UNIVERSITY OF CALICUT

(Abstract)

MSc programme in Polymer Chemistry under Credit Semester System (PG)-Course structure and Syllabus of Ist and IInd Semesters-approved –implemented-with effect from 2010 admission onwards-Orders issued

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GENERAL & ACADEMIC BRANCH-IV 'J' SECTION

No. GA IV/J2/8619/07 Dated, Calicut University PO, 24.07.2010

Read:1. U.O.No. GAIV/J1/1373/08 dated, 23.07.2010.

2. Item no. 1 of the minutes of the meeting of the Board of Studies in Polymer Chemistry held on 16.06.2010

O R D E R

As per University Order read as first, Credit Semester System was implemented to the PG programmes in affiliated Arts and Science Colleges and Self Financing Centres of the University with effect from 2010 admission onwards.

The Board of Studies in Polymer Chemistry,vide paper read as second, decided to restructure the syllabus of MSc programme in Polymer Chemistry as Credit Semester System (CUCSS-PG)-and finalized the syllabus of CUCSS-PG-2010 of Ist and IInd Semesters of MSc Polymer Chemistry, with Course Structure.

The Vice Chancellor approved the minutes subject to ratification by the Academic Council.

Sanction has therefore been accorded for implementing the Course Structure and Syllabus of Ist and IInd Semesters of MSc programme in Polymer Chemistry

with effect from 2010 admission.

Orders are issued accordingly. Scheme and Syllabus appended.

Sd/-

` **DEPUTY REGISTRAR (G & A-IV)**

For REGISTRAR

To

The Principals of affiliated Colleges offering MSc programme in Polymer Chemistry

Copy to:

PS to V. C
PA to Registrar
Chairman,B/SPolymerChemistry/CE/EX/DRIII/DR,PG/EGI/Enquiry/System Administrator with a request to upload in the University website/Information Centres/G&A I `F``G`Sns/GAII,III

Forwarded/By Order

Sd/-
SECTION OFFICER.

MSc Programme in Polymer Chemistry under CUCSS(PG) 2010-Course Structure

Semester I:

Exam: 3 hours(Internal 25 %; External 75%)

Sl No.	Code No	Course Title	Hrs/week	Credits
1.	PC1 CO1	Inorganic Chemistry-I	4	4
2.	PC1 CO2	Organic Chemistry I	4	4
3.	PC1 CO3	Theoretical ChemistryI	4	4
4.	PC1 PO1	Inorganic Chemistry(Practicals)	4	-
5.	PC1 PO2	Organic Chemistry(Practicals)	4	-
6.	PC1 PO3	Physical Chemistry(Practicals)	5	-
		Total	**25**	**12**

Semester II

Exam: 3 hours(Internal 25 %; External 75%)

Sl. No.	**Code No**	**Course Title**	**Hrs/Week**	**Credits**
1.	PC2 CO4	Organic Chemistry-II	4	4
2.	PC2 CO5	Physical Chemistry-I	4	4
3.	PC2 CO6	Theoretical Chemistry-II	4	4
4.	PC2 PO1	Inorganic Chemistry(Practicals)	4	4
5.	PC2 PO2	Organic Chemistry(Practicals)	4	4
6.	PC2 PO3	Physical Chemistry(Practicals)	5	4
		Total	**25**	**24**

SYLLABUS– THEORY COURSES

UNIVERSITY OF CALICUT

M. Sc. POLYMER CHEMISTRY- SEMESTER I

PC1 C 01 *INORGANIC CHEMISTRY- I* Credits: 4

MODULE I (8 h)

Acid base theories - strength of acids and bases, solvent leveling effect, hard and soft acids and bases, super acids. Chemistry of non-aqueous solvents- liquid NH_3, SO_2, H_2SO_4 and HF. Heterogeneous acid- base reactions- surface acidity, solid- and molten acids in industrial processes.

MODULE II (8 h)

Synthesis, structure, reactions and bonding in boron hydrides, carboranes, metalloboranes and borazines. Synthesis, structure and applications of silicones.

Phosphorus- nitrogen, phosphorus- sulphur and sulphur- nitrogen ring and chain compounds- synthesis, structure, bonding and applications.

References (MODULE I and II)

1. D. F. Shriver, P. W. Atkins, C. H. Langford, *Inorganic Chemistry*, ELBS, 1990.
2. J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic chemistry, Principles, Structure and Reactivity,* Pearson Education, 1990.
3. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry,* 5th Edn., John Wiley and sons, 1988.

MODULE III (20 h)

Crystalline solids, crystal systems, Bravais lattices, crystal symmetry, symmetry elements, transitional and rotational transition symmetry, point groups, space groups, indices, Braggs law, X- ray diffraction.

Close packing, factors affecting crystal structure, radius ratio, coordination number, lattice energy, Born- Haber cycle, structure of AX, AX_2, AO_2, AO_3, A_2, O_3, ABO_3, AB_2O_4 type crystal defects, non- stoichiometry, sharing of polyhedra, structure of silicates, aluminosilicates, molecular sieves, polyoxyanions.

Electronic properties of solids, band theory, k- space, Brillouin zones, band structure. Fermi level, Fermi energy, density of states, metals, insulators, semiconductors, types and structure of semiconductors, super conductors.

Alloys, classification, intermetallic compounds, Hume Rothery rules.

Solid state reactions, solid-solid, solid-gas and solid-liquid reactions, kinetics, thermal analysis, borides, carbides, silicides, preparation and properties, preparative methods in solid state chemistry.

References

1. A. R. West, *Solid State Chemistry and its Applications*, John- Wiley, Chilchester, 1984.
2. F. D. Bloss, *Crystallography and Crystal Chemistry*, Holt Reinhart, Winston, New York, 1971.
3. A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1954.
4. A. K. Galway, *Chemistry of Solids*, Chapman- Hall, London, 1967.
5. M. F. C. Ladd, *Structure and Bonding in Solid State Chemistry*, Elliz Harwood, Chichester, 1979.

6. P. A. Cox, *The Electronic Structure and Chemistry of Solids*, Oxford University Press.
7. L. V. Azaroff, *Introduction to Solids*. Mc Graw Hill, 1960.

MODULE IV Nuclear *Chemistry* (10 h)

Radioactive decay and equilibrium- nuclear reactions- Q value, types of reactions- chemical effects of nuclear transformation, γ- recoil- effects of radiation on materials- fission and fusion, fusion products and fusion yields- Radioactive techniques, tracer techniques- neutron activation analysis- counting techniques such as G. M.-, ionization- and proportional counter.

References

1. J. B. Rajam, *Atomic Physics*, S. Chand and Co. Pvt. Ltd., 1974.
2. J. W. T. Spinks, R. J. Woods, *An Introduction to Radiation Chemistry*, John Wiley and Sons, 1964.
3. H. J. Anikar, *Essentials of Nuclear Chemistry*, 4th Edn., New Age International, 1995.
4. S. Glasston, S*ource Book on Atomic Energy*, 3rd Edn., East- West Press Pvt. Ltd., 1967.
5. Friedlander, J. W. Kennedy, *Introduction to Radiochemistry*, John Wiley and Sons, 1981.
6. Friedlander, J. W. Kennedy, J. M. Miller, *Nuclear and Radiochemistry*, 3rd Edn., John Wiley and Sons, 1981.

MODULE V (6 h)

Errors and treatment of analytical data, standard deviation, least square analysis, statistical treatment of data sets, students tests, confidence limit, Q test.

Theory of acid- base-, redox-, adsorption- and complexometric indicators, titrations in non-aqueous solvents.

References

1. G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denny, *Vogel's Text book of Quantitative Chemical Analysis*, 5th Edn., ELBS, 1989.
2. Skoog, West, Holler, *Fundamentals of Analytical Chemistry*, 8th Edn., Thomson and Brooks, 2004.

MODULE VI (10 h)

Coordination chemistry formation and stability of complexes, chelate and macrocyclic effect. The crystal field and ligand field theories, orbital splitting in octahedral, tetrahedral and square planar fields, spectrochemical- and nephelauxetic series, Jahn-Teller effect. M.O. theory- composition of ligand group orbitats. M.O. diagrams of complexes with and without π- bonding.

Standard reduction potentials and their diagrammatic representation. Ellingham diagram, Latimer and Frost diagram. Pourbaix diagram.

MODULE VII (10 h)

Lanthanides and actinides- stable oxidation states, the lanthanide and actinide contraction, the f orbitals, lanthanide chelates, separation of lanthanides and actinides, transactinide elements.

References (MODULE VI and VII)

1. D. F. Shriver, P. W. Atkins, C.H. Langford, *Inorganic Chemistry*, ELBS, 1990.
2. J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry, Principles, Structure and Reactivity*, Pearson Education, 1990.

3. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry,* 5th Edn., John Wiley and Sons, 1988.

MODULE WISE WEIGHTAGE FOR QUESTIONS

MODULE	WEIGHTAGE
I	5
II	5
III	14
IV	7
V	5
VI	7
VII	7

PC1 C02 *ORGANIC CHEMISTRY I* Credits: 4

MODULE I (10 h)

Delocalised chemical bonding, Electron Delocalization, Resonance and Aromaticity: Qualitative application of Huckel MO theory and perturbation theory to systems containing delocalized electrons. Delocalized electrons and Resonance, Resonance hybrid and resonance energy. Criteria for Aromaticity and Antiaromaticity, MO description of Aromaticity and Antiaromaticity. Homoaromaticity, Mobius twist and Aromaticity. Aromaticity of Annuelens and heteroannulenes, Fullerines, and fused ring systems. Stability of benzylic cations and radicals, Effect of delocalized electrons on pKa.

Hydrogen Bonding:
Inter- and intramolecular hydrogen bonding. Range of the energy of hydrogen bonding. Volatility, acidity, basicity and stability of hydrates of carbonyl compounds. Stabilization of hydrates of glyoxal and chloral, and ninhydrin. Comparison of boiling points of ethanol and dimethyl ether (two isomeric compounds). High volatility of *o*-nitrophenol and salicylaldehyde compared to their *meta*- and *para*- isomers. High acid strength of maleic acid compared to fumaric acid.

MODULE II (10 h)

Basic Concepts in the Study of Organic Reaction Mechanisms
Application of Experimental criteria to mechanistic studies, Thermodynamic and kinetic data, Curtius- Hammet principles, Kinetic versus thermodynamic control. Acidity constant, Hammet acidity function. Reactive intermediates and their characterization. Isotope effect (labeling experiments), stereochemical correlations.

Structure and reactivity, Transition state theory, Potential energy vs Reaction co-ordinate curve, Substituent effects (inductive, mesomeric, inductomeric, electomeric and field effects) on reactivity. Qualitative study of substitution effects changing with mechanism in $S_N1 - S_N2$ reactions. Semiquantitative study of substituent effects on the acidity of carboxylic acids. Quantitative correlation of substituent effects on reactivity. Linear free energy relationships. Hammet and Taft equation for polar effects and Taft's steric substituent constant for steric effect.

References (MODULE I and II)

1. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and sons, 1992.

2. T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper Collins, 1987.
3. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.
4. R. A. Y. Jones, *Physical and Mechanistic Organic Chemistry*, Cambridge University Press, 1979.

MODULE III *Isomerism* (10 h)

Dissymmetry, asymmetry and chirality- simple and alternating axis of symmetry- Conditions for optical activity, Isotopic asymmetric variation and specific rotation of the same compound in sign and magnitude under different conditions. Relative and absolute configurations. Sequence rule– R and S notations in cyclic and acyclic compounds.

Optical isomerism of compounds containing one or more asymmetric carbon atoms, Enantiotopic, Homotopic, Diastereotopic hydrogen atoms, Prochiral centre.

Optical isomerism in Biphenyls: Structure of biphenyls in solid, liquid and vapour states. Structure of substituted biphenyls. Number of substituents and their size in relation to the stability of optical isomers. R and S notation. Atropisomers. Restricted rotation in biphenyls – Molecular overcrowding. Chirality due to folding of helical structures.

Conditions for optical activity in allenes and spiro compounds- R and S notation.

Optical isomerism of nitrogen and sulphur compounds- naming- stereochemistry. Conditions for optical activity, R and S notation.

Geometrical isomerism – E and Z notation of compounds with one and more double bonds in acyclic systems. Methods of determination of the configuration of geometrical isomers in acyclic and cyclic systems, interconversion of geometrical isomers.

Stereochemistry of aldoximes and ketoximes – naming – isomerism – methods of determining configurations of aldoximes and ketoximes.

References

1. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and Sons, 1992.
2. Nasipuri, *Stereochemistry of Organic Compounds*, 2nd Edn., New Age International.
3. Kalsi, *Stereochemistry of Organic Compounds*, Wiley Eastern.

Suggested Reading

E. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, John Wiley, 1994.

MODULE IV Conformational Analysis (16 h)

Conformation and configuration. Internal factors affecting the conformation – dipolar interaction, bond opposition strain, bond angle strain, intramolecular hydrogen bonding. Sawhorse and Newman projections. Eclipsed, gauche and staggered conformations. Conformations of acyclic compounds – Ethane, *n*-butane, ethylene dihalide, glycols, chlorohydrins, *meso* and *dl*-tartaric acids, acetaldehyde and acetone.

Conformation of cyclohexane, conformations of mono- and di- substituted cyclohexanes, conformation of decalins, and 2-halocyclohexanones. Anchoring group.

Effect of conformation on reactivity – Debromination of *dl* and *meso*-2,3-dibromobutane with KI, dehydrogenation of stilbene dihalides (*dl* and *meso*) and erythro- and threo-1-bromo-1,2-diphenylpropane.

Effect of conformation on the course and rate of reactions – S_N1 and S_N2 reactions of axial and equatorial substituents. E1 and E2 eliminations of

(i) 4-t-Butylcyclohexyl tosylates (*cis* and *trans*)
(ii) 2-Phenylcyclohexanols
(iii) Menthyl and *neo*menthyl chlorides, and benzene hexachlorides.

Esterification of axial and equatorial alcohols and acids- their hydrolysis.

ORD and CD. Plane and single CE curves- uses. Axial haloketone rule and its application. Octant rule- Determination of conformation and configuration of 3-Methylcyclohexanone- ORD curves of *cis*- and *trans*- decalones.

References

1. Nasipuri, *Stereochemistry of Organic Compounds*, 2nd Edn., New Age International.
2. Eliel, Allinger, Anggal, Morrison, *Conformational analysis*, Wiley International.
3. I. L. Finar, *Organic Chemistry, Vol. II*, 5th Edn., ELBS, 1975.

MODULE V *Reactions of Carbon-Heteromultiple Bonds* (6 h)

Addition to carbon-oxygen multiple bond: Addition of water, alcohols, amines and hydrazine. Aldol, Claisen, Dieckmann, and Stobbe condensation. Darzen, Knoevenagel, Wittig, Mannich and Prins reactions. MPV reduction and Oppenaur oxidation. Cram's rule. Hydrolysis, alcoholysis and reduction of nitriles. Ritter reaction and Thorpe condensation. Clemmenson and Wolf- Kishner reduction.

References

1. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and sons, 1992.
2. Morrison, Boyd, *Organic Chemistry*, Prentice Hall.
3. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.

MODULE VI (14 h)

i) Electrophilic and Nucleophilic substitution in aromatic systems. (7 h)

Friedel-Crafts alkylation and acylation. Orientation in monosubstituted benzene. *Ortho-para* ratio with reference to electronegativity and steric factors.

Nucleophilic aromatic substitution, Aromatic diazonium ions as synthetic intermediates. Nucleophilic substitution as illustrated by the hydrolysis of 2,4-dinitro-chlorobenzene. Amination of pyridine by sodamide (Chichibabin reaction). Aryne mechanism. Examples, Detection of benzyne intermediate, orientation of addition. Structure of benzyne.

ii) ***Nucleophilic Substitution at Saturated Carbon and Elimination Reactions*** (7 h)

The four types of nucleophilic substitution reactions based on charges on the nucleophile and leaving group. Nucelophilicity and size of nucleophile. Effect of changing the basic nature of the leaving group. Effect of solvent polarity - solvent effects on nucleophilic substitution of different charge types due to Ingold Y-value and Dimroth parameter.

Stereochemistry of S_N1 and S_N2 reactions. Reactions of epoxides and quaternary ammonium compounds. Neighbouring group participation- participation of carboxylate ion, halogen, hydroxyl group, acetoxy group, phenyl group and π bond.

Elimination at Bridgehead carbon - Bredt's rule. *Cis* elimination - pyrolysis of esters and Chugev reaction. E1cB mechanism

References

1. J. B. Hendrickson, D. J. Cram, G. S. Hammond, *Organic Chemistry*, McGraw Hill International Book Company, 1981.
2. Morrison, Boyd, *Organic Chemistry*, Prentice Hall.
3. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and Sons, 1992.

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4. J. B. Hendrickson, D. J. Cram, G. S. Hammond, *Organic Chemistry*, McGraw Hill International Book Company, 1981.
5. Morrison, Boyd, *Organic Chemistry*, Prentice Hall.
6. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and Sons, 1992.
7. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.

MODULE VII *Photochemical and Electrochemical Synthesis.* (6 h)

Basic concepts of electroorganic reactions. Electrochemical oxidation and reduction reactions. Cathodic reduction of organic functional groups like halo, nitro etc. Electrodimerisation and electropolymerisation reactions. Electrochemical sensors. Electrooxidations.

Industrial applications of organic photochemistry.

References

1. A. J. Fry, *Synthetic Organic Electrochemistry*, Harper and Row Publishers, New York.
2. R. O. Kan, *Organic Photochemistry*, Mc Graw Hill.
3. D. R. Julian, *Industrial Aspects of Heterocyclic Photochemistry*, (O. Buchardt Ed.), Wiley Interscience, New York.

MODULE WISE WEIGHTAGE FOR QUESTIONS

MODULE	WEIGHTAGE
I	7
II	7
III	7
IV	11
V	4
VI	10
VII	4

PC1 C 03 *THEORETICAL CHEMISTRY I* Credits: 4

MODULE I (10 h)

i) *Mathematical Concepts* (5 h)

Co-ordinate systems: Cartesian, cylindrical polar and spherical polar coordinates and their relationships. Complex numbers: definition, complex conjugate, absolute value of a complex number, complex functions. Operator algebra: linear and nonlinear operators, Hermitian operators, del and del-squared operators. Eigen function and eigen values of an operator, Eigen value equation, Eigen functions of commuting operators. Well behaved functions, Normalized and Orthogonal functions.

ii) *Quantum Mechanics - A Historical Sketch* (5 h)

Blackbody radiation and Planck's quantum postulate. Einstein's quantum theory of radiation, Milliken's verification of Einstein's photoelectric equation, Wave-particle duality of radiation. Compton effect. Louis de Broglie's matter waves, Electron diffraction.

Heisenberg's matrix mechanics (mention only), Uncertainty principle. Schreodinger's wave mechanics, Deduction of Schrodinger equation from classical wave equation.

MODULE II (8 h)

i) *Postulates of Quantum Mechanics* (4 h)

Detailed discussion of postulates: State function postulate. Operator postulate. Eigen value postulate. Expectation value postulate. Postulate of time dependent Schrodinger equation of motion, Conservative system and time-independent Schrodinger equation.

ii) *Quantum Mechanics of Translational Motion* (4 h)

Particle in a one-dimensional box, important features of the problem. Symmetry of the wave functions. Particle in a three-dimensional box, Separation of variables, Degeneracy, Symmetry breaking. Introduction to Tunneling.

MODULE III (10 h)

i) *Quantum Mechanics of Vibrational Motion* (5 h)

Harmonic oscillator (complete treatment): Method of power series, Hermite equation and Hermite polynomials, Recurssion formula, Rodrigue's formula, Wave functions and energies. Important features of the problem. Harmonic oscillator and molecular vibrations. Three-dimensional harmonic oscillator.

ii) *Quantum Mechanics of Rotational Motion* (5 h)

Rigid rotator (complete treatment): The wave equation in spherical polar coordinates. Planar rigid rotator (or Particle on a ring), The Phi-equation, Solution of the Phi-equation, Handling of Imaginary wave functions, Wave functions in the real form, Polar diagrams.

Non-planar rigid rotator (or particle on a sphere), Separation of variables, The Phi-equation and the Theta-equation and their solutions, Legendre and Associated Legendre equations, Legendre and Associated Legendre polynomials, Spherical harmonics (Imaginary and real forms). Polar diagrams of spherical harmonics. Spherical harmonics as eigen functions of angular momentum operators L^2 and L_z, Quantisation of angular momentum, Angular momentum quantum numbers, Space quantisation.

MODULE IV (11 h)

Quantum Mechanics of Hydrogen-Like Atoms

Potential energy of hydrogen-like systems. The wave equation in spherical polar coordinates, Separation of variables. The R, Theta and Phi equations and their solutions, Laguerre and Associated Laguerre polynomials, Wave functions and energies of hydrogen-like atoms, Orbitals. Radial functions and Radial distribution functions and their plots, Angular functions (Spherical harmonics) and their plots, Orbital diagrams.

Explanation of Hydrogen spectrum, Fine structure, The postulate of spin by Uhlenbeck and Goudsmith, Dirac's Relativistic Schrodinger equation for hydrogen atom and discovery of spin, Hydrogen wave functions including spin or Spin orbitals, Construction of Spin orbitals from Orbitals and Spin functions.

MODULE V (12 h)

i) Quantum Mechanics of Many- Electron Atoms and Approximation Methods (6 h)

Many-body problem, Approximation methods. Independent particle model, Distribution of electrons in many electron atoms, Stoner's rule.

Variation method, Variation theorem with proof, Illustration of variation theorem using a trial function [e.g., x (a-x)] for particle in a 1D-box, Variation treatment for the ground state of Helium atom, Effective nuclear charge.

Perturbation method, Time-independent perturbation method (non-degenerate case only), Illustration by application to particle in a 1D-box with slanted bottom, Perturbation treatment of the ground state of the helium atom.
Hartree-Fock Self-Consistent Field (HF-SCF) method. Slater's treatment of complex atoms, Slater Orbitals, Slater's rules for calculating Slater orbitals.

ii) *Electron Spin in Many-Electron Atoms* (3 h)
Construction of wave functions including spin for many electron atoms, Symmetric and antisymmetric wave functions, Pauli's antisymmetry principle, Slater determinants, Pauli's exclusion principle.

iii) *Vector Model of Atoms and Spectroscopic Terms* (3 H)
Coupling of angular momenta, LS and JJ- couplings, LS coupling and Spectroscopic term symbols for atoms. Electronic spectrum of hydrogen atom - the fine structure of H_α line of the Balmer series.

MODULE VI *Chemical Bonding I* (11 h)

i) Schrodinger equation for a molecule, Born - Oppenheimer approximation. (2 h)

ii) Molecular Orbital (MO) theory (4 h)

MO theory of H_2^+. MO theory of H_2. MO treatment of homonuclear diatomic molecules L_{i2}, B_{e2}, C_2, N_2, O_2, F_2 and heteronuclear diatomic molecules LiH, CO, NO, HF. Correlation diagrams, Noncrossing rule. Spectroscopic term symbols for diatomic molecules.

iii) Valence Bond (VB) theory (5 h)

VB theory of H_2. VB theory of more complex molecules: Bonding in BeH_2, H_2O, NH_3, orbital overlap. Molecular geometry, Hybridization, Examples: Methane, Water, Ethylene, and Acetylene, Multiple bonds, VSEPR theory.

MODULE VII *Chemical Bonding II* (10 h)

i) MO Theory for More Complex Molecules (6 h)

HMO theory of linear conjugated hydrocarbons (Ethylene, Butadiene, Allylic anion), Charge on an atom, bond order, Calculation of free valence. HMO theory of aromatic hydrocarbons (benzene). Formula for the roots of the Huckel determinantal equation, Frost-Huckel circle mnemonic device for cyclic polyenes.

ii) Intermolecular Forces (5 h)

Intermolecular forces - ion dipole, dipole-dipole, ion-induced dipole, dipole-induced dipole and dispersion interactions - mathematical expressions - donor-acceptor interactions - Lennard Jones potential.

References

1. F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, 1968.
2. P. W. Atkins, *Molecular quantum mechanics*, 2nd Edn., Oxford University Press, 1983.
3. M. W. Hanna, *Quantum mechanics in Chemistry*, 2nd Edn., W. A. Benjamin Inc., 1969.
4. I. N. Levin, *Quantum Chemistry*, 5th Edn., Pearson Education Inc., 2003.
5. D. A. McQuarrie, *Quantum Chemistry*, University Science Books, 1983.
6. J. P. Lowe, *Quantum Chemistry*, 2nd Edn., Academic Press Inc., 1993.
7. A. K. Chandra, *Introduction to Quantum Chemistry,* Tata McGraw-Hill, 1994.
8. L. Pauling, E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill, 1935 (A good source book for many derivations).
9. R. L. Flurry, Jr., Quantum Chemistry, Prentice Hall, 1983.

10. R. K. Prasad, *Quantum Chemistry*, 2nd Edn., New Age International, 2000
11. M. S. Pathania, *Quantum Chemistry and Spectroscopy (Problems & Solutions)*, Vishal Publications, 1984.

MODULE WISE WEIGHTAGE FOR QUESTIONS

MODULE	WEIGHTAGE
I	7
II	6
III	7
IV	7
V	8
VI	8
VII	7

M. Sc. POLYMER CHEMISTRY- SEMESTER II

PC2 C 04 *ORGANIC CHEMISTRY II* Credits: 4

MODULE I *Pericyclic Reactions* (10 h)

Definition and types of pericyclic reactions a)cycloaddition and cycloreversion
(b) electrocyclic ring closure and ring opening c) sigmatropic rearrangement .
Stereochemistry of pericyclic reactions and theory of molecular orbital symmetry. Application of theory of molecular orbital symmetry by the method of corelation diagram for cycloaddition and electrocyclic reactions by both thermal and photochemical paths. Stereochemistry of pericyclic reactions- thermal and photochemical by method of transition state aromaticity.
Stereochemistry of pericyclic reactions by FMO.
Selection rules. Sommelet-Hauser, Cope and Claisen rearrangements.

References

1. T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper Collins.
2. S. H. Pine, J. B. Hendrickson, D. J. Cram, G. S. Hammond, *Organic Chemistry*, McGraw Hill International Book Company, 1981.
3. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.

MODULE II *Chemistry of Free Radicals and Photochemistry* (12 h)

i) Stability of free radicals. Formation and detection of free radicals. Structure and stereochemical properties of radical intermediates characteristics and reaction mechanism involving radical intermediates. Free radical substitution and addition reactions. Rearrangement and fragmentation reactions. Carbenes and nitrenes.

ii) Fundamental Concepts, Molecular excitation, Jablonski diagram and the singlet and triplet states. Photosensitization.
Reactions involving the olefinic double bonds, reactions of carbonyl compounds and reactions of aromatic compounds. Photoreduction. Di-pi-methane rearrangement. Barton reaction and photo Fries rearrangement. Mechanism of photosynthesis, photochemistry of dyes and pigments, photochemistry of vision.

References

1. T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper Collins.
2. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and sons, 1992.
3. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.
4. R. O. Kan, *Organic Photochemistry*, McGraw Hill.
5. O. L. Chapman, *Organic Photochemistry Vol. I & II*, Marcel Decker.
6. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.

MODULE III *Molecular Rearrangements* (6 h)

Rearrangement involving electron deficient carbon, nitrogen and oxygen atoms, Wagner-Meerwein, Dienone–phenol, Wolff, Hoffmann, Curtius, Lossen, Beckmann, Schmidt and Baeyer-Villiger rearrangements.

Anionic rearrangements: Benzil-benzilic acid and Favorski rearrangements. Orten, Claisen and Fries rearrangements.

References

1. P. Sykes, *A Guide Book to Mechanisms in Organic Chemistry*, Orient Longmans, 2002.
2. S. H. Pine, J. B. Hendrickson, D. J. Cram, G. S. Hammond, *Organic Chemistry*, McGraw Hill International Book Company, 1981.
3. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and sons, 1992.

MODULE IV *Organic Spectroscopy* (18 h)

Application of UV, IR, NMR, and MS in the structure elucidation of organic compounds. Problem solving approach (Instrumentation not required).

UV: Characteristic absorption of organic compounds - Empirical rules for calculating absorption maxima of dienes and enones.

IR: Characteristic group absorptions of organic molecules - Alkanes, alkenes, alkynes, mononuclear aromatic hydrocarbons, alcohols, phenols, ethers, carbonyl compounds, amines, amides and nitriles.

NMR: The chemical shift, Local diamagnetic shielding and magnetic equivalence. Spin-spin coupling and coupling constants. Coupling of protons to other nuclei - quadrupole broadening. First and second order spectra. Homotopic, enantiotopic and diastereotopic protons. Spin decoupling and double resonance, Vicinal and geminal coupling in rigid systems. High resolution NMR. ^{13}C chemical shifts. Correlation charts. Proton coupled, off resonance decoupled and noise- decoupled spectra.

MS: Determination of molecular mass. Molecular formula from isotope ratio. Fragmentation pattern in different classes of compounds. Modern techniques of ionization.

References

1. R. M. Silverstein, G. C. Basslar, T. C. Morrill, *Spectroscopic Identification of Organic Compounds*, John Wiley and Sons Inc., 1991.
2. W. Kemp, *Organic Spectroscopy*, 3rd Edn., McMillan. 1991.
3. P. S. Kalsi, *Spectroscopy of Organic Compounds*, New Age International, 1998.

MODULE V *Organic Reactions and Mechanisms* (8 h)

Robinson annulation, Birch reductions, hydroboration, Favorski reaction, Stork enamine reaction, Michael addition, Sharpless asymmetric epoxidation, Hofmann- Loffler- Freytag reaction, Shapiro reaction and Bayer- Villiger reaction.

References

1. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.
2. H. O. House, *Principles of Organic Synthesis.*
3. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and sons, 1992.

MODULE VI *Heterocyctic Compounds and Natural Product Chemistry* (8 h)

Structure, synthesis and reactions of pyrazole, imidazole and thiazole. Synthesis of uracil, thymine, cytosine, adenine, guanine, caffeine and pyrazine. Biosynthesis of alkaloids, terpenoids, steroids, carbohydrates and proteins.

Reference

1. I. L. Finar, *Organic Chemistry Vol. II*, 5th Edn., ELBS, 1975.

MODULE VII *Synthetic Reagents* (10 h)

Uses of the following reagents in organic synthesis. Complex metal hydrides. Gilmans reagent, lithium diisopropyl amide (LDA), DCC, 1,3-Dithiane (reactivity umpolung), trimethylsilyl iodide, tri-n-butyl tin hydride, OsO_4, DDQ, SeO_2, Woodward and Prevost hydroxylation, phase transfer catalysts, crown ethers and Merrifield resin, Peterson's synthesis, Wilkinson catalyst and Baker yeast.

References

1. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry (Parts A & B)*, 3rd Edn., Plenum Press, 1990.
2. H. O. House, *Principles of Organic Synthesis*.
3. J. March, *Advanced Organic Chemistry*, 4th Edn., John Wiley and sons, 1992.

MODULE WISE WEIGHTAGE FOR QUESTIONS

MODULE	WEIGHTAGE
I	7
II	8
III	4
IV	13
V	5
VI	6
VII	7

PC2 C 05 *PHYSICAL CHEMISTRY I* Credits: 4

MODULE I *Thermodynamics I* (12 h)

i) Review of first and second laws. Third law of thermodynamics, need for the third law, Nernst heat theorem, Apparent exceptions to third law, Applications of third law, Determination of absolute entropies, Residual entropy.

Determination of relations connecting the thermodynamic partial derivatives by the method of Jacobians (discussion to be confined to closed thermodynamic systems).

ii) Thermodynamics of Solutions

Partial molar quantities, Chemical potential, Variation of Chemical Potential with temperature and Pressure, Partial molar volume and its determination, Gibbs-Duhem equation, Thermodynamics of ideal and real gases and gas mixtures. Fugacities of gases and their determinations, Activity, activity coefficient, standard states of substances (for solute and solvents). Duhem-Margules equation and its applications. Thermodynamics of ideal solutions, Deductions of the laws of Raoult, ebullioscopy, cryoscopy and osmotic pressure. Non-ideal solutions, Deviations from Raoult's law, Excess functions - excess free energy, excess entropy, excess enthalpy and excess volume.

MODULE II *Thermodynamics II* (8 h)

Thermodynamics of Irreversible Processes

Simple examples of irreversible processes. General theory of non-equilibrium processes. Entropy production. The phenomenological relations. Onsager reciprocal relations, Application to the theory of diffusion, thermal diffusion, thermoosmosis and thermomolecular pressure difference, Electrokinetic effects. The Glansdorf-Prigogine equation.

References (MODULE I & II)

1. S. Glasstone, *Thermodynamics for Chemists*, East-West, 1973
2. Rajaram, Kuriokose, *Thermodynamics* , East-West, 1986
3. R. P. Rastogi, R. R. Misra, *An Introduction to Chemical Thermodynamics*, New Age International.
4. D. A. McQuarrie, J. D. Simon, *Physical Chemistry, A Molecular Approach*, University Science Books, 1997.
5. K. J. Laidler, J. H. Meiser, B. C. Sanctuary, *Physical Chemistry,* Houghton Mifflin Company, New York, 2003.
6. Prigogine, *An Introduction to Thermodynamics of Irreversible Processes*, Interscience.
7. B. G. Kyle, *Chemical and Process Thermodynamics*, 2nd Edn., Prentice Hall of India.
8. G. K. Vemulapalli, *Physical Chemistry*, Printice Hall of India.

MODULE III *Electrochemistry – I* (10 h)

i) Debye-Huckel theory of electrolytic conduction - Derivation of Debye-Huckel-Onsager equation. Deviation from Debye-Huckel-Onsager equation and corrections. Degree of dissociation and its determination. Conductance ratio. Debye-Falkenhagen effect, Wein effect.

ii) Activity and activity coefficients of electrolytes. Ionic strength, variation of activity coefficient with concentration, Derivation of Debye-Huckel limiting law and its various forms, Qualitative and quantitative tests of the Debye- Huckel limiting law.

MODULE IV *Electrochemistry – II* (10 h)

Polarization, overvoltage and polarography. Electrolytic polarization, dissolution and deposition potentials, concentration polarization. Decomposition voltage and its determination. Over voltage - hydrogen over voltage, oxygen overvoltage, metal deposition over voltage and their determination. Theories of over voltage - Ionic diffusion as the slow process - Principles of polarography, dropping mercury electrode, the half wave potential. Electrode kinetics.

References

1. S. Glasstone, *Introduction to Electrochemistry*, East-West Press Pvt. Ltd., 1965

2. D. A. McInnes, *The Principles of Electrochemistry*, Dover Publications.
3. J. O. M. Bockris, A. K. N. Reddy, *Modern Electrochemistry, Vol. I and II*, Kluwer Academic / Plenum Publishers, 2000.

MODULE V *Surface Chemistry and Colloids* (10 h)

Langmuir's unimolecular theory of adsorption, Adsorption isotherms, BET equation, derivation, determination of surface area of adsorbents, heat of adsorption and its determination. Gibbs adsorption isotherm.

Colloids: Colloidal surfactants, classification – cationic, ionic and ionogenic surfactants. Micelles - causes of micellar formation. Micelle structure. Determination critical micellar concentration stabilizing action of surfactants. Practical importance of colloidal surfactants - Tannins and dyes.

MODULE VI *Photochemistry* (8 h)

Radiative and non-radiative transitions - chemiluminescence photoluminescence, cathodoluminescence, electroluminescence, bioluminescence, thermoluminescence, fluorescence, theory of fluorescence, stokes antistokes and resonance fluorescence - photosensitization - sensitised fluorescence - quenching of fluorescence. Theory of quenching of fluorescence. Principles of utilization of solar energy- solar cells.

References

1. F. Daniels, R. A. Alberty, Physical *Chemistry*, 5th Edn., Wiley Eastern, 1980.
2. S. Glasstone, *Physical Chemistry*, Mac Millan and Company, 1962.
3. G. Raj, H. Misra, *Photochemistry*, Goel Publishing House.
4. P. W. Atkins, Physical Chemistry, 6th Edn., Oxford University Press, 1998.
5. C. H. Dupeg, R. L. Chapman, *Molecular Reactions and Photochemistry* , Prentice Hall.
6. Cox, Kemp, *Introductory Photochemistry*, McGraw Hill.
7. P. Suppan, Chemistry *and Light*, RSC London.

MODULE VII *Nuclear and Radiation Chemistry* (14 h)

Nuclear binding energy, semi empirical mass equation, stability rules, magic numbers, nuclear models, shell, liquid drop, fermi gas, collective and optical models.

Nuclear reactions: Types, conservation, reaction cross section, compound nucleus theory, specific nuclear reactions, photonuclear and thermonuclear reactions.

Nuclear fission- theory of fission - spontaneous and reduced fission - neutron capture cross section and critical size, principle and working of nuclear power plants. Nuclear fusion. Neutron activation analysis.

Radiation chemistry - interaction of radiation with matter - processes responsible for energy loss, range and range energy relation. Methods of detection and measurement of radiation. Physical and chemical radiation effects in solids. Radiation chemistry of water and aqueous ferrous sulphate solution. Dosimetry. Principle and working of GM counter and scintillation counters.

References

1. Friedlander, J. W. Kennedy, *Introduction to Radiochemistry*, John Wiley and Sons, 1981.
2. S. Glasstone, *Source Book on Atomic Energy*, 3rd Edn., Affiliated East-West Press Pvt. Ltd., 1967.
3. H. J. Arnikar, *Essentials of Nuclear Chemistry*, 4th Edn., New Age International, New Delhi, 1995.
4. J. B. Rajam, *Atomic Physics*, S. Chand and Co. Pvt. Ltd., 1974.
5. Friedlander, J. W. Kennedy, J. M. Miller, *Nuclear and Radiochemistry*, 3rd Edn., John Wiley and Sons, 1981.

6. J. W. T. Spinks, R. J. Woods, *An introduction to Radiation Chemistry*, John Wiley and Sons, 1964.

MODULE WISE WEIGHTAGE FOR QUESTIONS

MODULE	WEIGHTAGE
I	8
II	6
III	7
IV	7
V	7
VI	5
VII	10

PC2 C 06 *THEORETICAL CHEMISTRY II* Credits: 4

MODULE I *Molecular Symmetry and Mathematical Groups* (10 h)

Symmetry elements and symmetry operations in molecules, Complete set of symmetry operations of a molecule, Point groups and their systematic identification.

Mathematical group, Finite and infinite group, Abelian and Cyclic groups. Group multiplication table. Classes in a group, Similarity transformation.

Matrix algebra, Addition and multiplication of matrices, Inverse of a matrix, Square matrix, Character of a matrix, Diagonal matrix, Direct product and direct sum of square matrices, Block diagonalized matrix, Solving linear equations by the method of matrices. Matrix representation of symmetry operations.

MODULE II *Theory of Molecular Symmetry* (10 h)

Representation of groups, Basis for a representation, Representations using vectors, atomic orbitals and Cartesian coordinates positioned on the atoms of molecule (H_2O as example) as the basis , Reducible and irreducible representations, Construction of irreducible representation by reduction (qualitative demonstration only), Great orthogonality theorem (GOT) (no derivation), Construction of irreducible representation using GOT, Construction of character tables (C_{2V}, C_{3V}, C_{2h} and C_{4V} as examples), Nomenclature of irreducible representations-Mulliken symbols, Symmetry species. Derivation of reduction formula using GOT, Reduction of reducible representations, (e.g., Γ_{cart}) using the reduction formula, Direct sum and direct product of irreducible representations. Connection between group theory and quantum mechanics.

MODULE III *Applications of Group Theory - I* (10 h)

i) Vanishing and non-vanishing integrals. Transition moment integral and selection rules. Overlap integrals and conditions for overlap.

ii) MO treatment of H_2O, Classification atomic orbitals involved into symmetry species, Group orbitals, Symmetry adapted linear combination (SALC), Projection operator, Construction of MOs, Electronic configuration of H_2O, Symmetries of the ground and excited states, Electronic transitions and selection rules, Laporte selection rule for centro symmetric molecules.

MODULE IV *Applications of Group Theory- II* (10 h)

i) Treatment hybridization in BF_3 and CH_4, Inverse transformation and construction of hybrid orbitals.

ii) Molecular vibrations, Symmetry species of normal modes of vibration, Construction of Γ_{cart}. Normal coordinates and drawings of normal modes (e.g., H_2O and NH_3), Selection rules for IR and Raman activities, Complementary character of IR and Raman Spectra, Determination of IR active and Raman active modes of molecules (e.g., H_2O, NH_3, CH_4 , SF_6).

MODULE V (11 h)

i) General Theory of Spectra

Electromagnetic radiation and its different regions, Interaction of matter with radiation and its effect on the energy of the molecule. Origin of molecular spectra, Theory of the origin of rotational, vibrational and electronic spectra. Intensity of spectral lines, Dependence of intensity on population, transition probabilities, Transition moment integral, Selection rules. Line widths, Doppler broadening, Lifetime broadening.

ii) Microwave Spectroscopy

Rotation spectra of diatomic and polyatomic molecules, Rigid and non-rigid rotator models, Asymmetric, symmetric and spherical tops. Isotope effect on rotation spectra, Stark effect, Nuclear and electron spin interactions. Rotational transitions and selection rules. Microwave spectrometer – Principles & Instrumentation. Applications.

iii) *Vibrational Spectroscopy*

Vibrational spectra of diatomic and polyatomic molecules, Harmonic oscillator model, Anharmonicity, Vibrational transitions and selection rules. Morse potential, Fundamentals, Overtones, Hot bands, Combination bands, Difference bands.

MODULE VI (11 h)

i) Vibration-rotation spectra of diatomic and polyatomic molecules, P,Q,R branches.

IR and FTIR spectrophotometer - Principles & Instrumentation, Applications.

ii) Raman Spectroscopy

Pure rotational, pure vibrational Raman spectra, Vibrational-rotational Raman spectra, Selection rules, Mutual exclusion principle.

Raman spectrophotometer- Principles & Instrumentation, Laser Raman spectroscopy, Applications.

iii) Electronic Spectroscopy

Basic principles, Beer - Lambert law, Molar extinction coefficient, Intensity of electronic transitions. Types of electronic transitions. Franck - Condon principle, Ground and excited electronic states of diatomic molecules. Electronic spectra of polyatomic molecules, Chromophores. The fate of electronically excited state species- Vibrational relaxation, External conversion, Internal conversion, Fluorescence, Phosphorescence. Jablonski diagram. Electronic spectra of conjugated molecules - dissociation and predissociation spectra.

UV-Visible spectrophotometer - Principles & Instrumentation. Applications.

MODULE VII (10 h)

i) NMR Spectroscopy

Magnetic properties of nuclei, Theory and measurement techniques, Solvents used, Chemical shift and factors influencing chemical shift, Shielding effects, Spin-spin interaction, Coupling constant, Factors influencing coupling constant, Effects of chemical exchange, Fluxional molecules, Hindered rotation on NMR spectrum, Karl's relationships, NMR spectrometer-Principles and instrumentation. Multiple NMR spectroscopy (brief account). Applications of NMR spectroscopy to structure elucidation of simple organic and inorganic molecules. FT NMR.

ii) ESR Spectroscopy

Theory and measurement techniques, Hyperfine interactions, Equivalent and nonequivalent protons, Kramer's theorem. ESR spectrometer- Principles and instrumentation. Applications in structure elucidation of simple molecules.

iii) MossBauer spectroscopy

The Moss Bauer effect. Instrumentation. Hyperfine interactions, isomer shift, electric quadruple and magnetic hyperfine interactions. Applications.

iv) Mass Spectrometry

Basic principles, Instrumentation - Mass spectrometer, interpretation of mass spectra, resolution, exact masses of nuclides, molecular ions, isotope ions. Fragmentation processes - McLafferty rearrangements, retro Diels - Alder fragmentation. Application in structure elucidation and evaluation of heats of sublimation and ionization potential.

References

1. F. A. Cotton, *Chemical applications of Group Theory*, 2nd Edn., Wiley Eastern, 1971.
2. Jaffe, Orchin, *Symmetry in Chemistry*, Wiley Eastern.
3. L. H. Hall, *Group Theory and symmetry in Chemistry*, McGraw Hill
4. R. McWeeny, *Symmetry: An Introduction to Group Theory and its Applications*, Pergamon Press, London, 1963.
5. P. H. Walton, *Beginning Group Theory for Chemistry*, Oxford University Press Inc., New York, 1998.
6. A. W. Joshi, *Elements of Group Theory for Physicists*, New Age International Publishers, 1997.
7. P. W. Atkins, *Physical Chemistry*, 6th Edn., Oxford University Press, 1998.
8. F. Daniels, R. A. Alberty, *Physical Chemistry*, 5th Edn., Wiley Eastern, 1980.
9. D. A. Mc Quarrie, J. D. Simon, *Physical Chemistry, A Molecular Approach*, University Science Books, 1997.
10. K. J. Laidler, J. H. Meiser, B. C. Sanctuary, *Physical Chemistry,* Houghton Mifflin Company, New York, 2003.
11. C. N. Banwell, *Fundamentals of Molecular Spectroscopy*, Tata McGraw Hill, New Delhi, 1994.
12. G. M. Barrow, *Introduction to Molecular Spectroscopy*, McGraw Hill, 1962.
13. H. H. Willard, L.L. Merritt, J. A. Dean, *Instrumental Methods of Analysis*, 4th Edn., Affiliated East-West Press Pvt. Ltd., 1965.
14. N. Sathyanarayana, *Electronic Absorption Spectroscopy and Related Techniques*, University Press, 2000.
15. R. S. Drago, *Physical Methods in Inorganic Chemistry*, Affiliated East-West Press Pvt. Ltd., 1977.

MODULE WISE WEIGHTAGE FOR QUESTIONS

MODULE	WEIGHTAGE
I	7
II	7
III	7
IV	7
V	7
VI	8
VII	7

***SYLLABUS - PRACTICAL COURSES* (I & II Semesters)**

PC1 & PC2 P 01 *INORGANIC CHEMISTRY* Credits: 4

MODULE I

Separation and identification of four metal ions of which two are less familiar elements like W, Se, Te, Mo, Ce, Th, Ti, Zr, V, U and Li. (Eliminating acid radicals not present). Confirmation by spot tests.

MODULE 11

Volumetric Determinations using:

a) EDTA (Al, Ba, Ca, Cu, Fe, Ni, Co, hardness of water, etc.)

b) Estimations, involving quantitative separation of suitable binary mixtures of ions Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, $Cr_2O_7^{2-}$, Ba, Ag, etc. in solution by volumetric, gravimetric, colorimetric and electroanalytical methods.

c) Analysis of ores and alloys like dolomite, galena, ilmenite, monazite, feldspar and kaoline and two alloys.

MODULE III

Colorimetric determination of chromium, iron, manganese, nickel, and titanium using either Dubosque or photoelectric colorimeter.

References

1. G.H. Jeffery, J. Bassett, J. Mendham, R. C. Denny, *Vogel's Text book of Quantitative Chemical Analysis*, 5th Edn., ELBS, 1989.
2. D A Skoog, D M West, *Analytical Chemistry*, *An Introduction*, 4th Edn., CBS Publishing Japan Ltd., 1986.
3. E. J. Meehan, S. Bruckenstein, I. M. Kolthoff, E. B. Sandell, *Quantitative Chemical Analysis*, 4th Edn., The Macmillan Company, 1969.
4. R. A. Day (Jr), A. L. Underwood, *Quantitative Analysis*, 6th Edn., Prentice Hall of India, 1993.

PC1 & PC2 P 02 *ORGANIC CHEMISTRY* Credits: 4

MODULE I *Laboratory Techniques*

Methods of separation and purification of organic compounds - fractional, steam and low-pressure distillations, fractional crystallisation and sublimation

MODULE II *Qualitative Organic Analysis*

Separation and identification of the components of organic binary mixtures (at least ten) by semimicro analytical techniques. Determination of M.P/B.P of the separated components. Separation of organic mixtures using paper, thin layer and column chromatography. Determination of Rf value.

MODULE III *Organic Preparations*

Preparation of about fifteen organic compounds (at least six double stage- including photochemical reactions) illustrating important synthetic methods and reactions such as Friedel-Crafts reaction, Grignard, Perkin, Reimer-Tiemann, Sandmeyer, and Cannizzaro reactions, Claisen, Aldol, and benzoin condensations. Selective reduction in polynitro aromatic compounds; diazocoupling, phthalein fusion, etc.

MODULE IV *Quantitative Organic Analysis.*

Estimation of nitrogen by Kjeldahl method, estimation of hydroxyl and carbonyl groups, determination of iodine number and saponification value of oils. Estimation of reducing sugar, amines, phenols, esters, vitamins (A and C), drugs (aspirin, paracetamol).

References

1. B. S. Furnis, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, ELBS/Longman, 1989.
2. Fieser, *Experiments in Organic Chemistry.*
3. Mann, Saunders, *Practical Organic Chemistry*, 1957.
4. Dey, Sitaraman, Govindachari, *A Laboratory Manual of Organic Chemistry*, 3rd Edn., 1957.
5. Cheronics an Fatrikin S*emi-micro Organic Analysis.*
6. A. J. Vogel, *Qualitative Organic Analysis.*
7. P. R Singh, D. C Gupta, K. S. Bajpal, *Experimental Organic Chemistry*, *Vol. I and II*, 1980.
8. R. Srinivasan, Ed. *Photochemical Synthesis, Vol. I and II*.

PC1 & PC2 P 03 *PHYSICAL CHEMISTRY* Credits: 4

MODULE I *Colligative Properties*

1. Molecular weight from depression by transition method- cooling curve method.
2. Molecular weight by cryoscopic method.
3. Molecular weight Rast method.

MODULE II *Viscosity*

1. Determination of viscosity of pure liquids (water, methanol, ethanol, glycerol, benzene, nitrobenzene, carbon tetrachloride).
2. Determination of composition of binary liquid mixtures (benzene-nitrobenzene, water-alcohol).
3. Determination of molecular weight of a polymer (polystyrene in toluene).

MODULE III *Conductivity Experiments*

1. Equivalent conductance of a weak acid- verification of Ostwald's dilution law- calculation of dissociation constant.
2. Equivalent conductance of strong electrolytes (KCl). Verification of Onsagar equation.
3. Activity coefficient of Zn in 0.002M $ZnSO_4$ using Debye-Huckel limiting law.
4. Solubility product of a sparingly soluble salt (e.g., AgCl, $BaS0_4$)
5. Conductometric titrations
    (a) HCl vs NaOH
    (b) (HCl + CH_3COOH) vs NaOH
    (c) $AgNO_3$ vs KCl.

MODULE IV *Potentiometry*

1. Electrode potentials of Zn and Ag electrodes in 0.1 M and 0.001 M solutions at 25 °C and determination of standard potentials.
2. Mean activity coefficient of an electroanalyte at different molalities by EMF method.
3. Dissociation constant of acetic acid by potentiometric titration.

4. Determination of strength of the given HCl solution by differential potentiometric titration.
5. Dissociation constant of acetic acid in DMSO, DMF, acetone and dioxane by titrating with NaOH.
6. Potentiometric titration.
    i) Mixture of chloride and iodide.
    ii) Mixture of HCl and CH_3COOH.

MODULE V *Chemical Kinetics*

1. Specific reaction rate of acid catalysed hydrolysis of methyl acetate.
2. Temperature coefficient and energy of activation of hydrolysis of methyl acetate. Determination of Arrhenius parameters.
3. Saponification of ethyl acetate (titration/conductance method).
4. Inversion of cane sugar in presence of HCl by polarimetry.
5. Iodination of acetone- determination of order.

MODULE VI *Adsorption* (3 experiments)

1. Verification of Freundlich and Langmuir adsorption isotherms.
2. Determination of concentration of acetic acid/oxalic acid using Freundlich and Langmuir adsorption isotherms.

MODULE VII *Phase Equilibria*

1. Phase diagram of a simple eutectic system.
2. Phase diagram of a binary solid system forming a compound.
3. Phenol-water system, aniline-water system.
4. Ternary liquid system with one pair of partially miscible liquids (DMSO-benzene-water, acetone-chloroform-water, etc.).

References

1. A. Finlay, J. A. Kitchener, *Practical Physical Chemistry*, Longman.
2. A. M. James, *Practical Physical Chemistry*, J. A. Churchil Ltd., 1961.
3. F. Daniel, J. W. Williams, P. Bender, R. A. Alberty, C. D. Cornwell, J. E. Harriman, *Experimental Physical Chemistry*, McGraw Hill, 1970.
4. W. G. Palmer, *Experimental Physical Chemistry*, 2nd Edn., Cambridge University Press, 1962.
5. D. P. Shoemaker, C. W. Garland, *Experimental Physical Chemistry*, McGraw Hill.

QUESTION PAPERS

MODEL ONLY

FIRST SEMESTER M Sc (POLYMER CHEMISTRY) DEGREE EXAMINATION

PC1 C 01 INORGANIC CHEMISTRY –I

Time: 3 Hours Max: 36 Weightage

Part A

(Answer **all** questions. Each question has 1 weightage)

1. Arrange the following in the order of acid strength.

    a) BCl_3, BI_3, BF_3 b) $SnCl_2$, $SnCl_4$

2. B_2O_3 is acidic, Al_2O_3 is amphoteric and Se_2O_3 is basic. Why?

3. Calculate the maximum radius ratio of an atom A to fit in the simple cubic lattice of an atom B
4. Explain the term K- space. What is its significance?.
5. What is meant by packing fraction? How does it predict the stability or other wise a nucleus.
6. How do the d orbital split when a transition metal ion is placed in octahedral crystal field of ligands.
7. Choose the stronger acid or base in the following pair
    a) CH_3NH_2 or NH_3 in reaction with H^+
    b) Pyridine or 2-methyl pyridine in reaction with tri methyl boron
8. Why lanthanides exercise oxidation states other than + 3
9. Name three types of determinate errors.
10. On what factors does the solubility of a precipitate depend
11. What are phosphazines? Draw structure of Hexachloro cyclotriphosphazine.
12. State and explain Jahn- Tellar effect.
13. What is meant by confidence limit? What is its significance?
14. What are radio active tracers? Mention two applications.

Part B

(Answer any **seven** questions. Each question has 2 weightage)

15. Calculate the binding energy per nucleon of oxygen $_8O^{16}$ which has a mass of 15.994910 a.m.u. Mass of neutron = 1.008665 a.m.u, mass of proton = 1.007277 a.m.u and mass of electron = 0.0005486 a.m.u.
16. Explain why a strong acid like HNO_3 behaves as a base in HF.
17. Explain the different steps involved in the formation of silicones.
18. Why strong oxidizing agents do not exist in liquid NH_3.
19. Write short note on nephelauxetic series.
20. Distinguish between nuclear fission reaction and nuclear fusion reaction.
21. What are Latimer diagram? Explain how a Latimer diagram is converted into reduction half - cell reaction in acid solution?
22. Define Fermi level. Show that it is located half way between the highest filled level and lowest unfilled level.
23. What are carboranes? How are boranes and carboranes classified?

24. Describe carefully the Q test which is applied for rejection or retention of an anomalous result.

Part C

(Answer any **two** questions. Each question has 4 weightage)

25. Discuss the various types of semiconductors and their applications.
26. Give a brief account of imperfections in solids and various types of defects.
27. How is the MO diagram for an octahedral complex modified on including pi bonding? Explain why CN^- and Cl^- occur in opposite ends of the spectrochemical series.
28. Describe briefly the ion exchange and solvent extraction separation of lanthanides.

MODEL ONLY

FIRST SEMESTER M Sc (POLYMER CHEMISTRY) DEGREE EXAMINATION

PC1 C 03 THEORETICAL CHEMISTRY-I

Time: 3hours Max: 36 Weightage

Part A

(Answer **all** Questions. Each question has **1** weightage)

1. What you understand by commutator operator?
2. Show that sin 2x is not an eigen function of the operator d/dx but of d^2/dx^2.
3. What do you understand by Hermitian operator?
4. Which of the functions sin3x, 6cos4x, 5x2 are eigen functions of d^2/dx^2?
5. If $A\hat{} = 3x^2$ and $B\hat{} = d/dx$ then show that $A\hat{} B\hat{} \neq B\hat{} A\hat{}$
6. For a particle in a cubic box of edge L, How many states have energies in the range zero and $16h^2/8mL^2$?
7. Sketch the molecular orbital scheme for N_2
8. What do you under stand by the term hybrid orbitals?
9. State and explain uncertainty principle.
10. Deduce spectroscopic term symbol for F_2molecule.
11. On the basis of MO theory predict on the relative stability of O_2, O_2^+ and O_2^{--}
12. Write down the Hamiltonian operators for electrons in He^+ and He.
13. Calculate the zero point kinetic energy of CO_2 molecule moving in side a cube of length 20 A^o
14. Draw ψ and ψ^2 functions for 2s and 2p orbitals.

Part B

(Answer any **seven** Questions. Each question has **2** weightage)

15. Briefly explain Slater's treatment of complex atoms.
16. Out line the valence bond treatment of bonding in H_2.
17. Explain the basic postulates of Huckels MO theory.
18. Discuss about Hermite polynomials.
19. Write a short note on Self-Consistent Field method.
20. Write briefly the Pauli's exclusion principle.
21. Apply Schrödinger wave equation for a particle in one dimensional box and find eigen functions.
22. Explain the essential features of MO and VB treatment of H_2 molecule.
23. Enumerate the experimental proof for the uncertainty principle.
24. Write a note on Laguerre and associated Laguerre polynomials

Part C

(Answer any **two** Questions. Each question has **4**weightage)

25. Treat the pi-bonding in benzene within the frame work of Huckel MO theory.
26. Write a detailed account of variation method. How is it different from perturbation method?
27. Write short note on a) Radial distribution curves b) Operators
28. Solve Schrödinger equation for a particle in three dimensional box, solve it and get expression for the energy of electrons.

MODEL ONLY

SECOND SEMESTER M Sc (POLYMER CHEMISTRY) DEGREE EXAMINATION

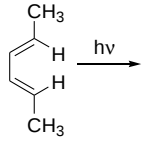
PC2 C 04 – ORGANIC CHEMISTRY – II

Time: 3hrs Max: 36 Weightage

Part A

(Answer all questions. Each question has 1 weightage)

1. Would the photochemical cyclisation of the following diene give *cis* or *trans* product? Explain.

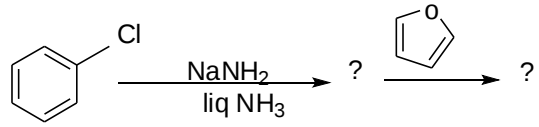


2. Write the stereostructure of the compound obtained by the Diels-Alder reaction of dimethylmaleate with butadiene.

3. What is *ortho* effect in aromatic electrophilic substitution reaction?

4. Alkylation of Benzene with MeI by Freidel - Crafts reaction gives toluene.However, a similar reaction to obtain *n*-propylbenzene using *n*-propyl iodide hardly succeeds.Explain why.

5. Predict the products and propose mechanism in the following



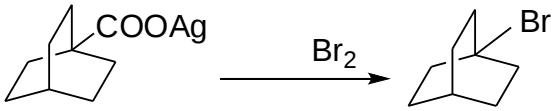
6. Write any two reactions of nitrenes.

7. Which butoxide, *t*-BuO^-K^+ or *n*-BuO^-K^+ is the best to prepare 1-pentene from MeCH(OTos) – CH_2 CH_2Me under E2 conditions? Why?

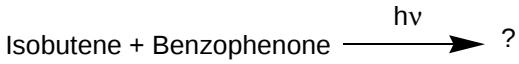
8. A benzyl radical is more stable than an ethyl radical.Give reason.

9. Explain why the E2 elimination rate of *trans*- 4- *t*- butylcyclohexyl tosylate is different from that of its *cis*- isomer.

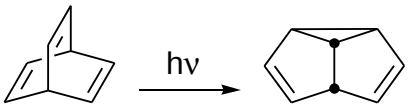
10. Is the following reaction, at a bridgehead position, a feasible one?Comment



11. Predict the products in the following



12. Provide mechanistic rationalization for the following reaction.



13. N-methylbenzamide does not undergo Hoffmann rearrangement.Give reason.

14. Is Fries rearrangement is temperature dependent?Explain

Part B

(Answer any seven questions. Each question has 2 weightages)

15. Write an account of the mechanism of Cope rearrangement and explain using examples why it is classified as a [3,3] sigmatropic rearrangement.

16. Write briefly on

(i) E1cB mechanism of elimination and

(ii) mechanism and stereochemistry of Chugev reaction.

17. (a) Why the reactivity of the diene is increased by electron releasing substituents?

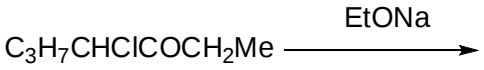
    (b) Cycloaddition of an unsymmetrically substituted diene and dienophile can in principle lead to regeoisomers.Write the structures of the products by taking examples.

18. Give the stereochemistry of the products formed when

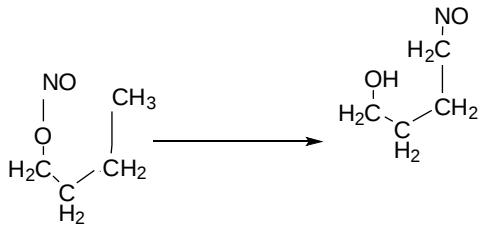
    (a) *cis,trans*-2,4- hexadiene reacts thermally and

    (b) *trans,trans*-2,4- hexadiene reacts photochemically.

19. (a) Complete the following equation, give its name and mechanism.



    (b) How will you convert the following?



20. Write briefly on the structure and reactivity of singlet and triplet Carbenes.

21. How does the branching on α and β- carbon atom of alkyl halide affect the rate of S_N2 reaction?

22. Deduce the mechanism of Wolff rearrangement.Discuss its utility in Arndt-Eistert synthesis.

23. Discuss the (i) photochemistry of vision and

    (ii) mechanism of di-π- methane rearrangement.

24. Derive the W-H rules for thermal electrocyclisation of 4n and 4n+2 systems.

Part C

(Answer any two questions. Each question has 4weightages)

25. Write an account of (i) Photopolymerisation reactions and

    (ii) the different mechanisms of aromatic substitutions.

26. (i) What is Favorskii reaction?

    (ii) Which side reaction occurs with Favorskii rearrangement?

    (iii) What is quasi- Favorskii rearrangement?

27. Using correlation diagram approach, derive the selection rules for thermal electrocyclisation in 4π and 6π electron systems.

28. Write an account of (i) photopolymerisation reactions and

    (ii) the different mechanisms of aromatic nucleophilic substitutions.

MODEL ONLY

SECOND SEMESTER M Sc (POLYMER CHEMISTRY) DEGREE EXAMINATION

PC2 C 05 PHYSICAL CHEMISTRY I

Time: 3 hours Max: 36 Weightage

Part A

(Answer all questions. Each question has 1 weightage)

1. Explain the term residual entropy.
2. What is Debye Falkenhagen effect?
3. Explain the term isosteric heat of adsorption
4. What are the major products of water radiolysis?
5. Explain with example an ideal non polarisable electrode
6. Define phenomenological coefficient. Explain it's significance
7. Distinguish between inter system crossing and internal conversion
8. Write down Debye Huckel limiting law and explain the terms
9. Define excess enthalpy. What is it's significance?
10. What is meant by chemiluminiscence? Give one example.
11. Calculate the ionic strength of a solution containing 0.001 mole Calcium phosphate.
12. Explain thermal osmosis.
13. Explain the term thermal neutrons.
14. Distinguish between Stokes and anti Stokes lines.

Part **B**

(Answer any **seven** questions. Each question has **2** weightage)

15. Derive Duhem Margules equation. What is it's importance?
16. Derive Gibb's adsorption isotherm.
17. Write IIkovic equation. Explain it's significance.
18. Write a note on colloidal surfactants.
19. Explain how irreversible process generates entropy.
20. Discuss briefly the theory of fluorescence.
21. Explain the principle and working of a solar cell.
22. How will you determine the surface area of an adsorbent?

23. Discuss the shell model of nucleus.
24. Explain the term dosimetry. Describe the function of a Fricke Dosimeter.

Part C

(Answer any **two** questions. Each question has **4** weightage)

25. Derive Debye Huckel Onsagar equation.
26. Give an account of determination of thermodynamic partial derivatives by the method of Jacobians
27. Write notes on
    a) Polarography
    b) Activity and activity coefficient
28. Describe the principle and working of a scintillation counter

MODEL ONLY

SECOND SEMESTER M Sc (POLYMER CHEMISTRY) DEGREE EXAMINATION

PC2 C 06 - THEORETICAL CHEMISTRY-II

Time: 3hours Max: 36 Weightage

Part A

(Answer **all** Questions. Each question has **1** weightage)

1. Show that $S_6^2 = C_3$.
2. Assign Schoenflies symbol of point groups to a) $C_6H_4R_2$ (ortho), b) *cis*- butadiene c) PCl_5 d) $CH_2 = CH_2$
3. Explain pre dissociation spectrum
4. Explain the Lande splitting factor (g).
5. Explain with examples, conjugate operations.
6. Generate the matrix representation of C_3 operation.
7. What are the factors responsible for lifetime broadening?
8. What is Stark effect?
9. What are *prolate* and *oblate* molecules? Give examples.
10. Stokes lines are more intense than antistokes lines. Why?
11. Calculate energy in wave numbers per mol for a radiation of wave length 500nm.
12. Delete σ_h from D_3h point group. What would be the resultant point group?
13. What do you mean by resonance Raman spectrum?

14. Explain the origin of laser.

Part B

(Answer any **seven** Questions. Each question has **2** weightage)

15. Show that E, C_3, C_3^2, σ_v, σ_v', and σ_v" form a mathematical group.
16. Construct the character table for C_{3v} point group by using GOT.
17. Write a shirt note on Mullikan's notations for irreducible representations.
18. Explain the fragmentation pattern of ketones on the basis of EIMS.
19. Reduce the representation Γr. You are provided with the character table.

C_{2v}	E	C_2	σ_{vxz}	σ_{vyz}		
A1	1	1	1	1	Tz	x^2, y^2, z^2
A2	1	1	-1	-1	Rz	xy
B1	1	-1	1	-1	Tx, Ry	xz
B2	1	-1	-1	1	Ty, Rx	yz

20. What is meant by PQR branches of lines? How are they formed?
21. How will you determine the dissociation energy of a diatomic molecule from vibration spectrum? Explain.
22. Explain the terms: a) Vanishing integrals b) Overlap integrals c) Exchange integrals
23. Explain the electronic spectra of conjugated molecules.
24. HCl shows absorption at 2990cm^{-1}. Calculate the force constant of the molecule.

Part C

(Answer any **two** Questions. Each question has **4** weightage)

25. Get the representation of normal modes of vibration of NH_3 molecule. Predict the IR and Raman activity of these modes. Character table is given.

C_{3v}	E	$2C_3$	$3\sigma_v$		

A1	1	1	1	Tz	x^2+y^2, z^2
A2					
E	1	1	-1	Rz	
	2	-1	0	(Tx, Ty)	(x^2-y^2, xy)
				(Rx,Ry)	(x^2,y^2)

26. Comment on the rotational spectrum of polyatomic molecules. How is it helpful in the determination of different bond lengths in a polyatomic molecule?
27. Find the molecular orbital of HCHO. C_{2v} character table is given below. Comment on the various electronic transitions in this molecule.

C_{2v}	E	C_2	σ_{vxz}	σ_{vyz}		
A1	1	1	1	1	Tz	x^2, y^2, z^2
A2	1	1	-1	-1	Rz	xy
B1	1	-1	1	-1	Tx, Ry	xz
	1	-1	-1	1	Ty, Rx	yz
B2						

28. Discuss briefly the principle of electron paramagnetic resonance spectroscopy.