry for the Environment – edited by Paul T. Anastas & Tracy C. Williamson. Second Edition, (1998).

3. Green Chemistry – Frontiers in benign chemical synthesis and processes- edited by Paul T. Anastas & Tracy C. Williamson. Oxford University Press, (1998).

4. Green Chemistry – Environment friendly alternatives- edited by Rashmi Sanghi & M. M. Srivastava, Narora Publishing House, (2003).

5. C.N.R. Rao, A. Muller, A.K. Cheetam (Eds), The Chemistry of Nanomaterials, Vol.1, 2, Wiley – VCH, Weinheim, 2004.

6. C.P. Poole, Jr: F.J. Owens, Introduction to Nanotechnology Wiley Interscience, New Jersey, 2003

7. Kenneth J. Klabunde (Ed), Nanoscale materials in Chemistry, Wiley- Interscience, New York, 2001.

8. T. Pradeep, Nano: The Essentials in understanding nanoscience and nanotechnology, Tata McGraw Hill, New Delhi, 2007.

9. H. Fujita (Ed.), Micromachines as tools in nanotechnology, Springer- Verlag, Berlin, 2003.

10. Bengt Nolting, Methods in modern biophysics, Springer-Verlarg, Berlin, First Indian Reprint, 2004. (Pages 102-146 for Unit II and 147 – 163 for Unit V)

11. H. Gleiter , Nanostructured Materials: Basic Concepts, Microstructure and Properties

12. W. Kain and B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, John-Wiley R Sons, New York.

13. T. Tang and p. Sheng (Eds), Nano Science and Technology Novel Structures and Phenomena, Taylor & Francis, New York, 2004. 10. A. Nabok, Organic and Inorganic Nanostructures, Artech House, Boston, 2005. 11. Edward A. Rietman, Molecular engineering of Nanosystems, Springer- Verlag, New York, 2001.

Major Paper IX - PHYSICAL CHEMISTRY PRACTICAL (6 hours)

NON ELECTRICALS

Any six experiments (to be decided by the course teacher) out of the following experiments.

1. Kinetics- Acid hydrolysis of ester- Comparison of strengths of acids.
2. Kinetics- acid hydrolysis of Ester- Determination of energy of activation (Ea).
3. Kinetics- Persulphate- Iodine reaction- Determination of order, effective of ionic strength on rate constant.
4. Determination of molecular weight of substance by Transition Temperature method.
5. Determination of molecular weight of substances by Rast method.
6. Determination of Critical Solution Temperature (CST) of phenol- water system and effect of impurity on CST.
7. Study of phase diagram of two components forming a simple eutectic.
8. Determination of molecular weight of substances by cryoscopy.
9. Adsorption- Oxalic acid/Acetic acid on charcoal using freundlich isotherm.

ELECTRICALS

Any eight experiments (to be decided by the course teacher) out of the following experiments.

1. Conductometry- Acid- alkali titrations.
2. Conductometry- Precipitation titrations.
3. Conductometry- Determination of dissociation constant of weak acids.
4. Conductometry- solubility product of sparingly soluble silver salts.
5. Verification of Onsager equation- conductivity method.
6. Potentiometric titrations- Acid alkali titrations.
7. Potentiometric titrations- Precipitation titrations.
8. Potentiometric titrations- Redox titrations.
9. Potentiometry- Determination of dissociation constant of weak acids.
10. Potentiometry- Determination of solubility of silver salts.

Reference books (Practical I and II)

1. J.B.Yadav, " Advanced Practical Physical chemistry", 20th edn. GOEL publishing House, Krishna Pakashan Media Ltd., (2001).
2. Findlay's "Practical Physical Chemistry" Revised and edited by B.P. Levitt 9th ed., Longman, London, 1985.
3. J.N. Gurtu and R.Kapoor, "Advanced Experimental chemistry", Vol.I. Chand & Co., Ltd, New Delhi.

MAJOR PAPER X

Practical IV (Analytical Chemistry)

I **Quantitative analysis of organic compounds** Estimation of phenol, aniline, glucose.

II Preparation of organic compounds (Double stage)

a. p-bromo acetanilide from aniline (acetylation and bromination).

b. 1,3,5-tribromobenzene from aniline (bromination, diazotization and hydrolysation). d. p-nitroaniline from acetanilide (nitration and hydrolysis).

c. benzillic acid from benzoin (rearrangement).

d. p-amino benzoic acid from p-nitro toluene (oxidation and reduction).

e. benzanilide from benzophenone (rearrangement).

f. p-bromoaniline from acetanilide (bromination and hydrolysis).

g. m-nitroaniline from nitrobenzene (nitration and reduction).

III Titrimetry and Gravimetry

A mixture of solution(s) should be given for estimation

a. Cu (V) and Ni (G)
b. Cu (V) and Zn
c. (G) Fe (V) and Zn (G)
d. Fe (V) and Ni (G)
e. Zn (V) and Cu (G)

IV **Preparation of the following compounds** a. Tetramminecopper (II) sulphate. b. Potassium trioxalatochromate (III). c. Potassium trioxalatoaluminate (III). d. Trithioureacopper (I) chloride. e. Trithioureacopper (I) sulphate.

In the University Practical Examinations for students either I and II OR III and IV ,may be given.

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