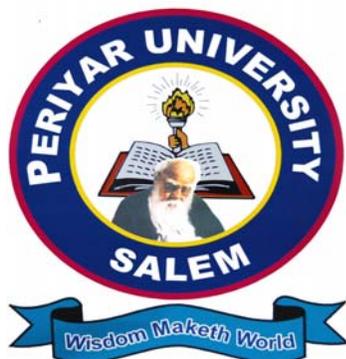


**PERIYAR UNIVERSITY
PERIYAR PALKALAI NAGAR
SALEM – 636 011**



**DEGREE OF MASTER OF SCIENCE
CHOICE BASED CREDIT SYSTEM
SYLLABUS FOR BRANCH IV (B) M.Sc. CHEMISTRY
FOR THE STUDENTS ADMITTED FROM THE
ACADEMIC YEAR 2012 – 2013 ONWARDS**

REGULATIONS AND SYLLABUS

Course of Study FIRST YEAR Semester I

| Code No. | Course | Subject | Work load per Semester (hours) |
|----------|----------------------|---------------------------------|--------------------------------|
| | Core Paper – I | Organic Chemistry I | 75 |
| | Core Paper – II | Inorganic Chemistry I | 75 |
| | Core Paper – III | Physical Chemistry I | 75 |
| | Elective Paper - I | Polymer Chemistry | 90 |
| | Core Practical – I | Organic Chemistry Practical I | 45 |
| | Core Practical – II | Inorganic Chemistry Practical I | 45 |
| | Core Practical - III | Physical Chemistry Practical I | 45 |

M. Sc. Chemistry
 (For the Candidates admitted from the academic year 2012 – 2013
 and onwards)
Course of Study
FIRST YEAR
Semester I

| Semester | Code | Course | Course Title | Hrs. | Credit | Marks | | |
|----------|------|----------------------|---------------------------------|------|--------|-------|----|-------|
| | | | | | | CIA | EA | Total |
| I | | Core Paper – I | Organic chemistry I | 5 | 4 | 25 | 75 | 100 |
| | | Core Paper – II | Inorganic chemistry I | 5 | 4 | 25 | 75 | 100 |
| | | Core Paper – III | Physical chemistry I | 5 | 4 | 25 | 75 | 100 |
| | | Elective Paper – I | Polymer chemistry | 6 | 4 | 25 | 75 | 100 |
| | | Core Practical – I | Organic chemistry practical I | 3 | - | - | - | - |
| | | Core Practical – II | Inorganic chemistry practical I | 3 | - | - | - | - |
| | | Core Practical - III | Physical chemistry practical I | 3 | - | - | - | - |

FIRST SEMESTER
Core Paper - I
ORGANIC CHEMISTRY – I
(75 Hours)

UNIT – I Nomenclature and Reaction Mechanism (15 Hours)

IUPAC Nomenclature for Aliphatic and Aromatic organic compounds and Heterocyclic compounds such as purine and pyrimidine.

Reaction Mechanisms : Types of mechanisms : Heterolytic, Homolytic and Pericyclic mechanisms – a general study.

Reaction intermediates : Formation, stability and structure of carbonium ions, carbanions, carbenes, nitrenes and free radicals.

Free radical reactions : Sandmeyer reaction, Gomberg-Bachmann reaction, Pschorr reaction and Ullmann reaction, mechanism of Hunsdiecker reaction.

UNIT – II Structure and Reactivity (15 Hours)

Effect of structure on reactivity – resonance and fields effects, steric effects, quantitative treatment – the Hammett equation and linear free energy relationship, substituent and reaction constant, Taft equation. Thermodynamic and kinetic requirements for reactions, thermodynamic and kinetic control reactions, Hammonds postulate, Microscopic reversibility. Potential energy diagrams, transition states and intermediates, methods of determining mechanisms – identification of products and determination of the presence of an intermediate, isotopic labeling, isotope effects.

UNIT – III Stereochemistry (15 Hours)

Homotopic, enantiotopic, diastereotopic H atoms, groups in organic molecules. Fischer, Newman and Sawhorse projections and their interconversion. Optical activity in the absence of chiral carbon – biphenyls, allenes and spiranes – R and S notations. Chirality due to helical shape, trans cyclooctene. E – Z isomerism of olefins containing one double bond and more than one double bond. Stereospecific and stereoselective synthesis with suitable examples, asymmetric synthesis – Cram's rule.

UNIT – IV Aliphatic Nucleophilic Substitution Reactions (15 Hours)

The S_N^2 , S_N^1 , mechanisms. The neighbouring group mechanism, neighbouring group participation by π and σ bonds, anchimeric assistance. Nucleophilic substitution at an allylic, aliphatic trigonal and vinylic carbon.

Reactivity effects of substrates structure, attacking nucleophile, leaving group and reaction medium, ambident nucleophile, regioselectivity. Williamson reaction, Vofbraun reaction, hydrolysis of esters, Claisen and Dieckmann condensation.

UNIT – V Heterocyclic Compounds

(15 Hours)

Synthesis and properties of imidazole, oxazole and thiazole.

Synthesis, properties and structural elucidation of flavones, isoflavones and anthocyanins.

Synthesis of pyrimidines, synthesis and structural elucidation of purines (uric acid and caffeine).

Text Books

1. Jerry March, **Advanced Organic Chemistry-Reactions, Mechanisms and Structure**, Fourth Edition, John Wiley & Sons (1992)
2. Francis A. Carey, **Organic Chemistry**, Third Edition, The McGraw-Hill Companies, Inc., 1996.
3. P.S. Kalsi, **Organic Reactions and Mechanisms**, Second Edition, New Age International Publishers, 2002.
4. Ernest L. Eliel, **Stereochemistry of Carbon Compounds**, T.M.H Edition, Tata McGraw-Hill Publishing Company, 1995.
5. P.S. Kalsi, **Stereochemistry – Conformation and Mechanism**, 6th Edition, Wiley Eastern Limited, 2005.
6. I.L. Finar, **Organic Chemistry**, Volume II, Fifth Edition, First Indian reprint, Pearson Education Asia Pte. Ltd., (2000)

Reference Books

1. P.S. Kalsi, **Stereochemistry and Mechanism through solved problems**, Second Edition, New Age International Publishers, 1994.
2. D. Nasipuri, **Stereochemistry of Organic Compounds**, 2nd Edition, New Age International Publishers, 1994.
3. S.M. Mukherji and S. P. Singh, **Reaction Mechanism in Organic Chemistry**, 1st Edition, Macmillan, 1976.
4. R.T. Morrison and R.N. Boyd, **Organic Chemistry**, 6th Edition, Prentice-Hall, 1992.
5. R.O.C. Norman, **Principles of Organic Synthesis**, Second Edition, Chapman and Hall, 1978.

6. R.M. Acheson, **Introduction to Chemistry of Heterocyclic Compounds**, 2nd Edition, Interscience Publishers, 1967.
7. J.A. Joule and G.F. Smith, **Heterocyclic Chemistry**, Van Nostrand Reinhold Co., London, 1978.

Core Paper - II
INORGANIC CHEMISTRY-I
(75 Hours)

UNIT-I Structure and Bonding (15 Hours)

Hard and Soft acids and bases-classifications, Acid-Base strength, hardness, symbiosis, Theoretical basis of Hardness and Softness, applications of HSAB.

Rings-Phosphazenes-Structure, Craig and Peddock model, Dewar model, polyorganophosphazenes, Polysulphur –nitrogen compounds.

Inorganic polymers-Silicates-structure, Pauling's rule, properties, correlation and application; Molecular sieves.

Polyacids- Isopolyacids of V, Cr, Mo and W; Heteropolyacids of Mo and W (only structural aspects).

UNIT-II Nuclear Chemistry-I (15 Hours)

Nuclear properties –Nuclear spin and moments, origin of nuclear forces, features of the liquid drop and the shell models of the nucleus; Modes of radioactive decay-orbital electron capture, nuclear isomerism, internal conversion; Detection and determination of activity-GM, Scintillation and Cherenkov counters.

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

UNIT III Nuclear Chemistry-II (15 Hours)

Applications relating to Nuclear Chemistry-Neutron activation analysis, Radio pharmacology, Radiation protection and safety precautions, Isotope dilution analysis.

Radiation Chemistry- radiation dosimetry, radiolysis of water, the hydrated electron.

UNIT IV Properties of Solids (15 Hours)

Electrical properties of solids – Band Theory, semiconductors, super conductors, solid state electrolytes; Magnetic properties – dia, para, ferro, antiferro and ferrimagnetism; hysteresis; Optical properties – solid – state lasers and Inorganic phosphors.

Reactions in solid state and phase transitions – diffusion coefficient, diffusion mechanism, vacancy and interstitial diffusions, formation of spinels; solid solutions, order-disorder transformations and super structure.

UNIT V Solid-State chemistry (15 Hours)

Defects in solids- Point defects, line defects and surface defects; Dislocations- Non-stoichiometric compounds; Use of X-ray powder data in identifying inorganic crystalline solids; details for cubic systems; Structures of NiAs, CdI₂, Pervoskite, rutile, fluorite and antiferroite-zinc blende and wurtzite.

Text books

1. J.E.Huheey, E.A.Keiter and R.L.Keiter, **Inorganic chemistry-principles of structure and reactivity**, 4th edition, Pearson-Education, 2002
2. F.A.Cotton and G.Wilkinson, **Advanced Inorganic Chemistry**, Wiley Eastern, 5th edition, 1988.
3. E.A.V.Ebsworth, D.WH.Rankine and S.Craddock, **Structural methods in Inorganic Chemistry**, Black well Scientific publication, 1987
4. R.S.Drago, **Physical methods in chemistry**, Reinhold, NewYork,1968
5. Charles A.Depuy and Orville L.Chapman, **Molecular reactions and photochemistry**, Prentice Hall, 1992
6. A.W.Adamson and P.Fleischauer, **Concepts of Inorganic Photochemistry**, Wiley, 1975.
7. H.J.Emelius and Sharpe, **Modern aspects of Inorganic chemistry**, Universal book stall, New Delhi, 1989
8. S.Glasstone, **Source book of Atomic Energy**, Van Nonstrand Co.,1969.
9. H.J.Arniker, **Essentials of Nuclear Chemistry**, 2nd edition Wiley eastern Co.,1987.
10. D.M.Adams, **Inorganic Solids**, John Wiley Sons, 1974
11. A.R.West, **Basic Solid State Chemistry**, John Wiley,1991.

Reference Books

1. N.H. Ray , Inorganic Polymers, Academic Press, 1978.
2. K.F. Purcell and J.C. Kotz, Inorganic Chemistry, WB Saunders Co., USA 1977.
3. G.S. Manku, Inorganic Chemistry, T.M.H. Co., 1984.
4. N.J.Turro, Modern moleculer photochemistry, Benjamin/Cummings, Menlo Park, California, 1978.
5. H.A.O. Hill and P.Day, Physical methods in advanced Inorganic chemistry, John Wiley, 1986.

6. A.K. Srivatsava and P.C. Jain, Elements of Nuclear Chemistry, S.Chand and Co., 1989.
7. G. Friedlander, J.W.Kennedy and J.M. Miller, Nuclear and Radio Chemistry, Wiley., 1964.
8. Mullor, Inorganic structural chemistry, Wiley, New York, 1993.

Core Paper - III

PHYSICAL CHEMISTRY – I

(75 Hours)

Unit – I Classical Thermodynamics – I (15 Hours)

Maxwell's relations and thermodynamic equations of state – applications in the evaluation of $C_p - C_v$ for solids and for vanderwaals gases, $C_p - C_v$ in terms of coefficient of expansion and coefficient of compressibility – Relation between C_p and C_v – Partial molar properties – Gibbs – Duhem equation – Partial molar free energy (Chemical Potential) – Determination of chemical potential [Direct Method and Method of Intercepts] and partial molar volume – variation of chemical potential with Temperature and Pressure

Unit – II Chemical Kinetics – I (15 Hours)

Theories of Reaction rates – Arrhenius theory – effect of temperature on reaction rate – Hard – Sphere collision theory of reaction rates – molecular beams – Reaction cross section – effectiveness of collisions – Probability factor.

Transition state theory of reaction rates – Potential energy surface – Partition functions and activated complex – Eyring equation – Comparison of collision theory and activated complex theory – Estimation of free energy, enthalpy and entropy of activation and their significance.

Unit – III Quantum Chemistry – I (15 Hours)

Black body Radiation – Experimental results of Black body radiation – Photoelectric effect – De – Broglie equation – Heisenberg uncertainty principle – Compton effect – operators and commutation relations – quantum mechanical postulates – Schrodinger equation and its solution to the problem of a particle in one and three dimensional boxes – the harmonic oscillator.

Unit – IV Group Theory – I (15 Hours)

Symmetry elements and symmetry operations – Point groups – identification and representation of groups – comparison of Molecular symmetry with Crystallographic symmetry – Reducible and irreducible representation – Direct product representation – Great orthogonality theorem and its consequences – Character Table and their uses.

Unit – V Spectroscopy – I (15 Hours)

Interaction of matter with radiation– Rotation spectroscopy – Rigid Rotor – Intensity of spectral lines – Molecular parameters from rotation spectra - Effect of

isotopic substitution on the rotation spectra . Vibrational spectroscopy – harmonic oscillator – anharmonic oscillator – Hot bands – selection rules – Vibrational spectra of polyatomic molecules – Overtones and combination frequencies – Fermi Resonance.

Raman spectroscopy – Raman effect – Rotational and vibrational Raman Spectra – Mutual Exclusion Rule. Electronic spectroscopy – Electronic spectra of diatomic molecules – vibrational coarse structure – Franck – Condon Principle.

Text Books:

1. S.Glasstone, Thermodynamics for chemists, Affiliated East West press, New Delhi, 1960.
2. J. Rajaram and J.C. Kuriacose, Thermodynamics for students of chemistry, Lal Nagin Chand, New Delhi, 1986.
3. J. Rajaram and J.C. Kuriacose, Kinetics and mechanism of chemical transformation Macmillan India Ltd., 1993.
4. K.J.Laidlar, Chemical Kinetics, Harper and Row Newyork, 1987.
5. D.A. Mcquarrie, Quantum chemistry, University science books, Mill Valley, California (1983)
6. R.K. Prasad, Quantum Chemistry, Wiley Eastern, New Delhi, 1992.
7. V.Ramakrishnan and M.S.Gopinathan, Group theory in chemistry, Vishal Publications, 1988.
8. K.V.Raman, Group theory and its application to chemistry, Tata McGraw Hill Publishing Co., 1990.
9. Raymond chang, Basic principles of Spectroscopy, McGraw Hill Ltd., New York, 1971.
10. C.N. Banwell, Fundamentals of Molecular Spectroscopy, Mc Graw Hill, Newyork 1966.

Reference Books:

1. W.J. Moore, Physical Chemistry, Orient Longman, London, 1972.
2. K.G. Den beigh, Thermodynamics of Steady state, Meklien and Co., London, 1951.
3. L.K. Nash, Elements of Chemical Thermodynamics, Addison Wesley, 1962.
4. R.G.Frost and Pearson, Kinetics and Mechanism, Wiley, Newyork, 1961.
5. J.W. Moore and R.G. Pearson, Kinetics and Mechanism, 1981.

6. C.Capellos and B.H.J. Bielski, Kinetic systems, Willey interscience, Newyork, 1968.
7. G.M.Harris, Chemical Kinetics, D.C. Heath and Co., 1966.
8. I.N.Levine, Quantum chemistry, Allyn and Bacon, Boston, 1983.
9. J.Goodman, Contemporary Quantum Chemistry, An Introduction, Plenum Press, Newyork, 1977.
10. F.J.Bockhoff, Elements of Quantum theory, Addison Wesley, Reading, Mass, 1976.
11. P.W.Atkins, Physical Chemistry, Oxford University Press, Oxford., 1990.
12. P.W.Atkins, Molecular Quantum Mechanics, Oxford University Press, Oxford., 1983.
13. H.Eyring, J.Walter and G. Kimball, Quantum chemistry, John wiley and sons, Newyork, 1944.
14. L.S.Pauling and E.B.Wilsob, Introduction to Quantum Mechanics, Mc Graw Hill book Co., Newyork, 1935.
15. F.A. Cotton, Chemical Application of Group Theory, John wiley and Sons Inc., Newyork, 1971.
16. N. Tinkham, Group Theory and Quantum Mechanics, McGraw Hill Book Company, Newyork, 1964.
17. Alan Vincent, Molecular Symmetry and Group theory – Programmed Introduction to chemical applications, Wiley, Newyork, 1977.
18. G.M. Barrow, Introduction to Molecular Spectroscopy, Mc Grawhill, Newyork, 1962.
19. G.W.King, Spectroscopy and Molecular Structure, Holt, Rienehart and Winston, 1964.
20. E.B.Wilson, J.C. Decius and D.C.Cross, Molecular Vibrations, Mc Graw Hill Book Co., 1955.
21. B.P. Straughan and S.Walker, Spectroscopy Vol-I, Vol-II and Vol-III, Chapmann and Hall, 1976.

Elective Paper - I
POLYMER CHEMISTRY
(90 Hours)

UNIT – I Basic Concepts (18 Hours)

Monomers, repeat units, degree of polymerization, Linear, branched and network Polymers. Condensation Polymerization : Mechanism of stepwise polymerization. Kinetics and statistics of linear stepwise polymerization. Addition polymerization : Free radical, cationic and anionic polymerization. Polymerization conditions. Polymerization in homogeneous and heterogeneous systems.

UNIT – II Co-ordination Polymerization (18 Hours)

Kinetics, mono and bimetallic mechanism of co-ordination polymers. Zeigler Natta catalyst, co-polymerization: Block and graft co-polymers, kinetics of copolymerization. Types of co-polymerization. Reactivity ratio.

UNIT – III Molecular Weight and Properties (18 Hours)

Polydispersion – average molecular weight concept, number, weight and viscosity average molecular weights. Measurement of molecular weights. Viscosity, light scattering, osmotic and ultracentrifugation methods. Polymer structure and physical properties – crystalline melting point T_m . The glass transition temperature. Determination of T_g . Relationship between T_m and T_g .

UNIT – IV Polymer Processing (18 Hours)

Plastics, elastomers and fibres. Compounding, processing techniques: calendaring, die casting, rotational casting, film casting, injection moulding, blow moulding extrusion, moulding, thermoforming, foaming, reinforcing and fibre spinning.

UNIT – V Properties of Commercial Polymers (18 Hours)

Polyethylene, polyvinyl chloride, polyamides, polyesters, phenolic resins, epoxy resins and silicone polymers. Functional polymers, Fire retarding polymers and electrically conducting polymers. Biomedical polymers – contact lens, dental polymers, artificial heart, kidney, skin and blood cells.

Text Books

1. F.W. Billmeyer, **TextBook of Polymer Science**, 3rd Edition, J.Wiley, 2003.
2. V. R. Gowariker, N.V. Viswanathan and J. Sreedhar, **Polymer Science**, New Age Int., 1986.

Reference Books

1. H.R. Alcock and F.W. Lamber, **Contemporary Polymer Chemistry**, Prentice Hall, 1981.
2. P.J. Flory, **Principles of Polymer Chemistry**, Cornell University press, New York, 1953.
3. G. Odian, **Principles of Polymerization**, 2nd Edition, John Wiley & Sons, New York, 1981.

FIRST YEAR

Semester II

| Code No. | Course | Subject | Work load per Semester (hours) |
|----------|---------------------------|---------------------------------|--------------------------------|
| | Core Paper – IV | Organic Chemistry II | 75 |
| | Core Paper – V | Physical Chemistry II | 75 |
| | Elective Paper – II | Co-ordination Chemistry | 75 |
| | Extra Disciplinary Course | Biological Chemistry | 60 |
| | Core Practical – I | Organic Chemistry Practical I | 45 |
| | Core Practical – II | Inorganic Chemistry Practical I | 45 |
| | Core Practical - III | Physical Chemistry Practical I | 45 |
| | | Human Rights | 30 |

**FIRST YEAR
Semester II**

| Semester | Code | Course | Course Title | Hrs. | Credit | Marks | | |
|----------|------|----------------------|---------------------------------|--------------|--------|-------|----|-------|
| | | | | | | CIA | EA | Total |
| II | | Core Paper – IV | Organic chemistry II | 5 | 4 | 25 | 75 | 100 |
| | | Core Paper – V | Physical chemistry II | 5 | 4 | 25 | 75 | 100 |
| | | Elective Paper – II | Co-ordination chemistry | 5 | 4 | 25 | 75 | 100 |
| | | EDC * | Extra Disciplinary Course * | 4 | 4 | 25 | 75 | 100 |
| | | Core Practical – I | Organic chemistry practical I | 3 | 4 | 40 | 60 | 100 |
| | | Core Practical – II | Inorganic chemistry practical I | 3 | 4 | 40 | 60 | 100 |
| | | Core Practical - III | Physical chemistry practical I | 3 | 4 | 40 | 60 | 100 |
| | | | | Human Rights | 2 | 2 | | |

***EDC papers- for syllabus refer appendix I.**

SECOND SEMESTER
Core Paper - IV
ORGANIC CHEMISTRY – II
[75 Hours]

UNIT – I Elimination Reactions (15 Hours)

E1, E2, E1cB mechanisms, Orientation of the double bond- Hofmann and Saytzeff rule, competition between elimination and substitution, dehydration and dehydrohalogenation reactions, stereochemistry of E2 eliminations in cyclohexane ring systems, mechanism of pyrolytic eliminations, chugaev reaction and Cope elimination.

UNIT II Aromaticity (15 Hours)

Aromaticity of benzenoid, heterocyclic and non-benzenoid compounds, Huckel rule, aromatic systems with pi electron compounds other than six pi electrons, non – aromatic (cyclooctatetraene, etc.) and anti aromatic systems (cyclobutadiene, etc.), systems with more than 10 pi electrons - annulenes.

UNIT III Aromatic electrophilic and nucleophilic substitution reactions (15 Hours)

The arenium ion mechanism, typical reactions like nitration, sulphonation, halogenation, Friedel – Crafts alkylation, acylation and diazonium coupling, electrophilic substitution on monosubstituted benzene, orientation and reactivity – ortho, meta and para directing groups, ortho-para ratio, ipso attack, Gatterman, Gatterman- Koch, Vilsmeier, Reimer – Tiemann reaction.

Aromatic nucleophilic substitution reactions, the S_NAr mechanism, the aryl cation mechanism, the benzyne intermediate mechanism, aromatic nucleophilic substitution of activated halides – Ziegler alkylation, Chichibabin reaction.

UNIT – IV Conformational Analysis (15 Hours)

Conformational analysis of simple cyclic (chair and boat cyclohexanes) and acyclic (n-butane) systems, conformation of simple 1,2 disubstituted derivatives – (ethylene chlorohydrin and ethylene glycol), Conformational analysis and stereochemical features of disubstituted cyclohexanes (1,2 ; 1,3 ; 1,4 dialkyl cyclo hexanes),

conformation and stereochemistry of cis and trans decalins, effects of conformation on reactivity in acyclic and cyclohexanes, Oxidation and acylation of cyclohexanols, reduction of cyclohexanones, esterification and hydrolysis of cyclohexane carboxylic acid derivatives.

UNIT – V Reagents in Organic Synthesis (15 Hours)

Synthesis of simple organic molecules using standard reactions like acylation and alkylation of enamines and active methylene compounds. Sulphur ylides. Robinson annulation, protection and deprotection of functional groups (R-OH, R-CHO, RCOR, R- NH₂ and R-COOH) Reagents and their uses: DCC, trimethyl silyl iodide, trimethyl silyl chloride, 1,3 – dithiane (umpolung), diisobutylaluminium hydride (DIBAL), 9BBN, Baker's yeast and Gilman's reagent.

Text Books

1. Jerry March, **Advanced Organic Chemistry-Reactions, Mechanisms and Structure**, Fourth Edition, John Wiley & Sons (1992)
2. Francis A. Carey, **Organic Chemistry**, Third Edition, The McGraw-Hill Companies, Inc., 1996.
3. P.S. Kalsi, **Organic Reactions and Mechanisms**, Second Edition, New Age International Publishers, 2002.
4. P.S. Kalsi, **Stereochemistry – Conformation and Mechanism**, 6th Edition, Wiley Eastern Limited, 2005.
5. I.L. Finar, **Organic Chemistry**, Volume II, Fifth Edition, First Indian reprint, Pearson Education Asia Pte. Ltd., (2000)

Reference Books

1. S. H. Pine, J.B. Hendrickson, D.J. Cram and G.S. Hammond, **Organic Chemistry**, IV Edn., McGraw Hill Company, 1980.
2. S.M. Mukherji and S. P. Singh, **Reaction Mechanism in Organic Chemistry**, 1st Edition, Macmillan, 1976.
3. R.T. Morrison and R.N. Boyd, **Organic Chemistry**, Prentice-Hall, 1992.
4. R.O.C. Norman, **Principles of Organic Synthesis**, Second Edition, Chapman and Hall, 1978.

5. S.M. Mukherji and S.P. Singh, **Reaction Mechanism in Organic Chemistry**, III Edn. 1984. MacMillan.

Core Paper - V
PHYSICAL CHEMISTRY – II

[75 Hours]

UNIT – I Classical Thermodynamics – II (15 Hours)

Thermodynamics of ideal and real gases, gas mixtures – Fugacity – definition – Methods of determination of fugacity – Variation of fugacity with temperature and pressure.

Standard states for gases, liquids, solids and components of solutions – determination of activities and activity coefficient from Vapour pressure, Freezing point, Boiling point and EMF – measurements.

Solution of Electrolytes – mean ionic activity, mean ionic molality and mean ionic activity coefficients – determination of activity coefficient from Freezing Point, EMF and Solubility measurements – Concept of ionic strength.

UNIT – II Chemical Kinetics – II (15 Hours)

Reactions in solutions – comparison between gas phase and solution reactions – the influence of solvent, ionic strength, dielectric constant and pressure on reaction in solution – Kinetic isotope effects – Linear free energy relationship – Hammett and Taft equations.

UNIT – III Quantum Chemistry –II (15 Hours)

Schrödinger equation for the rigid rotator and Hydrogen atom – arriving solution for energy and wave function – the origin of quantum numbers and their physical significance – Probability distribution of electrons.

Approximation methods – Perturbation and Variation methods – application of Variation method to Hydrogen and Helium atom – Spin - orbit interaction – LS coupling and JJ coupling – Term symbols and spectroscopic states. Ground state term symbols for simple atoms.

UNIT – IV Group Theory – II

(15 Hours)

Symmetry selection rules for vibrational, Electronic and Raman Spectra – determination of representation of vibrational modes in non-linear molecules such as H₂O, CH₄, XeF₄, SF₆ and NH₃ – symmetry of Hybrid orbitals in non-linear molecule (BF₃, CH₄, XeF₄, PCl₅ and SF₆) – Electronic spectra of formaldehyde.

UNIT – V Surface Chemistry and Catalysis

(15 Hours)

Kinetics of surface reactions: Physical and chemical adsorption – adsorption isotherms – types of adsorption isotherms – Langmuir adsorption isotherm – B.E.T theory for multilayer adsorption – measurement of surface area – Mechanism of heterogeneous catalytic reactions – the adsorption coefficient and its significance.

Acid – Base catalysis – mechanism – Bronsted catalysis Law – catalysis by enzymes – rate of enzyme catalysed reactions – effect of substrate concentration, pH and temperature on enzyme catalysed reactions – Michael – Menton's equation.

Text Books:

1. S.Glasstone, **Thermodynamics for chemists**, Affiliated East West press, New Delhi, 1960.
2. J. Rajaram and J.C. Kuriacose, **Thermodynamics for students of chemistry**, Lal Nagin Chand, New Delhi, 1986.
3. J. Rajaram and J.C. Kuriacose, **Kinetics and mechanism of chemical transformation**, Macmillan India Ltd., 1993.
4. K.J.Laidlar, **Chemical Kinetics**, Harper and Row, Newyork, 1987.
5. R.K. Prasad, **Quantum Chemistry**, Wiley Eastern, New Delhi, 1992.
6. M.W. Hanna, **Quantum mechanics in chemistry**, W.A. Benjamin INC, London (1965)
7. V.Ramakrishnan and M.S.Gopinathan, **Group theory in chemistry**, Vishal Publications, 1988.
8. K.V.Raman, **Group theory and its application to chemistry**, Tata McGraw Hill Publishing Co., 1990.
9. Gurudeep raj, **Advanced Physical Chemistry**, Goel Publishing House, Meerut.

Reference Books:

1. W.J. Moore, **Physical Chemistry**, Orient Longman, London, 1972.
2. K.G. Den beigh, **Thermodynamics of Steady state**, Meklien and Co., London, 1951.
3. L.K. Nash, **Elements of Chemical Thermodynamics**, Addison Wesley, 1962.
4. R.G.Frost and Pearson, **Kinetics and Mechanism**, Wiley, Newyork, 1961.
5. J.W. Moore and R.G. Pearson, **Kinetics and Mechanism**, 1981.
6. C.Capellos and B.H.J. Bielski, **Kinetic systems**, Willey interscience, Newyork, 1968.
7. G.M.Harris, **Chemical Kinetics**, D.C. Heath and Co., 1966.
8. A.K. Chandra, **Introductory Quantum Chemistry**, Tata Mc Graw Hill.
9. D.A. Mc Quarrie, **Quantum Chemistry**, University science books, Mill Valley, California (1983).
10. P.W.Atkins, **Molecular Quantum Mechanics**, Oxford University Press, Oxford., 1983.
11. I.N.Levine, **Quantum chemistry**, Allyn and Bacon, Boston, 1983.
12. F.J.Bockhoff, **Elements of Quantum theory**, Addison Wesley, Reading, Mass, 1976.
13. H.Eyring, J.Walter and G. Kimball, **Quantum chemistry**, John wiley and sons, Newyork, 1944.
14. L.S.Pauling and E.B.Wilsob, **Introduction to Quantum Mechanics**, Mc Graw Hill book Co., Newyork, 1935.
15. F.A. Cotton, **Chemical Application of Group Theory**, John wiley and Sons Inc., Newyork, 1971.
16. N. Tinkham, **Group Theory and Quantum Mechanics**, McGraw Hill Book Company, Newyork, 1964.
17. Alan Vincent, **Molecular Symmetry and Group theory – Programmed Introduction to chemical applications**, Wiley, Newyork, 1977.

Elective Paper - II
CO - ORDINATION CHEMISTRY

[75 Hours]

UNIT – I Metal - Ligand Bonding (15 Hours)

Crystal field theory – splitting of d- orbitals under various geometries, factors affecting splitting, CFSE, evidences for CFSE (Structural and thermodynamic effects), Spectrochemical series, Jorgensen relation, site preferences; Jahn – Teller distortion – Splitting pattern in trigonal pyramid, square pyramidal and cubic symmetries, Dynamic and Static J.T. effect, Jahn – Teller effect and Chelation; Limitations of CFT; Evidences for metal – ligand overlap; M.O. theory and energy level diagrams, concept of weak and strong fields, sigma and pi bonding in complexes, nephelauxetic effect, magnetic properties of complexes.

UNIT – II Stability and stereochemical aspects of complexes (15 Hours)

Stability of complexes – Factors affecting stability of complexes, thermodynamic aspects of complex formation, Stepwise and overall formation constants, stability correlations, statistical and chelate effects; Determination of stability constant – Polarographic, photometric and potentiometric methods.

Stereochemical aspects – Stereoisomerism in inorganic complexes, isomerism arising out of ligand distribution and ligand conformation, chirality and nomenclature of chiral complexes; application of ORD and CD in the identification of chirality of complexes.

Macrocyclic ligands – types – porphyrins, corrins, Schiff's bases, crown ethers and cryptates. (simple complexes)

UNIT – III Reaction mechanisms in Complexes (15 Hours)

Electron transfer reactions – Outer and inner sphere processes; atom transfer reaction, formation and rearrangement of precursor complexes, the bridging ligand, successor complexes; Cross reactions and Marcus – Hush theory (no derivation)

Reaction mechanism of coordination compounds – Substitution reactions, Labile and inert complexes. Substitution in square planar complexes – General mechanism;

reactivity of Platinum complexes; influences of entering and leaving groups; the trans effect – theories, trans influence.

Substitution in octahedral complexes – general mechanism, discussion of A, D, I_A, I_D and DC_B mechanism, replacement of coordinated water; mechanism of acid hydrolysis and base hydrolysis – Conjugate base mechanism; direct and indirect evidences in favour of the mechanism; application of substitution reaction in the synthesis of Platinum and Cobalt complexes.

UNIT – IV Organometallic Chemistry (15 Hours)

Carbonyls – 18 electron rule, isolobal concept – application to structure of carbonyls (simple and polynuclear); Chain Carbon donors - Olefins, acetylene and allyl complexes – Synthesis, structure and bonding; Cyclic carbon donors -Metallocene – synthesis, structure and bonding (Ferrocene only). Nitrosyls – bridging and terminal nitrosyls, bent and linear nitrosyls;

Substitution – electrophilic and nucleophilic attack on ligands. Carbonylation and decarbonylation; oxidative addition and reductive elimination to organometallics; fluxional isomerism.

UNIT – V Catalysis (15 Hours)

Hydrogenation of olefins (Wilkinson's catalyst); hydroformylation of olefins using Cobalt or Rhodium catalysts (oxo process); Oxidation of olefins to aldehydes and ketones (Wacker process); polymerization (Ziegler- Natta catalyst); Cyclo oligomerization of acetylene using Nickel catalyst (Reppé's catalyst); polymer bound catalysts.

Text Books:

1. H.J.Emelius and Sharpe, **Modern aspects of Inorganic chemistry**, Universal book stall, New Delhi, 1989
2. F. Basolo and R.G. Pearson, **Mechanism of Inorganic Reactions**, Wiley Eastern, 1967.
3. J.E.Huheey, E.A.Keiter and R.L.Keiter, **Inorganic chemistry-principles of structure and reactivity**, 4th edition, Pearson-Education, 2002
4. F.A.Cotton and G.Wilkinson, **Advanced Inorganic Chemistry**, Wiley Eastern, 5th edition, 1988.

5. S.F.A. Kettle, **Coordination compounds**, ELBS, 1973.
6. K.F. Purcell and J.C. Kotz, **Inorganic Chemistry**, WB. Sanders Co. USA. 1977.
7. D.F. Shriver, P. W. Atkins and C.H. Longford, **Inorganic Chemistry**, ELBS, 2nd Edition, 1994.
8. R.B. Heslop and K. Jones, **Inorganic Chemistry**, Elsevier, 1976.

Reference Books

1. D. Bannerjea, **Coordination Chemistry**, Tata – McGraw Hill, 1993.
2. M.L. Tobe, **Inorganic Reaction Mechanism**, Nelson, 1972.
3. K. Burger, **Coordination Chemistry Experimental Methods**, Butterworths, 1973.
4. B.N. Figgis, **Introduction to Ligand Fields**, Wiley Eastern Ltd, NewDelhi, 1976.
5. W.E. Addison, **Structural Principles of Inorganic Chemistry**, Longman, 1961.

Core Practical - I

ORGANIC CHEMISTRY PRACTICAL – I

1. Identification of components in a two component mixture and preparation of their derivatives. Determination of boiling point / melting point for components and melting point for their derivatives.

II Preparation

1. Beta naphthyl methyl ether from beta naphthol
2. Beta glucose penta acetate from glucose
3. Ortho-benzoyl benzoic acid from phthalic anhydride
4. Resacetophenone from resorcinol
5. para- Nitro benzoic acid from para nitro toluene
6. meta-Nitroaniline from meta dinitrobenzene
7. Methyl orange from sulphanilic acid
8. Anthraquinone from anthracene
9. Benzhydrol from benzophenone
10. S-benzyl isothiuronium chloride from benzyl chloride

Reference :

1. B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, **Vogel's Practical Organic Chemistry**. 5th edn. ELBS, 1989.
2. Raj K. Bansal, **Laboratory manual of Organic Chemistry**, III Edn., New Age International (P) Ltd. 1996.

Distribution of Marks for Practical –I

| | |
|------------------------------|-------------------|
| Qualitative organic analysis | : 30 marks |
| Preparation | : 15 marks |
| Viva-voce in practical | : 10 marks |
| Record | : 5 marks |
| Total | : 60 marks |
| Duration | : 6 hours |

Core Practical - II

INORGANIC CHEMISTRY PRACTICAL – I

Part –I

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

Part – II

- a) Colorimetric analysis: Visual and photometric; determination of iron, nickel, manganese and copper.
- b) Preparation of the following :
 - i) Potassium trioxalatoaluminate (III) trihydrate
 - ii) Trithioureacopper (I) chloride
 - iii) Potassium trioxalatochromate (III) trihydrate
 - iv) Sodium bis (thiosulphato) cuprate (I)
 - v) Tetramminecopper (II) sulphate
 - vi) Potassium Tetrachlorocuprate (II)
- c) Separation of mixture of two metal ions by paper chromatography.

Reference Books

1. G. Svehla, **Vogel's qualitative Inorganic analysis**, VI Edition, Orient Longman, 1987.
2. V.V. Ramanujam, **Inorganic Semimicro Qualitative analysis**. National Publishing Co., 1971.

Distribution of Marks for Practical –I

| | |
|--------------------------|-------------------|
| Qualitative analysis | : 20 marks |
| Colorimetric analysis | : 15 marks |
| Preparation | : 10 marks |
| Viva – voce in practical | : 10 marks |
| Record | : 5 marks |
| Total | : 60 marks |
| Duration | : 6 hours |

Core Practical - III

08PCHP03 PHYSICAL CHEMISTRY PRACTICAL - I

Experiments in chemical kinetics, phase rule, Chemical equilibrium and Conductivity measurements:

DETAILED LIST OF EXPERIMENTS

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

1. Study the kinetics of acid hydrolysis of an ester, determination of the temperature coefficient of the reaction and determination of the activation energy of the hydrolysis of ethylacetate.
2. Study the kinetics of the reaction between acetone and iodine in acidic medium by half life method and determine the order with respect to iodine and acetone.
3. Study of the saponification of ethylacetate by sodium hydroxide conductometrically and determine the order of the reaction.
4. Determination of association factor of benzoic acid in benzene by distribution method.
5. Study the phase diagram for m-toluidine and glycerine system.
6. Construction of phase diagram for a simple binary system (naphthalene – phenanthrene and benzophenone – diphenylamine)
7. Construction of the phase diagram of the three component of partially immiscible liquid systems (DMSO – Water – Benzene; Water-Benzene –Acetic acid; Ethyl alcohol – Benzene – Water; Acetone-Chloroform – Water; Chloroform – Acetic acid-Water).
8. Determination of equivalent conductance of a weak acid at different concentrations and verify Ostwald's dilution law and calculation of the dissociation constant of the acid.

9. Determination of equivalent conductivity of a strong electrolyte at different concentrations and examine the validity of the Onsager's theory as limiting law at high dilutions.
10. Conductometric titrations of a mixture of HCl and CH₃COOH against Sodium hydroxide.
11. Compare the relative strength of acetic acid and monochloroacetic acid by conductivity method.

Reference Books

1. B.P. Levitt (Ed.). Findlay's Practical Physical Chemistry, 9th Edn., Longman, London, 1985.
2. J.N. Gurtu and R.Kapoor, Advanced Experimental Chemistry, Vol I. S. Chand & Co. Ltd., New Delhi, 1980.

Distribution of Marks for Practical –I

| | |
|------------------------|-------------------|
| Experiment | : 45 marks |
| Viva-voce in practical | : 10 marks |
| Record | : 5 marks |
| Total | : 60 marks |
| Duration | : 6 hours |

Distribution of Marks Theory

University Examinations (UE) : 75 Marks

Internal Assessment (IA) : 25 Marks

Classification of Internal Assessment Structure

| | | |
|------------|---|----------|
| Test | - | 10 Marks |
| Attendance | - | 5 Marks |
| Assignment | - | 5 Marks |
| Seminar | - | 5 Marks |

Total - **25 Marks**

Passing Minimum : IA : 50% - 12 Marks

Passing Minimum : UE : 50% - 38 Marks

Total Passing Minimum : - 50 Marks

PRACTICALS

University Examination (UE) : 60 Marks

Internal Assessment (IA) : 40 Marks

Passing Minimum (IA) : 50 % 20 Marks

Passing Minimum (UE) : 50 % 30 Marks

Total Passing Minimum : 50 Marks

Distribution of Internal Assessment Structure

| | |
|---------------------|-----------------|
| No of Experiments- | 10 Marks |
| Experimental Skill- | 10 Marks |
| Test - | 20 Marks |
| ----- | |
| Total | 40 Marks |
| ----- | |

Everything should be supported by proper record

Question Paper Pattern

Time : 3 Hours

Max Marks : 75

PART – A : 5 X 5 = 25

(Answer all questions)

(One question from each unit with internal choice)

PART – B : 5 X 10 = 50

(Answer all questions)

(One question from each unit with internal choice)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. DEGREE Branch IV - CHEMISTRY

First Semester
Core Paper - I

ORGANIC CHEMISTRY – I

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1.a) How do you classify the given reaction as substitution, addition or elimination reaction? give an example for each of the reactions.

Or

b) Write notes on the following reaction:

i) Ullmann reaction

ii) Hunsdiecker reaction

2. a) With chosen example, illustrate the terms kinetic and thermodynamic control of reactions.

Or

b) State and explain Hammonds postulate with potential energy diagram.

3. a) Discuss briefly the optical activity of spiranes and allenes.

Or

b) Explain what is meant by Fischer projection and state an example.

4. a) What are known as ambident nucleophiles and mention some important ambident nucleophiles?

Or

b) Explain the nature of attacking nucleophile and mention the important principles.

5 a) Give the synthesis and properties of Imidazole.

Or

b) Give the synthesis of purines.

PART – B (5 X 10 = 50 Marks)

Answer all the questions

6. a) (i) How do you explain the stability of t-butyl and benzyl cations ? (4)

(ii) Discuss the mechanism of Hunsdiecker reaction (6)

Or

b) (i) Give any two methods of generation of carbenes and nitrenes (4)

(ii) Discuss Sandmeyer reaction (3)

(iii) Discuss the characteristics of pericyclic reactions. (3)

7. a) i) State the Hammett equation and explain the significance of σ and ρ (3)

ii) Discuss the principle of microscopic reversibility. (3)

iii) Draw the potential energy diagrams for the reactions involving (a) no intermediate (bi) an intermediate. (4)

Or

- b) Explain the usefulness of the following methods in determining the mechanism of a reaction. Give suitable examples.
- Isotopic labelling
 - Primary isotope effect
 - Determination of the presence of an intermediate. (3 + 3 + 4)
8. a) i) Explain the homotopic, enantiotopic, and diastereotopic H atoms with examples. (6)
- ii) Discuss the optical activity in transcyclooctene and biphenyls. (4)
- Or**
- b). (i) Draw the Fischer projection, Newman and Sawhorse formulae of meso – tartaric acid. (6).
- (ii) Give examples for Stereo selective and Stereo specific reactions. What is the difference between them. (4)
- 9) a) i.) Briefly discuss the effects of substrates structure, attacking nucleophile, leaving group and reaction medium on the SN^1 and SN^2 reaction . (6)
- ii) Describe the mechanism of Von-braun reaction. (4)
- Or**
- b) Account for the following
- SN^1 reaction proceeds with retention of configuration.
 - Nucleophilic substitution at allylic substrate gives mixture of products.
 - Vinyl chloride is not easily hydrolysed by NaOH. (4+3+3)
- 10 a) i) Give the synthesis and structural elucidation of flavones. (7)
- ii) Give the synthesis of uric acid. (3)
- Or**
- b) i) Write the synthesis of thiazole and oxazole (6)
- ii) Give the synthesis of Caffeine (4).

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. DEGREE Branch IV – CHEMISTRY

First Semester
Core Paper - II
INORGANIC CHEMISTRY – I

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

- 1) a) Briefly explain any one theory of Hardness – Softness of acid bases

Or

- b) What are Phosphazenes? Give their formulae and shape.

2. a) Give the features of liquid drop model of the nucleus.

Or

b) Describe the construction and working of G.M. Counter.

3. a) Give a brief account of neutron activation analysis.

Or

b) Briefly explain the radiolysis of water

4. a) Write a short notes on solid state electrolytes.

Or

b) Write a note on super conductors.

5. a) Distinguish between spinels & inverse spinels.

Or

b) What are Frenkel and Schottky defects. Explain with examples.

PART – B (5 x 10 = 50 Marks)

Answer all questions.

6. a) Draw and explain the various silicate structure in detail (10)

Or

b) Write briefly about the heteropoly acids of molybdenum and tungsten (10)

7 a) i) Write notes on Compound nuclear theory (5)

ii) Discuss the types of photonuclear reaction. (5)

Or

b) i) Explain orbital electron capture with an example. (5)

ii) Discuss briefly the types of nuclear isomerism encountered in the radio elements. (5)

8. a) Write a note on

i) Radiation dosimetry (5)

ii) Isotope dilution analysis. (5)

Or

b) Write a note on

i) Radio Pharmacology (5)

ii) Radiation protection and safety precautions. (5)

9. a) What is phase Transition? Describe briefly order-disorder transitions. (10)

Or

b) i) Distinguish between Dia, Para and ferromagnetic substances. (6)

ii) Describe Band theory of solids (4)

10 a) i) Illustrate the use of X-ray powder technique in determining the structure of sodium chloride (5)

ii) What are the three types of cubic lattices? How are they distinguished using X- ray diffraction?. (5)

Or

b) Outline the features of the crystal structures.

i) Pervoskite

ii) Rutile

iii) Zinc blende (6)

iv) How do the crystal structure of Nickel arsenide differ from Cadmium

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. DEGREE Branch IV - CHEMISTRY
First Semester
Core Paper - III
PHYSICAL CHEMISTRY – I

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Write the maxwell's relationships

Or

b) Using Maxwell's relation derive the thermodynamic equations of state.

2. a) List out the postulates of transition state theory.

Or

b) Explain the significance of enthalpy and entropy of activation.

3. a) When lithium is irradiated with light, the kinetic energy of the ejected electron is 2.935×10^{-19} J for $\lambda = 300$ nm. Calculate the threshold frequency of Lithium atom ($h = 6.626 \times 10^{-34}$ JS)

Or

b) Discuss the properties of a Hermitian Operator.

4. a) Define the different types of symmetry elements present in a molecule.

Or

b) Compare molecular symmetry with crystallographic symmetry.

5. a) Discuss the effect of isotopic substitution on the rotation spectra.

Or

b) Define (i) Overtone (ii) Fermiresonance.

Part – B (5 x 10 = 50 Marks)

Answer all questions.

6. a) Define chemical potential. Explain its dependence on pressure and temperature

(2 + 4 + 4)

Or

b) (i) Explain the use of thermodynamic equation of state in the evaluation of $C_p - C_v$ for solids. (5)

(ii) Derive Gibbs Duhem equation. (5)

7 a) i) Explain the effect of temperature on reaction rate. (3)

ii) Give a detailed account on collision theory. (7)

Or

b) (i) Write notes on potential energy surfaces. (5)

(ii) Deduce Eyring equation under thermodynamic considerations. (5)

8 a) i) Apply Schrodinger wave equation and find the solution for a particle in one dimensional box. (6)

- ii) Explain Heisenberg's uncertainty principle. (4)
- Or**
- b) i) Explain the Postulates of quantum mechanics. (5)
 ii) Define a black body? Discuss the experimental results of a black body radiation. (5)
- 9 a) i) Explain the construction of C_{3v} character table. (5)
 ii) What is a character table? What do the various areas of the character table represent? (5)
- Or**
- b) i) Write notes on direct product representation. (5)
 ii) Arrive at the point group for the following molecules : Allene and XeF_4 (5)
- 10 a) (i) Bring out the differences between IR and Raman Spectra. (4)
 (ii) Explain Franck Condon Principle (3)
 (iii) Discuss the selection rule for rotational transition (3)
- Or**
- b) i) Discuss the rotational – vibrational Raman spectrum of a diatomic molecule (7)
 ii) Calculate the force constant for $H^{35}Cl$ from the fact that its fundamental vibrational frequency is $8.667 \times 10^{13} \text{ sec}^{-1}$. (3)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. DEGREE Branch – IV - CHEMISTRY
First Semester
Elective Paper - I
POLYMER CHEMISTRY

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) With suitable examples, explain linear and branched polymers.
 Or
 b) Write the mechanism of anionic polymerization with a suitable monomer and initiator.
2. a) What are Zeigler – Natta catalysts composed of? Write down the composition of two such catalysts.
 Or
 b) Describe the methods of synthesis of copolymers.
3. a) What are T_g and T_m ? Discuss their relations to the structure of a polymer.
 Or
 b) With a neat sketch explain the distribution of molecular weight of a typical polymer.
4. a) Write the basic structure of rubber. Outline the industrial importance of rubber.

Or

- b) Write a note on injection moulding.
5 a) Describe the general method of preparation of
i) Polyamide
ii) Bakelite

Or

- b) Explain the biomedical applications of acrylic acid with examples.

Part – B (5 x 10 = 50 Marks)

Answer all questions.

6. a) i) Define an expression for the rate constant of a self catalysed step polymerization reaction. (6)
ii) What are the raw materials for the manufacture of polyurethanes? Which kind of polymers are they ? (4)

Or

- b) (i) What are the common initiators in a cationic polymerization reaction? Explain the mechanism of cationic polymerization with a suitable monomer. (6)
(ii) Write down the different types of terminations encountered in a free radical polymerization. (4)

7. a) (i) Illustrate the experimental determination of monomer reactivity ratio. (5)
(ii) Derive Co-polymer equation. (5)

Or

- b) (i) Discuss the mechanism of coordination polymerization. (6)
(ii) How can you obtain rate of copolymerization. (4)

8. a) (i) Explain in detail the molecular weight determination of viscosity measurements (5)
(ii) Discuss about viscosity method of determination of molecular weight of polymers (5)

Or

- b) (i) Explain the ultra centrifugation technique for the determination of molecular weight of polymers (5)
(ii) Describe light scattering method of determination of molecular weight of a polymer sample. How is it related to \overline{M}_n ? (5)

- 9 a) (i) Account on the following techniques.
(1) Thermoforming
(2) Reinforcing (6)
(ii) Describe how three dimensional articles are produced by thermoforming techniques. (4)

Or

- b) (i) Explain the importance of compounding technique ? (5)
(ii) How foamed plastics are produced. (5)

- 10 a) (i) Account on
(1) Epoxy resins
(2) Flame retardant polymers (4)

- (ii) Write a note on electrically conducting polymers. (3)
(iii) What do the numbers 6.6 in nylon 66 represent. (3)

Or

- b) (i) Define the term 'functional polymers'. How do they differ from ordinary polymers. (3)
(ii) Write a note on silicone polymers (4)
(iii) What polymeric material is useful as dialyser membrane in artificial kidney? How is it produced? (3)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Second Semester
Core Paper - IV

ORGANIC CHEMISTRY - II

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1.a) Account for the orientation of double bond in E2 eliminations under Hofmann and Saytzeff conditions.

Or

b) What is Chugaev reaction? Explain what are its advantages over conventional methods of alkene preparation.

2. a) Write down the structure of [18] annulene. Comment on whether it is aromatic or not. Give reasons for your answer.

Or

b) With suitable examples, bring out the differences between a non – aromatic and an anti – aromatic substance.

3. a) What is Zeigler alkylation? Comment on the uses of this reaction.

Or

b) Describe the chichibabin reaction. Explain its importance in synthesis of organic compounds.

4. a) Draw the energy profile diagram for cyclohexane as a function of conformation and explain the stability of the different conformations.

Or

b) Discuss the conformation and stability of decalins.

5. a) What is DIBAL? Mention any one application for this reagent

Or

b) Illustrate the utility of Baker's yeast in the synthesis of organic compounds.

PART – B (5 X 10 = 50 Marks)

Answer all the questions

All questions carry equal marks

6. a) Discuss the effect of changes of E2 elimination with respect to the following: substrate, base, leaving group and medium (10)

Or

- b) i) Discuss the E1 mechanism (4)
ii) What is cope elimination? Give its mechanism (3)
iii) Discuss the salient features of dehydrohalogenation reactions. (3)

7. a) Explain the aromaticity of five heterocyclic compounds of your choice. (10)

Or

b) Discuss the aromaticity of non - benzenoid aromatic compounds (10)

8. a) i) Discuss the evidences in support of arenium ion mechanism in aromatic electrophilic substitution reaction. (5)

ii) Explain the mechanism of sulphonation of benzene. (5)

Or

b) (i) Discuss the evidences in favour of the S_NAr mechanism for the nucleophilic aromatic substitution. (5)

(ii) Explain ortho, meta and para directing groups with examples. (5)

9. a) i) Discuss the conformation, relative stability and optical activity of cis and trans – 1, 3 dimethyl cyclohexanes. (5)

ii) Discuss the effect of conformation on reactivity in cis – and trans 4-t – butyl cyclohexanol during acetylation (5)

Or

b) Draw the preferred conformation of the following and justify your answer:

- i) 2-Fluorocyclohexanol
ii) cis – 4- methyl cyclohexanol
iii) 2- Chlorocyclohexanone
iv) trans – 1, 3-Di – t – butylcyclohexane.
v) Ethylene glycol (10)

10. a) i) Write short notes on Robinson annulation reaction. (5)

ii) What are ylides? Give an example of sulphur ylide and explain the nature of bonding in it. (5)

Or

b) Discuss the synthetic applications of the following reagents with suitable examples.

- i) PCC
ii) DCC
iii) Trimethyl silyl iodide (4 + 3 + 3)

Model Question Paper

(For the candidate admitted from 2012 – 2013 onwards)

M.Sc. Degree – Branch – IV Chemistry

Second Semester

Core Paper - V

PHYSICAL CHEMISTRY – II

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Explain how the fugacity varies with temperature and pressure.

Or

b) How activity coefficient of an electrolyte in a solution is determined from Emf measurements.

2. a) Deduce Hammett equation.

Or

b) Discuss the influence of pressure on reactions in solutions.

3. a) Solve Schrodinger equation for rigid rotor

Or

b) Write notes on Term Symbols.

4. a) Give the symmetry selection rules for vibrational, electronic and Raman spectra.

Or

b) Determine the representation of vibrational modes of H₂O molecule.

5. a) Derive Langmuir Adsorption isotherm. What are its limiting cases?

Or

b) Calculate how long a hydrogen atom will remain on the surface of the solid at 298 K if its desorption activation energy is (i) 15 KJ mol⁻¹ ii) 150 KJ mol⁻¹. Assume that T₀ = 10⁻¹³ S.

PART – B (5 X 10 = 50 Marks)

Answer all the questions

All questions carry equal marks

6. a) Describe any two methods of determining fugacity. (10)

Or

b) i) Define ionic strength (2)

ii) Define the terms activity, mean ionic activity and mean ionic activity coefficient
How are they related. (8)

7. a) i) Write briefly about Taft relationship (5)

ii) Explain the influence of ionic strength on the rate constant of a reaction (5)

Or

b) i) Compare gas phase reaction with solution reactions. (4)

ii) Write an account of kinetic isotope effects (6)

8. a) Derive Schrodinger wave equation for hydrogen atom. (10)

Or

b) i) Outline how variation method is used for the solution of helium atom problem (5)

ii) Explain the application of variation method to hydrogen atom. (5)

9 a) How will you find the IR and Raman activity of the vibrational modes of NH_3 molecule. (10)

Or

b) With the help of D_{4h} character table find the set of orbital suitable for hybridisation in XeF_4 (10)

10 a) Derive the rate expression for enzyme catalysed reaction following Michaelis – Menton kinetics. How the Michaelis parameters are evaluated. (10)

Or

b) i) Tabulate the distinction between physisorption and Chemisorption (4)

ii) Discuss Langmuir – Hinshel wood and Langmuir – Rideal mechanism for heterogeneous catalytic reactions. (6)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Second Semester
Elective Paper - II
CO-ORDINATION CHEMISTRY

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Explain the following term :

- i) CFSE and
- ii) Spectrochemical series

Or

b) Give a comparative account of MO and CFT.

2. a) Discuss the thermodynamic aspects of complex formation

Or

b) Discuss the importance of porphyrins.

3. a) Explain the substitution reactions occurring in square planar platinum complexes.

Or

b) Write the applications of substitution reactions used for the synthesis of Cobalt complexes.

4. a) Apply the EAN rule and 18 electron rule to $\text{Fe}(\text{CO})_5$.

Or

b) Explain with an example oxidative addition reaction.

5. a) Write the mechanism of conversion of olefin into aldehyde in Wacker process

Or

b) Write notes on the application of polymer bound catalysts.

PART – B (5 X 10 = 50 Marks)

Answer all the questions

All questions carry equal marks

6. a) Draw and explain M.O diagrams of $[\text{Fe F}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ complexes (10)

Or

b) Discuss the MO treatment for octahedral complexes. (10)

7. a) i) Bringout the relationship between stepwise stability constants and over-all stability constants. Taking the complex ML_n , derive them. (5)

ii) How are the absolute configurations of optically active complexes determined by ORD and CD curves? (5)

Or

b) i) What do you understand by the term chirality? How are chiral complexes named? (5)

ii) Describe the polarographic method of determination of stability constant of a complex. (5)

8. a) Discuss the A and DC_B mechanism for the substitution reactions of octahedral complexes (10)

Or

b) i) Explain the atom transfer process occurring in electron transfer reactions. (5)

ii) Give the general mechanism for the substitution reactions taking place in octahedral complexes. (5)

9. a) i) Draw a qualitative MO energy level diagram for ferrocene indicating the occupancy of the orbitals and comment on the bonding. (10)

Or

b) i) Write an account on the preparation and stereochemistry of allyl complexes (5)

ii) Write an account on the alkene complexes of platinum (5)

10. a) i) Explain the use of Wilkinson's catalyst in the hydrogenation of alkenes (5)

ii) Write a note on Hydroformylation of olefins. (5)

Or

b) i) Outline the mechanism of Zeigler – Natta Polymerisation and point out the importance of the reaction. (6)

ii) What is Reppe's catalyst? Explain its use in the cyclooligomerisation of acetylene (4)

SECOND YEAR Semester III

| Code No. | Course | Subject | Work load per Semester (hours) |
|----------|----------------------|-------------------------------------|--------------------------------|
| | Core Paper – VI | Organic Chemistry III | 75 |
| | Core Paper – VII | Inorganic Chemistry II | 75 |
| | Core Paper – VIII | Physical Chemistry III | 75 |
| | Elective Paper – III | Electro Chemistry & Photo Chemistry | 90 |
| | Core Practical – IV | Organic Chemistry Practical II | 45 |
| | Core Practical – V | Inorganic Chemistry Practical II | 45 |
| | Core Practical - VI | Physical Chemistry Practical II | 45 |

SECOND YEAR Semester III

| Sem ester | Code | Course | Course Title | Hrs. | Credit | Marks | | |
|-----------|------|----------------------|-------------------------------------|------|--------|-------|----|-------|
| | | | | | | CIA | EA | Total |
| III | | Core Paper – VI | Organic Chemistry III | 5 | 5 | 25 | 75 | 100 |
| | | Core Paper – VII | Inorganic Chemistry II | 5 | 5 | 25 | 75 | 100 |
| | | Core Paper – VIII | Physical Chemistry III | 5 | 5 | 25 | 75 | 100 |
| | | Elective Paper – III | Electro Chemistry & Photo Chemistry | 6 | 4 | 25 | 75 | 100 |
| | | Core Practical – IV | Organic Chemistry Practical II | 3 | - | - | - | - |
| | | Core Practical – V | Inorganic Chemistry Practical II | 3 | - | - | - | - |
| | | Core Practical - VI | Physical Chemistry Practical II | 3 | - | - | - | - |

Core Paper - VI
ORGANIC CHEMISTRY III
[75 Hours]

UNIT – I Alkaloids (15 Hours)

Occurrence, Extraction of alkaloids, Classification of alkaloids, structure elucidation, synthesis and stereochemistry of the following alkaloids: Quinine, Papaverine, Morphine and Reserpine. Biosynthesis of alkaloids.

UNIT – II Addition to Carbon – Carbon and Carbon – Hetero atom multiple bonds. (15 Hours)

Addition of halogen and nitrosyl chloride to olefins, hydration of olefins and acetylenes, hydroboration, hydroxylation, epoxydation, Michael addition, 1,3 dipolar addition, carbenes and their additions, Diels- Alder reaction.

Mechanism and reactivity. Mannich, Stobbe, Darzen Glycidic ester condensation, Benzoin condensation, Peterson olefination (Silyl Wittig reaction), Strecker synthesis, Wittig, Wittig - Horner, Perkin, Thorpe, Ritter, Prins reactions.

UNIT – III Molecular Rearrangements (15 Hours)

A detailed study of the mechanism of the following rearrangements: Nucleophilic, Electrophilic and Freeradical rearrangements – memory effects, migratory aptitudes, Pinacol - Pinacolone, Wagner – Meerwin, Demyanov, Dienone- Phenol, Favorski, Baeyer – Villiger, Wolff, Stevens, Von – Richter, Hofmann, Schmidt, Lossen, Curtius, Beckmann rearrangements (a few examples in each rearrangement are to be studied).

UNIT IV Oxidation and Reduction Reactions (15 Hours)

Study of the following oxidation reactions with mechanism: Oxidation of alcohols by CrO₃, DMSO alone, DMSO in combination with DCC; acetic anhydride and oxalyl chloride, oxidation of arylmethane, oxidation of methylene alpha to carbonyl, allylic oxidation of olefins, oxidative cleavage of glycols, oxidative cleavage of double bonds by ozonolysis.

Study of the following reduction reactions with mechanism; Reduction of carbonyl compounds by hydrides, selectivity in reduction of 4- ter – butyl cyclohexanone

using selectrides, clemmensen and Wolff Kishner reductions, Birch reduction, MPV reduction.

UNIT V Steroids

(15 Hours)

Structure and Stereochemistry of Cholesterol. Total synthesis of Cholesterol and estrone. Reactions of Oestrone, Conversion of cholesterol into progesterone, testosterone and oestrone. Artificial hormones – Stilboestrol and Hexoestrol.

Text Books :

1. Jerry March, **Advanced Organic Chemistry-Reactions, Mechanisms and Structure**, Fourth Edition, John Wiley & Sons (1992)
2. Francis A. Carey, **Organic Chemistry**, Third Edition, The McGraw-Hill Companies, Inc., 1996.
3. P.S. Kalsi, **Organic Reactions and Mechanisms**, Second Edition, New Age International Publishers, 2002.
4. I.L. Finar, **Organic Chemistry**, Volume II, Fifth Edition, First Indian reprint, Pearson Education Asia Pte. Ltd., (2000)
5. G. Chatwal, **Organic Chemistry of Natural Products**, Vol I & II, Himalaya Publishing House, 1988.

Reference Books :

1. S. H. Pine, J.B. Hendrickson, D.J. Cram and G.S. Hammond, **Organic Chemistry**, IV Edn., McGraw Hill Company, 1980.
2. S.M. Mukherji and S. P. Singh, **Reaction Mechanism in Organic Chemistry**, III Edition, Macmillan, 1984.
3. R.T. Morrison and R.N. Boyd, **Organic Chemistry**, Prentice-Hall, VI Edition, 1992.
4. Neil Issac, **Physical Organic Chemistry**, J. Wiley, New York, 1987.
5. Paul de Mayo, **Molecular Rearrangements**, Vol I, Vol II, Interscience, NY. 1963.
6. S.W. Pelletier, Van Nostrand, **Chemistry of Alkaloids**, Reinhold, 1970.
7. Hendry, **The Plant Alkaloids**, Churchill Publishers, IV Edn., 1949.
8. Fisher and Fisher, **Steroids**, Reinhold, 1959.
9. O.P. Agarwal, **Chemistry of Organic Natural Products**, Vol I & II, Goel Publishing House, 1988.

Core Paper - VII
INORGANIC CHEMISTRY II
[75 Hours]

UNIT – I Boron compounds and Clusters (15 Hours)

Boron hydrides – polyhedral boranes, hydroborate ions – a general study of preparation, properties and structure, styx numbers, Wade's rules.

Carboranes – types such as closo and nido – preparation, properties and structure. Metallo carboranes – a general study.

Metal clusters – Chemistry of low molecularity metal clusters only – structure of Re_2Cl_8 ; multiple metal – metal bonds.

UNIT – II Photoelectron Spectroscopy and Inorganic photochemistry (15 Hours)

Photoelectron Spectroscopy-Principle, PES of diatomic molecules and polyatomic molecules (HCl, HBr, HI, CO, NH_3 and H_2O); Core electron PES; X-ray photoelectron spectroscopy (ESCA) applications.

Inorganic photochemistry-Photosubstitution, Photoredox and isomerisation processes; application of metal complexes in solar energy conversion.

UNIT – III Electronic Spectra of Complexes (15 Hours)

Spectroscopic Term symbols for d^n ions – derivation of term symbols and ground state term symbol, Hund's rule; Selection rules – break down of selection rules, spin-orbit coupling, band intensities, weak and strong field limits- correlation diagram; Energy level diagrams; Orgel and Tanabe – Sugano diagrams; effect of distortion and spin orbit coupling on spectra; Evaluation of Dq and B values for octahedral complexes of Nickel; Charge transfer spectra. Spectral properties of Lanthanides and Actinides.

UNIT – IV Analytical Chemistry (15 Hours)

Polarography – Theory, apparatus, DME, diffusion, kinetic and catalytic currents, current voltage curves for reversible and irreversible systems; qualitative and quantitative applications to Inorganic systems.

Amperometric titrations – Theory, apparatus, types of titration curves, successive titrations and two indicator electrodes; applications; Complexometric titrations –

Chelating agents; types of EDTA titration – direct and back titrations; replacement titrations – masking and demasking reagents.

UNIT – V Inorganic Applications (15 Hours)

Combined uses of IR and Raman spectra in the structural elucidation of simple molecules like N_2O , ClF_3 , NO_3 , ClO_3 , NSF_3 . Effect of coordination on ligand vibrations, use of group vibrations in the structural elucidation of metal complexes of Urea, Thiourea, Cyanide, Thiocyanate, Nitrate and Sulphate. Effect of isotopic substitution on the vibrational spectra of molecules, vibrational spectra of metal carbonyls with reference to the nature of bonding, geometry and number of C-O stretching vibrations, Group theoretical treatment for C_{2V} molecules, limitations of IR.

Text Books :

1. J.E. Huheey, E.A. Keiter and R.L. Keiter, **Inorganic Chemistry – Principles of structure and reactivity**, 4th Edition, Pearson – Education, 2002.
2. F.A. Cotton and G. Wilkinson, **Advanced Inorganic Chemistry**, Wiley Eastern, 5th Edition, 1988.
3. S.F.A. Kettle, **Coordination compounds**, ELBS, 1973.
4. K.F. Purcell and J.C. Kotz, **Inorganic Chemistry**, WB. Saunders Co., USA 1977.
5. D.F. Shriver, P.W. Alkins and C.H. Longford, **Inorganic Chemistry**, ELBS, 2nd Edition, 1994.
6. R.B. Heslop and K. Jones, **Inorganic Chemistry**, Elsevier, 1976.
7. D. M. Adams, **Inorganic Solids**, John Wiley Sons, 1974.
8. R. West, **Basic Solid State Chemistry**, John Wiley Sons, 1991.
9. W.E. Addison, **Structural Principles in Inorganic Chemistry**, Longman, 1961.
10. E.A.V. Ebsworth, D.WH. Rankine and S. Craddock, **Structural methods in Inorganic Chemistry**, Black well Scientific Publ., 1987.
11. R.S. Drago, **Physical Methods in Chemistry**, Reinhold, New York, 1968.
12. D.A. Skoog and D.M. West, **Fundamentals of Analytical Chemistry**, Holt Rinehart and Winston Publications, IV Edn, 1982.
13. D.A. Skoog, **Principles of Instrumental Analysis**, Saunders College Pub. Co., III Edn., 1985.
14. J.G. Dick, **Analytical Chemistry**, McGraw Hill Publishers, 1974.

15. R.C. Kapoor and B.S. Agarwal, **Principles of polarography**, Wiley Eastern Ltd., 1991.

Reference Books:

1. D. Bannerjea, **Coordination Chemistry**, Tata – McGraw Hill, 1993.
2. K. Burger, **Coordination Chemistry Experimental Methods**, Butterworths, 1973.
3. A.R. West, **Solid - State chemistry and its applications**, Wiley, New York, 1984.
4. Muller, **Inorganic Structural Chemistry**, Wiley, New York, 1993.
5. C.N.R. Rao and J.R. Ferraro, **Spectroscopy in Inorganic Chemistry**, Methven Co., London, 1968.
6. G.W. King, **Spectroscopy and Molecular Structure**, Holt Rienehart and Winston, 1964.
7. A.F. Wells, **Structural Inorganic Chemistry**, Oxford, V Edn., 1984.
8. E.L. Mutteri, **Polyhedral boranes**, Academic Press, NY, 1975.
9. G.S. Manku, **Inorganic Chemistry**, TMH Co., 1984.
10. Willard, Merit, Dean and Settle, **Instrumental Methods of Analysis**, CBS Publishers and Distributors, IV Edn., 1989.

Core Paper - VIII PHYSICAL CHEMISTRY III [75 Hours]

UNIT – I Statistical Thermodynamics (15 Hours)

Objectives of Statistical thermodynamics – concept of thermodynamical and mathematical probabilities – Distribution of distinguishable and non – distinguishable particles.

Maxwell –Boltzmann, Bose-Einstein and Fermi-Dirac statistics - comparisons

Partition Functions – evaluation of Translational, Vibrational, Rotational and Electronic partition Function – Thermodynamic Functions in terms of partition Function – Application of partition Function to monoatomic and diatomic gases – Statistical expression for equilibrium constant – Calculation of Equilibrium Constant from Partition

Function – (isotopic exchange equilibria and dissociation of diatomic molecules) – Heat capacities of Monoatomic crystals – Einstein and Debye theory of heat capacities.

UNIT – II Irreversible Thermodynamics (15 Hours)

Postulates of Local equilibrium – Entropy production – Entropy Production in Heat flow – Entropy production in matter flow – Prigogine's principle of minimum entropy production – Forces and Fluxes – Linear force – flux relation – phenomenological equation – microscopic reversibility and Onsager's reciprocity relations.

Electrokinetic phenomena – diffusion – Non – equilibrium stationary states.

UNIT – III Chemical Kinetics – III (15 Hours)

Kinetics of complex reactions – reversible reactions, consecutive reactions – Parallel reactions and Chain reactions – General treatment of chain reaction – Chain length – Rice Herzfeld mechanism – explosion limits.

Study of Fast reactions: Luminescence and energy transfer process – Study of kinetics by relaxation methods-temperature and pressure jump methods - Stopped flow technique, flash photolysis and Crossed molecular beam method.

UNIT - IV Quantum Chemistry – III (15 Hours)

Theory of chemical bonding – Born – Oppenheimer approximation – LCAO – MO approximation for hydrogen molecule ion and Hydrogen – Valence Bond theory of Hydrogen molecule – Concept of Hybridisation – sp , sp^2 and sp^3 hybridisation – Huckel Molecular orbital (HMO) theory for conjugated π - system – applications to simple systems – (Ethylene, butadiene and benzene) – Physical Significance of HMO coefficients – Self consistent field approximation – Hartree's and Hartree – Fock Self Consistent field theory – Slater type orbitals – Slater rules.

UNIT – V Spectroscopy – II (15 Hours)

NMR spectroscopy – theory – nuclear zeeman effect- chemical shift – Spin-spin coupling – NMR of simple AX and AMX type molecules – Calculation of coupling constants - ^{13}C -NMR – a brief discussion of Fourier Transformation.

ESR Spectroscopy – Theory – hyperfine interactions – Spin densities – McConnell relationship – selection rules in ESR – ‘g’ value and coupling constants.

Text Books :

1. Gurudeep raj, **Advanced Physical Chemistry**, Goel Publishing House, Meerut.
2. M.C. Gupta, **Statistical Thermodynamics**, Wiley Eastern, New Delhi, 1990.
3. R. Hasse, **Thermodynamics of Irreversible Process**, Addison Wesley, Reading, Mass 1969.
4. I. Prigogine, **Introduction to Thermodynamics of Irreversible Process, Inter Science**, New York, 1961.
5. J. Rajaram and J.C. Kuriakose, **Kinetics and Mechanism of Chemical Transformations**, Macmillan India Ltd., 1993.
6. K.J. Laidlar, **Chemical Kinetics**, Harper and row, New york. 1987.
7. R.K. Prasad, **Quantum Chemistry**, Wiley Eastern, NewDelhi, 1992.
8. M.W. Hanna, **Quantum Mechanics in Chemistry**, W.A. Benjamin Inc, London 1965.
9. C.N. Banwell, **Fundamentals of Molecular Spectroscopy**, Mc Graw Hill, Newyork, 1966.
10. A. Carrington and A.D. McLachlan, **Introduction to Magnetic Resonance**, Harper and Row, New york (1967)

Reference Books

1. M. Dole, **Statistical Thermodynamics**, Prentice Hall, New York, 1954.
2. B.J. McClelland, **Statistical Thermodynamics**, Chapman and Hall, London 1973.
3. N.O. Smith, Elementary, **Statistical Thermodynamics, a Problem approach**, Pleunum Press, New York, 1980.
4. R.G. Frost and Pearson, **Kinetics and Mechanism**, Wiley New York, 1961.
5. J.W. Moore, and R.G. Pearson, **Kinetics and Mechanism**, 1981.
6. C. Capellos and B.H.J. Bielski, **Kinetics Systems**, Wiley inter science, New York, 1972.
7. I. Amdur and C.G. Hammes, **Chemical Kinetics, Principle and Selected Topics**, McGraw Hill, New York, 1968.

8. G.M. Harris, **Chemical Kinetics**, D.C. Heath and Co, 1966.
9. A.K. Chandra, **Introductory Quantum Chemistry**, Tata McGraw Hill.
10. D.A. McQuarrie, **Quantum Chemistry**, University Science Books, Mill Valley, California (1983).
11. P.W. Atkins, **Molecular Quantum Mechanics**, Oxford University Press, Oxford, 1983.
12. J.N. Murrell, S.F.A. Kettle and J.M. Tedder, **The Chemical Bond**, Wiley.
12. Raymond chang, **Basic Principle of Spectroscopy**, McGraw Hill Ltd., New York (1971).
13. G.M. Barrow, **Introduction to Molecular Spectroscopy**, McGraw Hill, New York, 1962.
14. W. Kemp, **NMR in Chemistry**, Mac Millan Ltd., (1986).
15. K.P. McLauchlan, **Magnetic Resonance, Oxford Chemistry series**, Oxford, (1972).
16. F.A. Rushworth and D.P. Tunstall, **Nuclear Magnetic Resonance**, Gordon and Breach Science Publishing, New York, (1973).
17. J.K.M. Sanders and B.K. Hunther, **Modern NMR Spectroscopy**, A guide for chemists, Oxford University press, Oxford, (1987).

Elective Paper - III
ELECTROCHEMISTRY AND
PHOTOCHEMISTRY
[90 Hours]

UNIT – I Electrochemistry – I **(18 Hours)**

Ions in solutions – Debye – Huckel theory of strong electrolytes – Debye – Huckel – Onsager equation – verification and limitation – Debye – Huckel limiting law and its extension.

Electrode – Electrolyte interface - adsorption at electrified interface – electrical double layers – Electro capillary phenomena – Lippmann capillary equation – structure of

double layers – Helmholtz Perrin, Gouy-Chapman and Stern models of electrical double layers – electro kinetic Phenomena – Tiselius method of separation of proteins – Membrane potential.

UNIT – II Electrochemistry – II (18 Hours)

Mechanism of electrode reactions – Polarisation and Over Potential – the Butler Volmer equation for one step and multi step electron transfer reactions – significance of equilibrium exchange current density and symmetry factor – transfer coefficient and its significance – Theory and applications of dropping mercury electrode – Polarography, Amperometry and Cyclic voltametry – Principles and applications – mechanism of Hydrogen and Oxygen evolution reactions.

UNIT – III Electrochemistry – III (18 Hours)

Electrochemical inorganic and organic reactions of technological interest (at least one example in each) – Corrosion and Passivation of metals – construction of Pourbaix and Evans diagrams – Prevention of Corrosion.

Electrochemical energy systems – Primary and Secondary batteries – (dry cells, lead acid - storage batteries, silver zinc cell, nickel cadmium battery, mercury cell) – Fuel cells – Electrodeposition – Principles and applications.

UNIT – IV Photochemistry – I (18 Hours)

Absorption and emission of radiation – Franck – Condon principle – decay of electronically excited states – radiative and non –radiative processes – spin allowed and spin forbidden transition.

Non – radiative process – theory of radiation less transition – Internal conversion and intersystem crossing. Radiative processes – Fluorescence and Phosphorescence – Theory of Fluorescence and Phosphorescence. Factors affecting Fluorescence and Phosphorescence – Prompt and delayed Fluorescence – Fluorescence and structure. quenching of Fluorescence – static and dynamic quenching – Stern – Volmer equation – concentration dependence of quenching and Excimer formation – quenching by added substance – Exciplex formation and decay.

UNIT – V Photochemistry – II (18 Hours)

Techniques and applications of Photochemistry – Quantum yield – Experimental determination of quantum yield – Actinometry – chemical Actinometry – Steady state treatment of quantum yield – Reasons for high and low quantum yield – life time measurements – radiative and non – radiative life time measurements – Kinetics of Photochemical reaction – Photosensitized reactions.

Photovoltaic and Photogalvanic cells – Photoelectrochemical cells – Photoassisted electrolysis of water – aspects of solar energy conversion.

Text Books:-

1. S. Glasstone, **Introduction to Electro Chemistry**, Affiliated East West Press, New Delhi, 1960.
2. D.R. Craw, **Principles and applications of Electro chemistry**, Chapman and Hall, 1991.
3. J. Robbins, **Ions in solution – An Introduction to Electro chemistry**, Clarendon Press, Oxford (1972).
4. K.K. Rohatgi Mukherjee, **Fundamentals of Photochemistry**, Wiley Eastern Ltd., 1978.
5. N.J. Turro, **Modern Molecular Photochemistry**, Benjamin / Cummings, Menlo park, California (1978).

Reference Books:-

1. J.O.M. Bockris and A.K.N. Reddy, **Electrochemistry, Vols, 1 and 2**, Plenum, New York. 1977.
2. C.M.A Brett and A.M.O. Brett, **Electrochemistry, Principles, Methods and Applications**, OUP, Oxford, 1993.
3. R.H. Rieger, **Electrochemistry**, Chapman and Hall, New York (1994).
4. P. Delahay, **Electrode Kinetics and Structure of Double Layer**, Interscience, 1965.
5. J.C. Calvert and J.N. Pitts, **Photochemistry**, Wiley, London, 1966.
6. R.P. Wayne, **Photochemistry**, Butterworths, London, 1970.
7. R.P. Cundell and A.Gilbert, **Photochemistry**, Thomas Nelson, London, 1970.
8. C.K. Depuy and O.L. Chapman, **Molecular reactions and Photochemistry**.

SECOND YEAR
Semester IV

| Code No. | Course | Subject | Work load per Semester (hours) |
|----------|---------------------|---|--------------------------------|
| | Core Paper – IX | Inorganic Chemistry III | 90 |
| | Elective Paper – IV | Organic Spectra, Photochemistry & Pericyclic reactions | 90 |
| | Core Practical – IV | Organic Chemistry Practical II | 60 |
| | Core Practical – V | Inorganic Chemistry Practical II | 60 |
| | Core Practical - VI | Physical Chemistry Practical II | 60 |
| | Project | Dissertation / Project Work | 90 |

Total 1800 Hours

SECOND YEAR
Semester IV

| Semester | Code | Course | Course Title | Hrs. | Credit | Marks | | |
|----------|------|---------------------|--|------|--------|-------|----|-------|
| | | | | | | CIA | EA | Total |
| IV | | Core Paper – IX | Inorganic Chemistry III | 6 | 6 | 25 | 75 | 100 |
| | | Elective Paper – IV | Organic Spectra, Photochemistry & Pericyclic reactions | 6 | 4 | 25 | 75 | 100 |
| | | Core Practical – IV | Organic Chemistry Practical II | 4 | 4 | 40 | 60 | 100 |
| | | Core Practical – V | Inorganic Chemistry Practical II | 4 | 4 | 40 | 60 | 100 |
| | | Core Practical - VI | Physical Chemistry Practical II | 4 | 4 | 40 | 60 | 100 |
| | | Project | Dissertation / Project Work | 6 | 5 | - | - | 200 |

Core Paper - IX
INORGANIC CHEMISTRY - III

[90 Hours]

UNIT – I Spectroscopic and Thermal methods of Analysis (18 Hours)

Atomic absorption spectroscopy – Principle; instrumentation; EMR sources – cells, furnaces, detectors; interferences and their corrections; applications of AAS. Flame photometry – Theory, instrumentation and a few important applications.

Principles and instrumentation of DTA, DSC and TGA

UNIT – II Basic aspects of Nanotechnology (18 Hours)

Introduction, importance – Various stages of nanotechnology - Nanoparticles – Carbon nanotubes – Fullerenes – Nanopore Channels – Fibers and scaffolds – CUP and FCUA technology and its applications – Nano imaging techniques- Top down and bottom up methods of synthesis Effect of size quantization on Optical properties.

UNIT – III EPR Spectroscopy and Mossbauer Spectroscopy (18 Hours)

Theory : EPR spectra of VO (II), Mn(II), Co(II), Ni(II) and Cu(II) complexes; covalency of metal – ligand bonding by EPR; John-teller distortions in Cu(II) complexes.

Mossbauer Spectroscopy – Doppler effect; isomer effect; electron – neutron hyperfine interactions; Quadrupole interactions and magnetic interactions; simple applications to Iron and Tin compounds.

UNIT – IV Analytical Techniques (18 Hours)

Chromatography – Gas liquid chromatography – Principle, retention volumes; instrumentation; carrier gas; columns preparations; stationary phase; detectors – thermal conductivity, flame ionization, electron capture; applications of GLC.

High Performance liquid chromatography – scope; column efficiency; instrumentation; pumping systems; columns; column packing; detectors; applications.

UNIT – V Computer Applications in Chemistry (18 Hours)

Input and Output Statements, Transfer and control statements, programming in BASIC only for calculation of equilibrium constants, pH of a buffer, potentiometric titrations and standard deviation.

MS-Word, MS-Excel and MS- Power Point, Internet usage.

Text Books:-

1. D.A. Skoog and D.M. West, **Fundamentals of Analytical Chemistry**, Holt Rinehart and Winston Publications, IV Edn, 1982.
2. D.A. Skoog, **Principles of Instrumental Analysis**, Saunders College Pub. Co, III Edn., 1985.
3. J.G. Dick, **Analytical Chemistry**, McGraw Hill Publishers, 1974.
4. A.I. Vogel, **Text Book of Quantitative Inorganic Analysis**, Pearson, V Edn., 2001.
5. R.S. Drago, **Physical Methods in Chemistry**, Reinhold, New York, 1968.
6. H. Kaur, **An Introduction to Chromatography**, Pragati Publishers, 2006.
7. P.C. Jurns, T.L. Isenhour and C.C. wilkins, **BASIC Programming for Chemists**, J.W. & Sons, 1987.
8. K.V. Raman, **Computers in Chemistry**, Tata McGraw Hill, New Delhi. 1993.

Reference Books:-

1. C.N.R. Rao and J.R. Ferraro, **Spectroscopy in Inorganic Chemistry**, Vol I and Vol II, Academic Press, 1970.
2. Willard, Merit, Dean and Settle, **Instrumental Methods of Analysis**, CBS Publishers and Distributors, IV Edn., 1989.
3. G.D. Christian and J.E.O Reilly, **Instrumental Analysis**, Allyn and Bacon Inc, II Edn., 1986.
4. G.W. Ewing, **Instrumental Methods of Chemical Analysis**, McGraw Hill Pub, 1975.
5. J.H. Knox (Ed), **High Performance Liquid Chromatography**, Edinburgh University Press, Edinburgh, 1982.
6. G.W. King, **Spectroscopy and Molecular Structure**, Holt Rinehart and Winston, 1964.
7. Albert Paul Malvino, **BASIC Programming**, PMH Publishers, III Edn., 1984.
8. N. Subramanian, **Programming for BASIC**, A.H. Wheeler and Co. Pvt. Ltd III Edn., 1987.
9. Mick Wilson, Kamali Kannangara, Geoff Smith, Michelle Simmons and Burkhard Raguse, **Nanotechnology Basic Science and emerging Technologies**, overseas press
10. Kenneth J. Klabundo, **Nanoscale materials in Chemistry**, John Wiley

Elective Paper - IV
ORGANIC SPECTRA, PHOTOCHEMISTRY AND
PERICYCLIC REACTIONS
[90 Hours]

UNIT – I Organic Spectra : UV – VIS, and IR Spectra (18 Hours)

UV – VIS : Woodward – Fieser rules for dienes, enones. Calculation of λ_{\max} for organic molecules. Chromophores and effect of conjugation, substituents with unshared electrons and their capability of π - conjugation. Colour in compounds.

IR : characteristic group frequencies of organic molecule, Factors influencing vibrational frequencies, interpretation of IR spectra of organic molecules.

UNIT – II ORD – CD and Mass Spectra (18 Hours)

ORD – CD : Definition, deduction of absolute configuration, octant rule for ketones, Cotton effect – axial haloketone rule.

Mass spectra – theory, applications, McLafferty rearrangement, fragmentation pattern, Examples of mass spectral fragmentation of organic compounds with respect to their structure determination.

UNIT – III NMR (^1H and ^{13}C) and ESR Spectra (18 Hours)

NMR spectroscopy: Chemical shift, factors influencing chemical shift, spin – spin coupling, NMR of simple AX and AMX type organic molecules, calculation of coupling constants, identification of H in various chemical environments to assign structure to the organic molecules using chemical shift values, resonance coupled and decoupled spectra, ^{13}C NMR, applications of ^{13}C NMR to find the different carbon functional groups. Lanthanide compounds as shift reagents.

ESR Spectroscopy: Basic principles, zero field splitting and Kramer's degeneracy, factors affecting the 'g' value. Isotropic and anisotropic hyperfine coupling constants. Applications of ESR spectroscopy.

UNIT – IV Organic Photochemistry (18 Hours)

Photochemical reactions : fate of excited molecules, Jablonski diagram, Norrish Type I and Norrish Type II reactions, photoreduction of ketone, photoaddition reactions, Paterno Buchi reaction, di - π methane rearrangement, photochemistry of arenes,

Photooxidation (Formation of peroxy compounds), Photoisomerization (Cis – trans isomerization), Photo addition of olefins and amines to aromatic compounds, Photo rearrangements: Photo – Fries rearrangement and Photo rearrangement of 2,5 – Cyclohexadienones.

UNIT – V Pericyclic Reactions (18 Hours)

Pericyclic reactions, classification, orbital symmetry, Woodward Hofmann rules, selection rules and stereochemistry of electrocyclic reactions, cycloaddition and sigmatropic shifts, analysis by correlaton diagram method and Frontier molecular orbital method, Sommelet, Hauser, Cope and Claisen rearrangements.

Text Books:-

1. P.S. Kalsi, **Organic Reactions and Mechanisms**, Second Edition, New Age International Publishers, 2000.
2. I.L. Finar, **Organic Chemistry**, Volume II, Fifth Edition, First Indian reprint, Pearson Education Asia Pte. Ltd., (2000)
3. F.A. Carey and Sundberg, **Advanced Organic Chemistry, Part A & B**, III Edn, Plenum Press, 1990.
4. Charles H. DePuy, **Molecular reactions and photochemistry**, Orville L.Chapman Prentice Hall of India Private Limited, New Delhi, 1988.

Reference Books:-

1. Y.R. Sharma, **Elementary Organic Spectroscopy**, I Edn, S.Chand & Company Ltd, New Delhi, 1980.
2. J. Dyer, **Applicaton of absorption spectroscopy of organic compounds**, Prentice Hall of India Pvt. Ltd., New Delhi, 2005.
3. R.M. Silverstein, C.G. Bassler and Monsil, **Spectrometric identification of organic compounds**, 6th Edn., John Wiley & Sons, New York, 2004.
- 4 William Kemp, **Organic Spectroscopy**, ELBS, New Delhi, 1982.
5. S. Kalsi, **Spectroscopy of organic compounds**, 5th Edn., Wiley Eastern Ltd., Madras, 2002.
6. C.N. Banwell, **Fundamentals of Molecular Spectroscopy**, McGraw Hill, New York, 1966.
7. A. Carrigton and A.D. McLachlan, **Introduction to Magnetic Resonance**, Harper and

- Row New York, 1967.
8. R. Drago, **Physical Methods in Inorganic Chemistry**, Reinhold, NY, 1968.
 9. G.M. Barrow, **Introduction to Molecular Spectroscopy**, McGrawHill, NewYork, 1962.
 10. W. Kemp, **NMR in Chemistry**, MacMillan Ltd., 1986.
 11. G.W. King, **Spectroscopy and Molecular Structure**, Holt, Rienehart and Winston, 1964.
 12. C.N.R. Rao, J.R. Ferraro, **Spectroscopy in Inorganic Chemistry**, Methven Co., London, 1968.
 13. Raymond Chang, **Basic Principles of Spectroscopy**, McGraw Hill Ltd, New York, 1993.
 14. Dudley. H. Williams, Ian Fleming, **Spectroscopic methods in Organic Chemistry**, 5th Edition, Tata McGraw Hill Publishing Co Ltd, 2004.

Core Practical - IV

ORGANIC CHEMISTRY – PRACTICAL – II

I. Organic Estimation

1. Phenol
2. Aniline
3. Methyl Ketone
4. Glucose
5. Iodine value of an oil
6. Saponification value of an oil.

II. Organic Preparation, Involving Two stages

1. Sym-tribromobenzene from aniline.
2. m- Nitrobenzoic acid from methyl benzoate.
3. para – Nitroaniline from acetanilide.
4. Benzanilide from benzophenone.

5. Aspirin from methyl salicylate
6. Anthraquinone from phthalic anhydride.

III. Extraction of Natural Products:

1. Caffeine from tea leaves.
2. Citric acid from lemon.

IV Chromatographic Separations

1. Column chromatography : separation of a mixture of ortho and para-Nitroanilines.
2. Thin layer Chromatography: separation of a mixture of ortho and para – Nitroanilines.
3. Paper chromatography – identification of natural alpha amino acids.

Reference :

1. B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, **Vogel's Practical Organic Chemistry**, 5th edn. ELBS. 1989.
2. Raj K. Bansal, **Laboratory manual of Organic Chemistry**, III Edn., New Age International (P) Ltd. 1996.

Core Practical - V

INORGANIC CHEMISTRY PRACTICAL – II

Part I Quantitative analysis of complex materials

A) Quantitative analysis:

Quantitative analysis of the following mixture

1. Iron and magnesium
2. Iron and nickel
3. Copper and nickel
4. Copper and Zinc

B) Analysis of Ores

1. Determination of percentage of calcium and magnesium in dolomite.
2. Determination of percentage of MnO₂ in pyrolusite

3. Determination of percentage of lead in galena.

C) Analysis of Alloys

1. Determination of tin and lead in solder
2. Determination of copper and zinc in brass.
3. Determination of Chromium and nickel in stainless steel.

Part II: Preparations of the following:

1. Sodium hexanitrocobaltate (III)
2. Sodium Trisoxalatoferrate (III)
3. Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
4. Bis (acetylacetonato) Copper (II)
5. Hexamminecobalt (III) chloride
6. Hexamminenickel (II) chloride

Reference Books:

1. G. Svehla, **Vogel's qualitative Inorganic analysis**, VI Edition, Orient Longman, 1987.
2. V.V. Ramanujam, **Inorganic Semimicro Qualitative analysis**. National Publishing Co., Chennai.1971.
3. J. Basset, R.C. Denney, G.H. Jeffery and J.Mendham **Vogel's Text book of quantitative inorganic analysis**, IV Edition, ELBS, 1985.
4. W.G. Palmer, **Experimental Inorganic Chemistry**, Van Nostrand Reinhold Co., London, 1972.
5. D.N. Grindley, **An advanced course in practical Inorganic Chemistry**, Butterworths, 1964.

Core Practical - VI

PHYSICAL CHEMISTRY PRACTICAL – II

Experiments in Electrochemistry, Polarography and Chemical Kinetics.

EMF Measurements

1. Determination of standard potentials (Cu and Ag)
2. Determination of thermodynamic quantities from EMF measurements
3. Potentiometric titrations.
4. Determination of pH and calculation of pKa.
5. Determination of stability constant of complex.
6. Determination of solubility product of a sparingly soluble salt, Redox titrations.

7. Precipitation titration of mixture of halides by emf measurements.

DETAILED LIST OF EXPERIMENTS

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

1. Determination of the activity coefficient of an electrolyte at different molalities by emf measurements.
2. Determination of the dissociation constant of acetic acid by titrating it with sodium hydroxide using quinhydrone as an indicator electrode and calomel as a reference electrode.
3. Determination of the strength of a given solution of KCl using differential potentiometric titration technique.
4. Determination of the pH of the given solutions with the help of the indicators using buffer solutions and by colorimetric method.
5. Determination of the pH of a given solution by emf method using hydrogen electrode and quinhydrone electrode.
6. Determination of the composition and instability constant of a complex by mole ratio method.
7. Calculation of the thermodynamic parameters for the reaction
$$\text{Zn} + \text{H}_2\text{SO}_4 \text{ -----} \rightarrow \text{ZnSO}_4 + \text{H}_2$$
 by emf method.
8. Determination of the formation constant of silver ammonia complex and stoichiometry of the complex potentiometrically.
9. Solubility and solubility products by emf method.
10. Determination of the activity coefficient of Zinc ions in the solution of 0.002M Zinc sulphate using Debye - Huckel Limiting law.
11. Determination of solubility product of Silver bromide and calculate its solubility in water and 0.1 M and 0.01 M KBrO_3 using Debye- Huckel limiting law.
12. Determination of the electrode potentials of Zn and Ag electrodes in 0.1 M and 0.001M solutions at 298 K and find the standard potentials for these electrodes and test the validity of Nernst equations.
13. Study the inversion of cane sugar in presence of acid using polarimeter.

14. Determination of the rate constant and order of reaction between potassium persulphate and potassium iodide and determine the temperature coefficient and energy of activation of the reaction.
15. Study the primary salt effect on the kinetics of ionic reactions and test the Bronsted relationship (iodide ion is oxidized by persulphate ion.)
16. Determination of the viscosities of mixtures of different compositions of liquids and find the composition of a given mixture.
17. Determination of the partial molar volume of glycine/methanol/formic acid/ sulphuric acid by graphical method and by determining the densities of the solutions of different compositions.
18. Study the surface tension – concentration relationship of solutions (Gibb's equation)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Third Semester

Core Paper - VI

ORGANIC CHEMISTRY - III

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Formulate the following

Quininic acid -----> (-) Quinine

Or

b) How is the position of methoxy group in reserpine established.

2. a) Write notes on Thorpe reaction and Strecker synthesis.

Or

b) Discuss the salient features of Darzens glycidic ester condensation.

3. a) Selecting a suitable example discuss the mechanism of Demjanov rearrangement.

Or

- b) Account for the following with suitable evidence.
- i) Favorski rearrangement proceeds through cyclopropanone intermediate.
 - ii) Carbonyl carbon of diazomethyl ketone becomes the carbonyl carbon of the product in Wolff rearrangement.
4. a) Discuss the oxidation of methylene alpha to a carbonyl group by SeO_2 with the mechanisms.

Or

- b) Write a note on allylic oxidation.
5. a) How do you synthesise testosterone from cholesterol.

Or

- b) Write the structure of cholesterol and indicate the chiral centres in it.

PART – B (5 X 10 = 50 Marks)

6. a) i) How is the position of hydroxyl group in quinine arrived at. (4)
ii) Prove the pentacyclic nature of reserpine (6)

Or

- b) Establish the structure of papaverine. Give a method of synthesis also. (10)

7. a) Give an account of the salient features, mechanism and synthetic utility of the Wittig reaction. (10)

Or

- b) Give an account of the salient features and mechanism of Mannich reaction and Stobbe condensation. (10).

8. a) i) Describe the mechanism of Pinacol – Pinacolone rearrangement. (5)
ii) What are crossover experiments? How are they useful in the elucidation of mechanism of a rearrangement. (5)

Or

- b) Explain the mechanism of the following and adduce suitable evidence.
- i) Baeyer-Villiger oxidation.
 - ii) Von – Richter rearrangement.

9. a) i) Explain Meerwein – Pounding – Verley reduction with suitable example. (5)
ii) Discuss the mechanism of oxidation of alcohols by CrO_3 and DMSO. (5)

Or

- b) i) Write a note on Clemmensen reduction and Wolff Kishner reduction. (5)
ii) Write notes on Birch reduction. (5)
10. a) i) Give any one method of synthesis of oestrone (5)
ii) How is cholesterol converted into progesterone. (5)

Or

- b) Discuss how the nature and the position of the side chain in cholesterol established. (10)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Third Semester
Core Paper - VII
INORGANIC CHEMISTRY - II

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Explain the bonding in diborane.

Or

- b) What are carboranes? Discuss their types, preparations and structures.

2. a) Explain photoisomerisation with an example

Or

- b) Discuss the PES of a HBr molecule.

3. a) Draw and explain Orgel diagram for Co^{2+} ion in tetrahedral and octahedral fields.

Or

- b) Describe the selection rules for electronic spectra.

4. a) What is known as the Half wave potential? Explain the significance of it.

Or

- b) Describe the various methods which are employed for performing EDTA titrations.
5. a) What are the different modes of coordination of thiourea with a metal atom? Explain how IR frequencies are useful to identify the coordinating atom of thiourea.

Or

- b) How could the structure of NSF_3 be unequivocally fixed on the basis of IR and Raman studies?

PART – B (5 X 10 = 50 Marks)

Answer all the questions

All questions carry equal marks

6. a) i) Describe the structure and bonding feature in $\text{Re}_2 \text{Cl}_8^{2-}$ (5)
ii) Discuss the applicability of the Wade's rule in the classification and structural elucidation of boranes and carboranes. (5)

Or

- b) Discuss the preparation, properties and structure of polyhedral hydroborate ions. (10)

7. a) i) Discuss the photochemistry of Ruthenium III complexes. (5)
ii) How does PES of oxygen molecule differ from that of nitrogen molecule (5)

Or

- b) i) In what respects XPES differ from uv-visible PES ? Illustrate with suitable example. (5)
ii) Discuss the applications of metal complexes in solar energy conversions (5)

8. a) Briefly discuss:

- i) Tanabe – Sugano diagram (5)
ii) Charge transfer transition (5)

Or

- b) i) Calculate Dq and B values for Ni^{2+} complexes. (4)
ii) Discuss the effect of distortion and spin orbit coupling on the spectra of octahedral complexes. (6)

9. a) Explain the basic instrumentation employed in polarographic analysis. Cite Example for inorganic qualitative analysis applications (10)

Or

b) Draw and explain the various types of curves obtained for Amperometric titrations
Cite one example for each type. (10)

10. a) Establish the structures of NO_3^- and ClO_3^- ions from their IR and Raman bands.
Compare their structures. (10)

Or

b) Apply group theory to identify the IR active stretching modes in C_{2v} molecule. (10)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Third Semester

Core Paper - VIII

PHYSICAL CHEMISTRY – III

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Explain the concepts of thermodynamic probability and statistical probability

Or

b) Derive Fermi-Dirac distribution law

2. a) What is entropy production? Derive an expression for the entropy production resulting from a heat flow in a system.

Or

b) What is a linear phenomenological relations ? What is phenomenological coefficient ? Explain.

3. a) What are consecutive reactions? Derive the rate equation for consecutive first order reaction.

Or

b) What are fast reactions? Explain the stopped flow method in the study of fast reactions.

4. a) What is Born – Oppenheimer approximation? Explain its usefulness.

Or

b) Explain LCAO- MO method. Treat H_2^+ ground state by LCAO – MO method.

5. a) Write notes on spin – spin coupling

Or

b) Write briefly about Fourier Transformations as applied to ^{13}C NMR.

PART – B (5 X 10 = 50 Marks)

Answer all the questions

All questions carry equal marks

6.a) (i) What are partition functions ? Show how they can be used to determine equilibrium constant for the dissociation of diatomic molecules (7)

(ii) Einstein frequency for copper is 7.1×10^{12} Hz. Calculate the molar heat capacity at 200K. (3)

Or

b) Explain Einstein's model for heat capacity of solids. Mention its limitations. Compare it with Debye model.

7.a) i) What are Onsager reciprocity relations? Discuss the utility of these relations in a coupled two – flow system (6)

ii) State and explain Prigogine's principle of minimum entropy production (4)

Or

b) i) What is seebeck effect? Explain the postulates local equilibrium (6)

ii) Explain the terms: "Force" and "Flux" (4)

8. a) i) What are chain reactions? Discuss the Rice – Herzfeld mechanism for the thermal decomposition of acetaldehyde. Derive the kinetic expression for the formation of methane. (7)

ii) If the relaxation time for the fast reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$ is $10 \mu s$ (micro seconds) and the equilibrium constant is 1.0×10^{-3} , Calculate the rate constant for the forward and reverse reaction. (3)

Or

b) Describe briefly the following methods for studying kinetics of fast reactions.

i) Flash Photolysis (5)

ii) Relaxation method (5)

9. a) Describe valence bond theory. Apply this theory to hydrogen molecule. (10)

Or

b) Discuss HMO theory of the conjugated system. Apply this theory to ethylene for calculating π - electron density and bond order. (10)

10. a) Discuss the principle of NMR spectroscopy. Taking suitable examples explain the spin – spin coupling involved in the NMR spectra of AX and AMX type molecules. (10)

Or

b) i) Write notes on Franck – Condon Principle (5)

ii) Explain the selection rule and hyperfine interactions in ESR spectroscopy (5)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Third Semester
Elective Paper - III
ELECTRO CHEMISTRY AND PHOTO CHEMISTRY

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Write a brief note on ion association in electrolyte solution.

Or

b) Explain Wien effect.

2. a) Write any five applications of polarography.

Or

b) What is supporting electrolyte ? Explain its significance in polarography.

3. a) Explain how corrosion can be prevented.

Or

b) Write a note on Hydrogen – Oxygen fuel cell.

4. a) Write a short note on phosphorescence.

Or

b) Write the selection rules for a radiative and radiationless transitions.

5. a) Discuss the reasons for high and low quantum yield.

Or

b) Distinguish between photo voltaic and photo galvanic cell.

PART – B (5 X 10 = 50 Marks)

Answer all the questions

All questions carry equal marks

6. a) Derive Debye Huckel limiting law and discuss its applications.

Or

b) Discuss Tiselius method of separation of proteins.

7. a) Discuss the principle and applications of cyclic voltammetry

Or

b) i) Define the following:

(1) Polarisable and non polarisable electrodes. (2)

(2) Exchange current density. (2)

ii) Discuss the mechanism of H₂ evolution reaction. (6)

8. a) Illustrate the principle and applications of electro deposition.

Or

b) Discuss the following

(i) Dry Cells (5)

(ii) Nickel cadmium battery (5)

9. a) Derive Stern volmer equation and discuss the effect of static and dynamic quenching on it.

Or

b) Discuss the following:

(i) Delayed Fluorescence (5)

(ii) Frank Condon principle (5)

10. a) Illustrate the experimental determination of quantum yield.

Or

b) (i) Illustrate photo sensitised decomposition of H₂O. (5)

(ii) Write short notes on photo voltaic and photo galvanic cells. (5)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Fourth Semester
Core Paper - IX
INORGANIC CHEMISTRY - III

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) Briefly discuss the chemical and spectral interferences encountered in AAS. How are they overcome?

Or

b) Discuss the theory of flame photometry

2. a) Define Nanotechnology and describe the various stages of it

Or

b) Describe CVD Diamond technology

3. a) Discuss the theory of EPR spectroscopy

Or

b) Discuss on Mossbauer effect.

4. a) Write about specific retention volume in Gas-Liquid Chromatography.

Or

b) What are the important requirements of a carrier gas in GLC ? Helium gas is generally preferred over hydrogen as a carrier gas. Why?

5. a) What are input and output statements in computer programming ?

Or

b) Write a program in BASIC for calculation of equilibrium constants for a redox reaction.

PART – B (5 X 10 = 50 Marks)

6 a) i) Explain the principle and working of Atomic Absorption spectroscopy. (5)

ii) Explain the terms sensitivity and detection limit with special reference to AAS. (5)

Or

- b) Discuss the principle, instrumentation and applications of Differential thermal analysis (10)
7. a) Explain FCVA technology and write its advantages over other techniques (10)
- Or**
- b) Write short notes on (i) Fullerenes (ii) Nanopore channels
8. a) i) Sketch the EPR spectrum of bis (salicylaldehyde) Copper (II) and interpret (5)
 ii) Outline the principle of Mossbauer Spectroscopy. (5)
- Or**
- b) i) How does the 'g' value of a transition metal ion differ from that of a free radical. (5)
 ii) The Mossbauer spectrum of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ exhibits a single line where as that of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ has a double line. Explain. (5)
9. a) i) Give the applications of GLC (4)
 ii) Write about the columns used in Gas – Liquid chromatography (6)
- Or**
- b) i) Write briefly about the pumps used in HPLC. (5)
 ii) Give the principles of Gas-Liquid chromatography. (5)
10. a) Discuss the application of MS-Powerpoint programme in teaching of chemistry. (10)
- Or**
- b) Explain the use of MS – Word in detail as applied to chemistry. (10)

Model Question Paper
(For the candidate admitted from 2012 – 2013 onwards)
M.Sc. Degree – Branch – IV Chemistry
Fourth Semester
Elective Paper - IV

**ORGANIC SPECTRA, PHOTOCHEMISTRY AND
PERICYCLIC REACTIONS**

Time : Three Hours

Maximum : 75 Marks

PART – A (5 X 5 = 25 Marks)

Answer all the questions

All questions carry equal marks

1. a) How does absorption maxima of an organic compound vary with solvent polarity.

Or

b) How do you distinguish intra molecular H-bonding from intermolecular type using IR spectroscopy.

2. a) Write notes on axial haloketone rule.

Or

b) Discuss the McLafferty rearrangement with an example.

3. a) Explain the spin-spin coupling in AX spectrum.

Or

b) Discuss the theory of ESR spectroscopy.

4. a) Explain Patterno – Buchi reaction.

Or

b) Explain di – π methane rearrangement.

5. a) Explain Woodward Hofmann rule with a suitable example.

Or

b) Briefly discuss the characteristics of Pericyclic reaction.

PART – B (5 X 10 = 50 Marks)

6. a) i) How do you distinguish between solution samples of o- and p- hydroxy acetophenones by uv absorption spectroscopy. (5)

ii) Account for $\nu_{C=O}$ of ethyl acetate in the IR spectrum appears at 1735 cm^{-1} whereas that of CH_3COCl appears at 1800 cm^{-1} (5)

Or

b) Explain the factors influencing vibrational frequencies. (10)

- 7.a) i) Explain the fragment pattern in carbonyl compounds and benzene derivatives (6)
ii) Explain cotton effect. (4)

Or

- b) i) What is meta stable ion peak and base peak in mass spectra ? (5)
ii) Explain the isotopic peak in mass spectra. (5)

- 8.a) i) Define chemical shift. What are the factors that influence the chemical shift? (5)
ii) Explain the calculation of coupling constant. (5)

Or

- b) i) Explain the splitting pattern in the NMR spectrum of ethyl bromide (5)
ii) Write notes on Kramer's degeneracy. (5)

- 9.a) i) Draw and explain the various photophysical processes in Jablonski diagram. (6)
ii) Write notes on Norrish Type II reaction. (4)

Or

- b) i) Give an account of the photo reduction of carbonyl compounds. (5)
ii) Illustrate using suitable examples the role of sensitizers in organic photochemistry. (5)

10. a) Write short notes on the following.

- i) Cope rearrangement (5)
ii) Claisen rearrangement. (5)

Or

- b) i) Analyse the sigmatropic reactions using FMO method. (5)
ii) With a aid of a correlation diagram, explain the electrocyclic reaction of butadiene to cyclobutene under thermal conditions. (5)

PERIYAR UNIVERSITY
M.Sc CHEMISTRY (C.B.C.S)
List of Board of studies members

| S.No. | Name and Address | | Mobile No | Signature |
|--------------|--|--------------------|----------------------------|------------------|
| 1 | Dr.A.K.Ramasamy Professor and Head Department of Chemistry Periyar University, Periyar palkalai Nagar, Salem – 636 011 | Chairman | 9944517524 | |
| 2 | Ms. P.Revathi Associate Professor Department of Chemistry J.K.K.Nataraja College of Arts and Science Komarapalayam – 638 183 Namakkal –Dt | Member | 9940922588 | |
| 3 | Ms.R.Thilakam Associate Professor Department of Chemistry Sri Sarada College for Women (Autonomus) Salem – 636 016 | Member | 9500636779 | |
| 4 | Thiru.V.Kumaravelan Associate Professor Department of Chemistry Mahendra College of Arts and Science Kalipatti – 637 501 Namakkal -Dt | Member | 9442580922 | |
| 5 | Thiru K.Perumal Raj Associate Professor, Department of Chemistry Vivekanandha College of Arts and Science for Women Thiruchengodi – 637 205 Namakkal - Dt | Member | 94433 16503 89034 69299 | |
| 6 | Dr.V.Murugesan Professor Department of Chemistry Anna University, Chennai – 600 025 | Member External | | |
| 7 | Dr.R.Renganathan Professor Department of Chemistry Bharathidasan University,Trichy – 6320 024 | Member External | 9994954236 | |

List of Examiners

| From Periyar Univ & Affiliated Colleges | | Outside Periyar University | |
|---|--|----------------------------|---|
| S.No. | Name and Address | S.No. | Name and Address |
| 1. | Dr. A.K. Ramasamy Professor and Head Department of Chemistry, Periyar University, Salem – 636 011. | 1. | Dr. S. Muthusubramaniyan Professor of Organic Chemistry School of Chemistry Madurai Kamaraj University Madurai- 625 021 |
| 2. | Dr.P.Viswanathamurthi Reader Department of Chemistry, Periyar University, Salem – 636 011. | 2. | Dr. A. Krishnaiah Dept.of Chemistry Sri Venkataswara (S.V.) University Tirupati-517502 |
| 3. | Dr.V.Raj Reader Department of Chemistry, Periyar University, Salem – 636 011. | 3. | Dr.M . Kandasamy Professor and Head Department of Inorganic Chemistry, University of Madras, Guindy campus Chennai- 600 025 |
| 4. | Dr.R.Rajavel Lecturer Department of Chemistry, Periyar University, Salem – 636 011. | 4. | Dr. S. Rajeswari Professor and Head Department of Analytical Chemistry University of Madras, Guindy campus Chennai- 600 025 |
| 5. | Dr.D.Gopi Lecturer Department of Chemistry, Periyar University, Salem – 636 011. | 5. | Dr.S. Kabilan Professor of Organic Chemistry Annamalai University Annamalai Nagar Chidambaram. |
| 6. | Dr.A. Lalitha Lecturer Department of Chemistry, Periyar University, Salem – 636 011. | 6. | Dr. S. Sriman Narayanan Professor Department of Analytical Chemistry University of Madras, Guindy campus, Chennai- 600 025 |
| 7. | Dr.V. Sujatha Lecturer Department of Chemistry, Periyar University, Salem – 636 011. | 7. | Dr.K.Pituchumani Professor of Organic Chemistry School of Chemistry Madurai Kamaraj University Madurai- 625021 |
| 8. | Mrs. Mariyammal SG Lecturer in Chemistry J.K.K. Nataraja College of Arts & Science, Komarapalayam. | 8. | Dr. P. Manisankar Professor and Head Department of Industrial Chemistry Alagappa University Karaikudi-630003 |
| 9. | Dr. V. Raghunathan Reader and Head | 9. | Dr. P.S. Mohan Department of Chemistry |

| | | | |
|--|---|--|---|
| | Department of Chemistry Kanadaswamy Kandar's College P. Velur, Namakkal | | Bharathiar University Coimbatore- 46 |
|--|---|--|---|