#### M. Sc. DEGREE Branch IV (D) ORGANIC CHEMISTRY REGULATIONS AND SYLLABUS

(For the Candidates admitted from the academic year 2008 – 2009 and onwards)

#### Course of Study FIRST YEAR

#### Semester I

	Course		Work load per
Code No.		Subject	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	45
		Practical I	
	Core Practical – II	Inorganic Chemistry	45
		Practical I	
	Core Practical - III	Physical Chemistry	45
		Practical I	

#### Course of Study FIRST YEAR Semester I

Sem ester	Codo Courso a mu		IJ	Caradit	Marks			
	Code	Course	Course Title	пгз.	Credit	CIA	EA	Total
Ι		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	-	-	-	-
	08POCP03	Core Practical - III	Physical Chemistry Practical I	3	-	-	-	-

#### **UNIT – III Stereochemistry**

# Homotopic, enantiotopic, diastereotopic H atoms, groups in organic molecules. Fischer, Newman and Sawhorse projections and their interconvertion. 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 – Crams rule.

#### **UNIT – IV Aliphatic Nucleophilic Substitution Reactions**

The  $S_N^2$ ,  $S_N^{-1}$ , mixed  $S_N^{-1}$  and  $S_N^2$ ,  $S_N^{-1}$  and SET mechanisms. The neighbouring group mechanism, neighbouring group participation by  $\pi$  and  $\sigma$  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. Reactions involving substitution at carbon doubly bonded to oxygen and nitrogen : Williamson reaction, Vonbraun reaction, hydrolysis of esters, Claisen and Dieckmann condensation.

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.

Pschorr reaction and Ullmann reaction, mechanism of Hunsdiecker reaction.

FIRST SEMESTER **Core Paper - I ORGANIC CHEMISTRY – I** (75 Hours) UNIT – I Types of Reactions, Mechanisms and Reaction intermediates (15 Hours)

Types of reactions : Substitutions, Additions, Eliminations, Rearrangements,

Reaction Mechanisms : Types of mechanisms : Heterolytic, Homolytic and

**Reaction intermediates :** Formation, stability and structure of carbonium ions,

Free radical reactions : Sandmeyer reaction, Gomberg-Bachmann reaction,

#### **UNIT – II Structure and Reactivity** Effect of structure on reactivity - resonance and fields effects, steric effects,

Pericyclic mechanisms – a general study.

carbanions, carbenes, nitrenes and free radicals.

Oxidations and Reductions reactions – a general study.

#### (15 Hours)

(15 Hours)

(15 Hours)

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#### **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.
- P.S. Kalsi, Stereochemistry Conformation and Mechanism, 6<sup>th</sup> 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**, 2<sup>nd</sup> Edition, New Age International Publishers, 1994.
- 3. S.M. Mukherji and S. P. Singh, Reaction Mechanism in Organic Chemistry, 1<sup>st</sup> Edition, Macmillan, 1976.
- 4. R.T. Morrison and R.N. Boyd, **Organic Chemistry**, 6<sup>th</sup> 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**, 2<sup>nd</sup> Edition, Interscience Publishers, 1967.
- 7. J.A. Joule and G.F. Smith, **Heterocyclic Chemistry**, Van Notrand Reishord 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 sleves.

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

#### UNIT-II Nuclear Chemistry-I

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)

(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 Photoelectron Spectroscopy and Inorganic photochemistry

#### (15 Hours)

Photoelectron Spectroscopy-Principle, PES of diatomic molecules and polyatomic molecules (HCl, HBr, HI, CO, NH<sub>3</sub> and H<sub>2</sub>O);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 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, CdI<sub>2</sub> ,Pervoskite, rutile, fluorite and antifluorite-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. C.N.R. Rao and J.R.Ferraro, Spectroscopy in Inorganic Chemistry, Vol I and Vol II, Academic press, 1970.

- H.A.O. Hill and P.Day, Physical methods in advanced Inorganic chemistry, John Wiley, 1986.
- 7. A.K. Srivatsava and P.C. Jain, Elements of Nuclear Chemistry, S.Chand and Co., 1989.
- G. Friedlander, J.W.Kennedy and J.M. Miller, Nuclear and Radio Chemistry, Wiley., 1964.
- 9. Mullor, Inorganic structural chemistry, Wiley, New York, 1993.

#### Core Paper - III PHYSICAL CHEMISTRY – I (75 Hours)

#### Unit – I Classical Thermodynamics – I

#### (15 Hours)

(15 Hours)

(15 Hours)

Maxwell's relations and thermodynamic equations of state – applications in the evaluation of Cp – Cv for solids and for vanderwaals gases, Cp – Cv in terms of coefficient of expansion and coefficient of compressibility – Relation between Cp and Cv – 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

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

# 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.

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#### Unit – IV Group Theory – I

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 – Einstein's theory of transition probability – 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.

#### (15 Hours)

- 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, Addision 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. Copolymerization : Block and graft co-polymers, kinetics of copolymerization. Types of co- polymerization. Evaluation of monomer. Reactivity ratio. Rate of copolymerization.

9

F.W. Billmeyer, **TextBook of Polymer Science**, 3<sup>rd</sup> Edition, J.Wiley, 2003. 1. V. R. Gowariker, N.V. Viswanathan and J. Sreedhar, Polymer Science, New 2.

H.R. Alcock and F.W. Lamber, Contemporary Polymer Chemistry, Prentice Hall, 1981.

Age Int., 1986.

**Text Books** 

1.

**Reference Books** 

- 2. P.J. Flory, Principles of Polymer Chemistry, Cornell University press, New York. 1953.
- G. Odian, Principles of Polymerization, 2<sup>nd</sup> Edition, John Wiley & Sons, 3. New York, 1981.

**UNIT – V** Properties of Commercial Polymers (18 Hours) Polyethylene, polyvinyl chloride, polyamides, polyesters, phenolic resins, epoxy Functional polymers, Fire retarding polymers and resins and silicone polymers. electrically conducting polymers. Biomedical polymers – contact lens, dental polymers, artificial heart, kidney, skin and blood cells.

calendering, die casting, rotational casting, film casting, injection moulding, blow

#### **UNIT – IV Polymer Processing**

average molecular weights. Measurement of molecular weights. Gel permeation chromatography, viscosity, light scattering, osmotic and ultracentrifugation methods. Polymer structure and physical properties - crystalline melting point  $T_m$ . The glass transition temperature. Determination of T<sub>g</sub>. Relationship between T<sub>m</sub> and T<sub>g</sub>. (18 Hours)

Polydispersion – average molecular weight concept, number, weight and viscosity

Plastics, elastomers and fibres.

#### **UNIT – III Molecular Weight and Properties**

#### (18 Hours)

#### moulding extrusion, moulding, thermoforming, foaming, reinforcing and fibre spinning.

Compounding processing techniques :

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 II

Semes	Cala	Comment				Caradit		Marks	
ter	Code	Course	Course Title	Hrs.	Credit	CIA	EA	Total	
		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	
		Extra Disciplinary Biological chemis course	Biological chemistry	4	4	25	75	100	
II		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			100	

#### 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, Vilsmeir, 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.

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#### 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- NH<sub>2</sub> and R-COOH) Reagents and their uses: DCC, trimethyl silyl iodide, trimethyl silyl chloride, 1,3 – dithiane (umpolung), diisobutylaluminium hydride (DIBAL), 9BBN, Osmium tetroxide, DDQ, Selenium dioxide, Phase transfer Catalysts.

#### **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.
- P.S. Kalsi, Organic Reactions and Mechanisms, Second Edition, New Age International Publishers, 2002.
- P.S. Kalsi, Stereochemistry Conformation and Mechanism, 6<sup>th</sup> 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**

- S. H. Pine, J.B. Hendrickson, D.J. Cram and G.S. Hammond, Organic Chemistry, IV Edn., McGraw Hill Company, 1980.
- S.M. Mukherji and S. P. Singh, Reaction Mechanism in Organic Chemistry, 1<sup>st</sup> Edition, Macmillan, 1976.
- 3. R.T. Morrison and R.N. Boyd, Organic Chemistry, Prentice-Hall, 1992.
- 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)

#### 12

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

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

### Schrodinger 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 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**

Symmetry selection rules for vibrational, Electronic and Raman Spectra – determination of representation of vibrational modes in non-linear molecules such as  $H_2O$ ,  $CH_4$ ,  $XeF_4$ ,  $SF_6$  and  $NH_3$  – symmetry of Hybrid orbitals in non-linear molecule (BF<sub>3</sub>,  $CH_4$ ,  $XeF_4$ ,  $PCl_5$  and  $SF_6$ ) – 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.

#### (15 Hours)

#### (15 Hours)

#### (15 Hours)

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 – inhibition of enzyme catalyzed reactions.

#### **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.
- 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.
- 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.
- 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.
- 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).
- 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**, Addision Wesley, Reading, Mass, 1976.
- 13. H.Eyring, J.Walter and G. Kimball, **Quantum chemistry**, John wiley and sons, Newyork, 1944.
- L.S.Pauling and E.B.Wilsob, Introduction to Quantum Mechanics, Mc Graw Hill book Co., Newyork, 1935.
- 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

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)

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

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 (Zeigler- Natta catalyst); Cyclo oligomerization of acetylene using Nickel catalyst (Reppe'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, 4<sup>th</sup> edition, Pearson-Education, 2002
- F.A.Cotton and G.Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern, 5<sup>th</sup> 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.
- D.F. Shriver, P. W. Atkins and C.H. Longford, Inorganic Chemistry, ELBS, 2<sup>nd</sup> 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. Addision, Structural Principles of Inorganic Chemistry, Longman, 1961.

### Extra Disciplinary Course BIOLOGICAL CHEMISTRY [60 Hours]

#### UNIT – I Bioorganic Chemistry – I (12 Hours)

Polypeptides and proteins – classification – the peptide linkage – sequential analysis of peptides – synthesis of polypeptides and synthesis of glutathione, oxytocin and thyroxine – solid phase synthesis (Merrifield synthesis).

Classification of proteins – primary, secondary, tertiary and quaternary structures of proteins – denaturation of proteins – determination of primary structure of proteins (end group assay).

#### **UNIT – II Bioorganic Chemistry – II** (12 Hours)

Nucleic acids - structure of nucleosides and nucleotides - synthesis of nucleosides and nucleotides – Structure and role of (genetic code) DNA and RNA. (Determination of structure is not required).

Biosynthesis of amino acids (phenylalanine, tyrosin, 3, 4 dopa, proline only) and cholesterol.

#### **UNIT – III Bioinorganic Chemistry** (12 Hours)

Metal ions in biological systems – essential and trace elements,  $Na^+ / K^+$  Pump; Biologically important complexes of Iron (transport proteins) – haemoglobin, myoglobin, iron – sulphur proteins, cytochrome – C, Magnesium (chlorophyll), Cobalt (vitamin  $B_{12}$ ), Zinc (carbonic anhydrase, carboxy peptidase); fixation of Nitrogen. (12 Hours)

#### **UNIT – IV Terpenoids**

Isoprene rule – Special isoprene rule, Classification of terpenoids with few examples. Structural elucidation and synthesis of menthol, Abietic acid, Squalene and Phytol.

#### **UNIT – V Carotenoids**

Synthesis of  $\alpha$  – carotene,  $\beta$  – carotene,  $\gamma$  – carotene, Vitamin A<sub>1</sub>, and Vitamin A<sub>2</sub>. Geometrical isomerism of Carotenes.

#### **Text Books:**

- 1. I.L. Finar, Organic Chemistry, Volume II, Fifth Edition, First Indian reprint, Pearson Education Asia Pte. Ltd., (2000)
- 2. G. Chatwal, Organic Chemistry of Natural Products, Vol. I & II, Himalaya Publishing House, 1988.
- 3. A.L. Leninger, **Biochemistry**, Nath Publishers
- 4. M.N. Hughes, The Inorganic chemistry of Biological Processes, Willy London (1982) II Edition.

#### (12 Hours)

- 5. S.J. Lippard and Berg, **Principles of Bioinorganic chemistry**, Univ. Science Books. 1994.
- 6. D.E. Fenton, Biocoordination Chemistry, Oxford Science Publication, 1995.

#### **Reference Books:**

- 1. J. Mann, R.S. Davidson, J.B. Hobbs, D.V. Banthropeand J.B. Harborne, Longman, Essex, Natural Products: Chemistry and Biological Significane.
- 2. Atta. Ur. Rahman and M.I. Choudhary, New Trends in Natural product chemistry, Harwood Academic Publishers.
- 3. J.A. Cowan, Inorganic biochemistry, wiley VCH, New York, 1997.
- 4. Voet and Voet, Biochemistry, John Wilay & Son 1990.
- R.K. Muray, D.K. Grammer, P.A. Mayer, V.W. Rodwell, Biochemistry, 24<sup>th</sup> Ed. 1990.
- O.P. Agarwal, Chemistry of Organic Natural Products, Vol I & II, Goel Publishing House, 1988.

#### Core Practical - I ORGANIC CHEMISTRY PRACTICAL I

- 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. s-Benzyl isothiuronium chloride from benzylchloride
- 3. Beta glucose penta acetate from glucose
- 4. ortho-Benzoyl benzoic acid from phthalic anhydride
- 5. Resacetophenone from resorcinol
- 6. para-Nitrobenzoic acid from para nitrotoluene
- 7. meta-Nitroaniline from meta dinitrobenzene
- 8. Methyl orange from sulphanilic acid

- 9. Anthraquinone from anthracene
- 10. Benzhydrol from benzophenone

#### Distribution of Marks for Practical –I

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

#### 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 cations 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:
  - a) Potassium trioxalatoaluminate (III) trihydrate
  - b) Tristhioureacopper(I) chloride
  - c) Potassium trioxalatochromate (III) trihydrate
  - d) Sodium bis (thiosulphato) cuprate (I)
  - e) Tetramminecopper (II) sulphate

f) Potassium Tetrachlorocuprate (II)

#### **Distribution of Marks for Practical –I**

Qualitative	analysis	: 20 marks
Colorimetric	analysis	: 15 marks

Duration	: 6 hours
Total	: 60 marks
Record	: 5 marks
Viva – voce in practical	: 10 marks
Preparation	: 10 marks

#### Core Practical - III PHYSICAL CHEMISTRY PRACTICAL I LIST OF EXPERIMENTS

- 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.
- 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.
- Construction of phase diagram for a simple binary system (naphthalene phenanthrene and benzophenone – diphenylamine).
- 4. Determination of the equilibrium constant of the reaction between Iodine and KI by partition method.
- 5. 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.
- 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.
- 7. 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.

- Conductometric titrations of a mixture of HCl and CH<sub>3</sub>COOH against Sodium hydroxide
- Determination of the activity coefficient of an electrolyte at different molalities by emf measurements.
- 10. 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.
- 11. Determination of the P<sup>H</sup> of a given solution by emf method using hydrogen electrode and quinhydrone electrode.
- 12. 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.
- 13. Study the surface tension concentration relationship of solution (Gibb's equation)
- 14. Determination of the viscosities of mixtures of different composition of liquids and find the composition of a given mixture.

#### **Distribution of Marks for Practical –I**

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

#### Distribution of Marks Theory University Examinations (UE) : 75 Marks Internal Assessment (IA) : 25 Marks Classification of Internal Assessment Structure - 10 Marks

Test

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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** 

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#### 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 Experime	ents-	10 Marks
Experimental S	kill-	10 Marks
Test -	20 N	larks

Total - 40 Marks

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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 2008 – 2009 onwards) M.Sc. DEGREE Branch IV (D) Organic Chemistry First Semester Core Paper - I ORGANIC CHEMISTRY – I

#### **Time : Three Hours**

Maximum: 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### 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 $(5 \times 10 = 50 \text{ Marks})$ 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 nitren	es (4)
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- (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 $\sigma$ and	ρ (3)
ii) Discuss the principle of microscopic reversibility.	(3)
iii) Draw the potential energy diagrams for the reactions involving (a) no	o intermediate
(b) an intermediate.	(4)
Or	
b) Explain the usefulness of the following methods in determining the	mechanism of a
reaction. Give suitable examples.	
i) Isotopic labelling	
ii) Primary isotope effect	
iii) Determination of the presence of an intermediate. $(3+3)$	+ 4)
8. a) i) Explain the homotopic, enantiotopic, and diastereotopic H atoms	s 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	2
meso – tartaric acid.	(6).
(ii) Give examples for Stereo selective and Stereo specific reactions	S.
What is the difference between them.	(4)
9) a) i.) Briefly discuss the effects of substrates structure, attacking nucl-	oephile, 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	
i) SN <sup>i</sup> reaction proceeds with retention of configuration.	
ii) Nucleophilic substitution at allylic substrate gives mixture of products.	
iii) 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 2008 – 2009 onwards) M.Sc. DEGREE Branch IV (D) Organic Chemistry First Semester Core Paper - II INORGANIC CHEMISTRY – I

#### **Time : Three Hours**

#### Maximum : 75 Marks

 $PART - A \quad (5 X 5 = 25 Marks)$ 

#### 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) Explain photoisomerisation with an example

#### Or

b) Discuss the PES of a HBr molecule.

5. a) Distinguish between spinels & inverse spinels.

#### Or

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

#### $PART - B (5 \times 10 = 50 \text{ Marks})$

#### 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		
ii) Discuss the types of photonuclear reaction.		
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) 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)	
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		
iodide	(4)	

#### Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. DEGREE Branch IV (D) Organic Chemistry First Semester Core Paper - III PHYSICAL CHEMISTRY – I

**Time : Three Hours** 

Maximum : 75 Marks

 $PART - A \quad (5 X 5 = 25 Marks)$ 

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 x 10<sup>-19</sup> J for  $\lambda = 300$  nm. Calculate the threshold frequency of Lithium atom (h = 6.626 x 10<sup>-34</sup> 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.

#### $Part - B (5 \times 10 = 50 \text{ Marks})$

#### 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	Cp – Cv	
for solids.	(5)	
(ii) Derive Gibbs Duhem equation.		
7 a) i) Explain the effect of temperature on reaction rate.		
ii) Give a detailed account on collision theory.		
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 or	ie	
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 radi	ation. (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	eter 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.		
(ii) Explain Franck Condon Principle	(3)	
(iii) Discuss the selection rule for rotational transition		
Or		
b) i) Discuss the rotational – vibrational Raman spectrum of a diatomic molect	ule (7)	
ii) Calculate the force constant for H <sup>35</sup> Cl from the fact that its fundamental v	ibrational	

frequency is 8.667  $\times 10^{13}$  sec<sup>-1</sup>.

(3)

Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. DEGREE Branch IV (D) Organic Chemistry First Semester Elective Paper - I POLYMER CHEMISTRY

#### **Time : Three Hours**

#### **Maximum : 75 Marks**

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### 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 Tg and Tm? 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)

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(ii) Write down the different types of terminations encountered in a fre	e 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 gel permeation chromatography in the polymer fractiona	tion and
molecular weight computation method.	(5)
Or	
b) (i) Explain the ultra centrifugation technique for the determination of n	ıolecular
weight of polymers	(5)
(ii) Describe light scattering method of determination of molecular wei	ght of a
polymer sample. How is it related to $\overline{Mn}$ ?	(5)
9 a) (i) Account on the following techniques.	
(1) Thermoforming	
(2) Reinforcing	(6)
(ii) Describe how three dimensional articles are produced by thermo-	oforming
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 neurons) How do they differ from	andinami

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 2008 – 2009 onwards) M.Sc. Degree Branch IV (D) Organic Chemistry Second Semester Core Paper - IV ORGANIC CHEMISTRY - II

#### **Time : Three Hours**

#### Maximum: 75 Marks

PART – A  $(5 \times 5 = 25 \text{ Marks})$ 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 Osmium tetroxide 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.	
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 SNAr 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-Fluoroehanol

ii) cis – 4- methyl cyclohexanol

iii) 2- Chlorocyclo hexanone

iv) trans -1, 3-Di -t – butylcyclo hexane.

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.

33

Or

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

i) 9BBN

ii) DDQ

iii) Trimethyl silyl iodide

(4+3+3)

#### Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. Degree – Branch IV (D) Organic 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 H<sub>2</sub>O 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<sup>-1</sup> ii) 150 KJ mol<sup>-1</sup>. Assume that  $T_o = 10^{-13}$  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 heliu	m 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<sub>3</sub> molecule. (10)

#### Or

b) With the help of  $D_4h$  character table find the set of orbital suitable for hybridisation in XeF<sub>4</sub> (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 physisorpton and Chemisorption (4)

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

#### Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. Degree – Branch IV (D) Organic Chemistry Second Semester Elective Paper - II CO-ORDINATION CHEMISTRY

**Time : Three Hours** 

Maximum : 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### 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 Fe (CO)<sub>5</sub>.

#### 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  $[Fe F_6]^{3-}$  and  $[Fe (CN)_6]^{3-}$  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 MLn, 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)

#### **Model Question Paper**

#### (For the candidate admitted from 2008 – 2009 onwards)

M.Sc. Degree – Branch IV (D) Organic Chemistry

#### **Second Semester**

#### **Extra Disciplinary Course**

#### **BIOLOGICAL CHEMISTRY**

**Time : Three Hours** 

#### Maximum: 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### Answer all the questions

#### All questions carry equal marks

1.a) How is solid phase peptide synthesised

#### Or

b) What is denaturation of protein ? How is it brought about? What happens to the structure of the protein during denaturation.

2. a) Discuss the biological function of RNA and DNA.

#### Or

b) Schematically outline the biosynthesis of L – Phenylalanine and proline.

3. a) Discuss the role of magnesium in photosynthesis.

#### Or

b) Write a short note on Cytochorme – C

4. a) How are the terpenoids classified.?

#### Or

b) Bring out the method of synthesis of squalene.

5. a) Write the synthesis of vitamin  $A_1$ .

#### Or

b) Write briefly about the synthesis of  $\gamma$  – Carotene.

#### PART - B (5 X 10 = 50 Marks)

#### Answer all the questions

#### All questions carry equal marks

6. a) i) Give an account of determination of the primary structure of proteins (5)

ii) Comment on the need for protection of -NH<sub>2</sub> and -COOH groups in peptide synthesis. (5)

#### Or

b) i) Write an account of the two possible secondary structure of proteins advanced by Pauling. (5)

ii) Discuss the tertiary structure of proteins	(5)
7. a) i) Discuss the structure of RNA	(6)

ii) In what way is DNA different from RNA. (4).

#### Or

b) i) Write notes on biological importance of nucleotides	(4)
ii) How is cholesterol biosynthesized from acetic acid?	(6)

- 8. a) i) Explain the functions of haemoglobin and myoglobin (5)
  - ii) Discuss the principal similarities in their structures. (5)

#### Or

b) i) Discuss the bioinorganic chemistry of nitrogen fixation.	(6)
ii) Write a short note on the structure of Vitamin $B_{12}$ .	(4)
9. a) i) Indicate a method of synthesis of abietic acid.	(7)
ii) State and explain isoprene rule	(3)
Or	

b) Elucidate the structure of menthol (10)

10. a) i) Draw the molecular structures of  $\beta$  – carotene. How is its structure confirmed by synthesis. (6)

11) Write an account of geometrical isomerism of carotenes. (4)
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#### Or

b) Write briefly about the following

i) Syntheis of vitamin A <sub>2</sub>	(5)
ii) Synthesis of $\alpha$ - carotene	(5)

#### SECOND YEAR Semester III

	Semester III			
Code No.	Course	Subject	Work load per Semester (hours)	
	Core Paper – VI	Organic Chemistry – III	75	
	Core Paper – VII	Organic Chemistry – IV	75	
	Core Paper – VIII	Organic Chemistry – V	75	
	Elective Paper – III	Instrumental methods of Analysis	90	
	Core Practical – IV	Organic Chemistry Practical – II	45	
	Core Practical – V	Organic Chemistry Practical – III	45	
	Core Practical - VI	Organic Chemistry Practical – IV	45	

#### SECOND YEAR Semester III

Sem ester	Code	Course	Course Title	Hr s	Credit	Marks		
						CIA	EA	Total

	Core Paper – VI	Organic Chemistry – III	5	5	25	75	100
	Core Paper – VII	Organic Chemistry – IV	5	5	25	75	100
	Core Paper – VIII	Organic Chemistry – V	5	5	25	75	100
III	Elective Paper – III	Instrumental methods of Analysis	6	4	25	75	100
	Core Practical – IV	Organic Chemistry Practical – II	3	-	-	-	-
	Core Practical – V	Organic Chemistry Practical – III	3	-	-	-	-
	Core Practical - VI	Organic Chemistry Practical – IV	3	-	-	-	-

#### Core Paper - VI ORGANIC CHEMISTRY - III [75 Hours]

#### **UNIT – I Molecular Rearrangements**

#### (15 Hours)

A detailed study of the mechanism of the following rearrangements: Nucleophilic, Electrophilic and Free radical rearrangements – memory effects, migratory aptitudes; Pinacol – Pinacolone, Wagner – Meerwin, Demyanov, Dienone-Phenol, Favorski, Benzidine, Baeyer – Villiger, Wolff, Stevens, Von – Richter, Claisen, Cope, Sommlet – Hauser, Pummerer, Hofmann, Schmidt, Lossen, Curtius, Beckmann and Fries rearrangements (Few examples in each rearrangement are to be studied).

#### **UNIT – II Name Reactions**

#### (15 Hours)

A study of the following name reactions: Dieckmann cyclization, Shapiro reaction, Stork enamine, Barton, Sharpio, and ene reactions; Sharpless asymmetric epoxidation, Robinson annulation; Grignard reactions, Duff reactions, Simmons Smith reaction, Chichibabin reaction, Hoffmann – Loffler – Freytag reaction, Gilman's reagent reaction.

#### UNIT - III Addition to carbon - carbon multiple bonds (15 Hours)

40

Electrophilic, Nucleophilic and Free radical additions – Addition to conjugated dienes – orientation and reactivity – Additions of halogen, halogen acids and nitrosyl chloride to C-C double bonds; Markovnikov and Anti Markovnikov addition; Stereochemistry of additions; 1,3 dipolar addition; Hydration of olefins and acetylenes; Hydroxylation, Hydroboration and Diels - Alder reactions, carbenes and their additions.

#### UNIT – IV Addition to Carbon – Hetero Atom multiple bonds

#### (15 Hours)

(15 Hours)

Reactions of carbonyl group – Mechanisms of Aldol, Perkin, Mannich, Stobbe, Benzoin, Darzen Glycidic ester and Dieckmann condensations; Strecker synthesis, Wittig, Thorpe, Ritter and Prins reactions; Conjugate additions to  $\alpha,\beta$ - unsaturated carbonyl and nitrile systems – Michael addition; Formation of enamine and their synthetic applications. Wittig – Horner reaction.

#### UNIT – V Retro synthesis

# Retro synthetic analysis – definition; synthon approach – synthetic equivalent, reagent, functional group interconversions; Linear and convergent method in organic synthesis; Disconnection approach – one group disconnection; retro synthesis of alcohols; retro Diels – Alder reaction; retro synthesis of olefins, aliphatic and aromatic ketones; protective groups in organic synthesis.

#### **Text Books:**

- 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. I.L. Finar, **Organic Chemistry**, Volume II, Fifth Edition, First Indian reprint, Pearson Education Asia Pte, Ltd. 2000.
- Paul de Mayo, Molecular Rearrangements, Vol. I, Vol. II, Interscience, NY, 1963.
- R.T. Morrision and R.N. Boyd, Organic Chemistry, Prentice Hall, 6<sup>th</sup> Edn, 1992.

#### **Reference Books**

- P.S. Kalsi, Organic Reactions and Mechanisms, Second Edition, New Age International Publishers, 2000.
- S.H. Pine, J.B Hendrickson, D.J. Cram and G.S. Hammond, Organic Chemistry, IV Edn, McGraw Hill Company 1980.
- S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry, III En. 1984. MacMillan.
- R.O.C Norman, Principles of Organic Synthesis, Second Edition, Chapman and Hall, 1978.
- R.K. Mackie and Smith, Organic Synthesis, II Ed., Longman Group UK Ltd, 1990.
- V.K. Ahluwalia and R.K. Parashar, Organic Reaction Mechanisms, Narosa Publishing House, 2002.
- 7. W. Carrothers, Some modern methods of organic synthesis, OUP, 1982.
- 8. H.O. House, Modern synthetic reactions, Allied Publishers.

#### **Core Paper - VII**

#### **08POC07 ORGANIC CHEMISTRY – IV**

Organic Spectroscopy [75 Hours]

#### UNIT – I UV – VIS and ORD – CD

# UV – VIS: Laws of light absorption – chromophores and auxochromes – types of electronic transitions – bathochromic, hypsochromic, hypochromic and hyperchromic effects; Applications of UV – VIS spectroscopy – use of model compounds and additivity – dienes, polyenes and $\alpha$ , $\beta$ – unsaturated carbonyl compounds – Woodward – Fieser rules – Calculation of $\lambda_{max}$ for organic molecules; absorption spectra of polyenes, polyenyenes and aromatic compounds; stereochemical factors in electronic spectroscopy; charge transfer complexes.

**ORD** – **CD:** Definition – circular birefringence and circular dichroism; plain dispersion curves and their applications; single and multiple cotton effect curves; structural and stereochemical applications – axial haloketone rule, octant rule for ketones; comparison of ORD and CD.

#### UNIT – II IR and Raman

#### (15 Hours)

(15 Hours)

**IR** : Molecular vibrations – stretching and bending vibrations, Hooks law – Overtone and combination band; Factors influencing vibrational frequencies – effect of substituents,

conjugation, distortion, geometry, hydrogen bonding – Fermi resonance; Characteristic group frequencies of organic molecules; interpretation of IR spectra of organic molecules.

**Raman :** Theory, application of Raman spectra to organic, inorganic and biological species, quantitative applications, Resonance Raman spectroscopy.

#### UNIT – III $^{1}$ H NMR

#### (15 Hours)

Origin – relaxation and saturation; Chemical shift, factors influencing chemical shift; magnetic equivalence – homotopic, enantiotopic and diastereotopic protons; spin – spin coupling – Criteria for first order and non – first order spectra – representation of non-equivalent hydrogens by alphabets; geminal, vicinal and long range couplings – Karplus equation – NMR of simple AX and AMX type organic molecules, identification of H in various chemical environments to assign structure to the organic molecules using chemical shift values and coupling.

Simplification of spectra – high fields, deuterium exchange, shift reagents – satellite spectra – multiple resonance – spin decoupling, spin tickling and INDOR.

#### UNIT – IV <sup>13</sup>C NMR and ESR

#### (15 Hours)

 $^{13}$ C NMR : Distinction between <sup>1</sup>H and <sup>13</sup>C NMR – theory and experiment – factors affecting intensity of signals – nuclear Overhauser effect – chemical shift and its dependence on polar and steric effects (gamma gauche effect); additivity relationships - C-C and C-H couplings – off resonance, gated and single frequency decouplings – relationship between coupling constant and 's' character; effect of shift reagents on <sup>13</sup>C chemical shifts; applications of <sup>13</sup>C NMR to find the different carbon functional groups.

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 – V Mass Spectroscopy and conjoined problems (15 Hours)

**Mass Spectra:** Theory, applications, McLafferty rearrangement, fragmentation pattern, Examples of mass spectral fragmentation of organic compounds with respect to their structure determination.

**Conjoined problems:** Structural elucidation of organic compounds using a combination of all the above spectral methods – a problem solving approach. **Text Books:-**

- 1. William Kemp, Organic Spectroscopy, ELBS II Edition, Spectroscopy of organic compounds.
- 2. P.S. Kalsi, Organic Spectroscopy, Wiley Eastern Ltd, Madras.

3. R.M. Silverstein, C.G. Bassler and Monsil, Spectrometric identification of organic compounds, John Wiley & Sons, New York.

#### **Reference Books:-**

- 1. J. Dyer, Application of absorption spectroscopy of organic compounds, Prentice Hall of India Pvt. Ltd., New Delhi.
- 2. W.Kemp, NMR in Chemistry, MacMillan Ltd, 1986.
- 3. J.B. Lambert, H.F. Shunnel, L. Verbit, R.G. Cooks and G.H. Stout, Organic structural analysis, MacMillan, 1976.
- 4. G.C. Levy and G.L. Nelson, Carbon 13 Nuclear Magnetic Resonance for organic chemists, Wiley - Interscience, 1972.
- 5. R.A.W. Johnstone, Mass spectrometry for organic chemists, Cambridge, 1972.
- 6. M.C. Hamming and N.G. Foster, Interpretation of Mass spectra of organic compounds, Academic Press, 1972.
- 7. C.Djerassi, Optical rotatory dispersion application to organic chemistry, McGraw Hill, 1960.
- 8. R.J. Abraham and P. Loftus, Proton and carbon 13 spectroscopy, Heydon & Sons., 1978.
- 9. D.H. Williams and I.Fleming, Spectroscopic methods in organic chemistry, Tata McGraw Hill, 4<sup>th</sup> Edition, 1988.

#### **Core Paper - VIII**

#### 08POC08 ORGANIC CHEMISTRY - V [75 Hours]

#### **UNIT – I Carbohydrates**

# Introduction, definition and classification; Monosaccharides - configuration of aldotrioses, aldotetroses, aldopentoses, aldohexoses, Ketohexoses; Deoxy - sugars; Ring structure of monosaccharides; mutarotation; a brief introduction on the structure of disaccharides (sucrose and maltose as representative examples) and polysaccharides (starch, cellulose and cyclodextrins as representative examples).

#### **UNIT – II** Vitamins

Structure and synthesis of the following : Retinol, thiamine, riboflavin, pyridoxine, pantothenic acid, ascorbic acid, tocopherols, vitamin k and cyanocobalamine.

#### **UNIT – III Alkaloids**

Definition; Occurrence; Extraction of alkaloids; General properties; Classification of alkaloids; Structure elucidation, synthesis and stereochemistry of the following alkaloids : Quinine, Morphine, Yohimbine, Reserpine, Strychnine, Lysergic acid.

#### **UNIT – IV Oxidation Reactions**

Study of the following oxidation reactions with mechanism: Oxidation of alcohols by CrO<sub>3</sub>, DMSO alone. DMSO in combination with DCC, acetic anhydride and oxalyl chloride, oxidation of arylmethane, oxidation of methylene alpha to carbonyl, allylic

44

(15 Hours)

(15 Hours)

#### (15 Hours)

#### (15 Hours)

oxidation of olefins, oxidative cleavage of glycols, oxidative cleavage of double bonds by ozonolysis, Lead tetra acetate, Periodic acid, MnO<sub>2</sub>, Oppenauer oxidation.

#### **UNIT – V Reduction Reactions**

#### (15 Hours)

Study of the following 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, Homogeneous and heterogeneous hydrogenation (Reduction of alkenes, alkynes, and aromatic compound with hydrogen), Use of complex metal hydrides as reagent.

#### **Text Books:**

- 1. I. L. Finar, **Organic Chemistry**, Vol II, 5<sup>th</sup> Edn. Pearson Education Asian Pvt. Ltd. 2000.
- Atta-Ur-Rahman and M.I. Choudhary, New Trends in Natural Product Chemistry, Gordon & Breach Science Publishers, I Edn., 1998.
- Jerry March, Advanced Organic Chemistry Reactions, Mechanisms and Structure, 4<sup>th</sup> Edition, John Wiley & Sons, 1992.
- G. Chatwal, Organic Chemistry of Natural Products, Vol I & II, Himalaya Publishing House, 1988.
- 5. Organic reaction mechanisms, K. Ahluvalia, R.K. Parashar, Narosa Publishing House.

#### **Reference Books:**

- 1. S.W. Pelletier, Van Nostrand, Chemistry of Alkaloids, Reinhold, 1970.
- 2. Hendry, The Plant Alkaloids, Churchill Publishers, IV Edn., 1949.
- 3. Bentley, The Natural Pigments, Interscience, 1960.
- O.P. Agarwal, Chemistry of Organic Natural Products, Vol I & II, Goel Publishing House, 1988
- S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry, III Edn, 1984. Macmillan.

# Elective Paper - III 08POCZ03 INSTRUMENTAL METHODS OF ANALYSIS [90 Hours]

#### UNIT – I Absorption, Emission and Reflection Spectroscopy (18 Hours)

Absorption spectrometry – Beer Lamberts law; Principles of UV visible spectroscopy – photometric titrations; Principles and applications of Fluorimetry, turbidimetry and nephelometry.

Flame Photometry – Theory, instrumentation and a few important applications; Atomic absorption spectroscopy (AAS) – Theory, instrumentation and applications; Atomic fluorescence.

#### UNIT – II Thermal and Magnetic Methods of Analysis (18 Hours)

DTA/DSC – Principle and instrumentation, Different techniques. Application to organic and inorganic compounds.

TGA – Principle, instrumentation of TGA curves, Application to organic and inorganic compounds.

Magneto chemical Analysis – Magnetic susceptibility and its measurements, Guoy's, Quink's curie's, and Ranking's balances. Application to simple compounds and ranking's transition metal complexes, Lanthanides and Actinides.

#### UNIT – III Nuclear Magnetic Resonance and Electron Spin Resonance Spectroscopy (18 Hours)

Nuclear Magnetic Resonance Spectroscopy – Theory, relaxation and saturation processes, Environmental effects, instrumentation – type of magnets, source, detector and sample handling; few application of proton NMR; qualitative and quantitative analysis. Lanthanide, compounds as shift reagents.

Electron Spin Resonance – Theory, instrumentation and a few applications in qualitative and quantitative analyses.

#### UNIT – IV Polarography and Amperometry (18 Hours)

Polarography – Theory, apparatus, DME, diffusion kinetic and catalytic currents, current voltage curves for reversible and irreversible system, qualitative and quantitative application to inorganic systems.

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

#### **UNIT – V** Chromatography

#### (18 Hours)

Principle, method and applications of column and thin layer chromatographies; Gas liquid chromatography – principle, retention time values, instrumentation, carrier gas, column, detectors – thermal conductivity, flame ionization and electron capture; few applications of GLC; HPLC – theory, instrumentation and applications.

#### **Text Books:-**

- 1. Williard, Merit, Dean and Settle, Instrumental Methods of Analysis, CBS Publishers and Distributors, IV Edn. 1986.
- Schoog, Holler, Nieman, Principles of Instrumental Analysis, Thomson Asia Pvt Ltd., Singapore. 2004.
- D.A. Skoog, Principles of Instrumental Analysis, Saunders College Pub. Co, III Edn., 1985.
- 4. A.I. Vogel, Text Book of Quantitative Inorganic Analysis. ELBS III Edn, 1987.
- 5. J.O.M. Bockris and AKN Reddy, Modern Electrochemistry, Plenum, 1970.
- D.A. Skoog and D.M.West, Fundamentals of Analytical Chemistry, Holt Rinehart and Winston Publications, IV Edn, 2004.
- 7. W.Kemp, NMR in Chemistry, MacMillan Ltd, 1986.

#### **Reference Books:**

- 1. Albert Paul Malvino, Electronic Principles, PMH Publishers, III Edn, 1984.
- 2. J.G. Dick, Analytical Chemistry, McGraw Hill Publishers, 1974.
- G.W. Ewing, Instrumental Methods of Chemical Analysis, McGraw Hill Pub, 1975.

- 4. B.H. Vassos and G.W. Ewing, Electroanalytical Chemistry, John Wiley and Sons, NY, 1983.
- R. Greef, R.Peat, L.M. Peter, D. Pletcher and J.Robinson, Instrumental methods in Electrochemistry, Ellis Horwood, Chichester, 1985.
- 6. A.J. Bard and L.R. Faulkner, Electrochemical methods; Fundamentals and applications, J. Wiley and Sons, NY, 1980.

#### SECOND YEAR

#### Semester IV

			Work load per	
Code No.	Course	Subject	Semester	
			(hours)	
08POC09	Core Paper – IX	Organic Chemistry – VI	90	
08000704	Elective Depor	Industrial and Medicinal	00	
08FUC204	Elective rapei – Iv	Organic Chemistry	90	
	Core Practical IV	Organic Chemistry	60	
08100104	Core Fractical – IV	Practical – II		
	Core Practical – V	Organic Chemistry	60	
001 001 05	Core i lactical V	Practical – III	00	
08000006	Core Practical VI	Organic Chemistry	60	
08100100		Practical – IV	00	
	Project	Dissertation / Project Work	90	
UOF UCD/ FW	riojeci	in Organic Chemistry.	70	

#### **SECOND YEAR**

#### Semester IV

Sem ester	Code	Course Course Title	Hrs.	Cre dit	Marks			
					CIA	EA	Total	
IV	08POC09	Core Paper – IX	Organic Chemistry – VI	6	6	25	75	100
	08POCZ04	Elective Paper – IV	Industrial and Medicinal Organic Chemistry	6	4	25	75	100
	08POCP04	Core Practical – IV	Organic Chemistry Practical – II	4	4	40	60	100
	08POCP05	Core Practical – V	Organic Chemistry Practical – III	4	4	40	60	100
	08POCP06	Core Practical – VI	Organic Chemistry Practical – IV	4	4	40	60	100
	08POCD/P W	Project	Dissertation / Project Work in Organic Chemistry.	6	5	-	-	200

# 50

#### UNIT – IV Steroids – I

#### (Organic Photochemistry, Pericyclic reactions and Steroids) [90 Hours]

#### UNIT – I Symmetry and perturbation theory and introduction to

#### photochemistry

#### (18 Hours)

Symmetry and perturbation theory: Definition – interaction between molecular orbitals, basic orbitals of the same energies and different energies; symmetry applications of symmetry to orbital interactions - localized and delocalized models; application of perturbation theory and symmetry to pi systems.

Basic concepts of organic photochemistry: Thermal versus photochemical reactions – electronic excitations – n –  $\pi^*$  and  $\pi - \pi^*$  transitions, singlet and triplet energy states - comparison of energies, lifetimes and reactivates; allowed and forbidden transitions; fluorescence, phosphorescence and internal conversion - intersystem crossing; Jablonski diagram; quantum yields and their determination; sensitization and quenching.

#### **UNIT – II Organic Photochemistry**

#### Photochemical reactions of saturated ketones – Norrish Type I and Norrish Type II reaction; photoreduction of ketone, photoaddition reactions, Paterno Buchi reaction.

Photochemistry of simple olefins - cis - trans isomerization, 1,3-dienes, 1,4dienes, di – pi methane rearrangement, 1,5 – dienes – sigmatropic rearrangement.

Photooxidation – Formation of peroxy compounds – oxidative couplings – Barton reaction.

Photo rearrangements : Photo – Fries rearrangement and Photo rearrangement of 2,5 – Cyclohexadienones.

#### **UNIT – III Pericyclic Reactions**

# Pericyclic reactions, classification, orbital symmetry, Woodward Hofmann rules, selection rules and stereochemistry of electrocyclic reactions, cycloaddition and signatropic shifts, analysis by correlation diagram method and Frontier molecular orbital method, comparison of Woodward - Hofmann and Dewar - Zimmermann pericyclic selection rules.

Sommelet, Hauser, Cope and Claisen rearrangements.

#### (18 Hours)

(18 Hours)

#### (18 Hours)

Classification with examples, nomenclature of steroids; Structure, Steroechemistry and synthesis of the following:

Sterols: Cholesterol, Ergosterol, Lanosterol, Stigmasterol, Ergocalciperol.

Bile acids: Cholic acid

Biosynthesis of Sterols

#### UNIT – V Steroids – II

#### (18 Hours)

Synthesis and structure of the following :

Steroidal glycosides: Saponis and Sapogenins

Cardiotonic glycosides; Strophanthidin

General discussion on Steroidal alkaloids

Male sex harmones: Androsterone and testosterone

Female sex harmones: Eqilenin, Oestrone, Oestradiol and Oestriol

#### **Text Books:-**

- 1. I. L. Finar, **Organic Chemistry, Volume II**, Fifth Edition, First Indian Reprint, Pearson Education Asia Pvt Ltd., 2000.
- 2. F.A. Carey and Sundberg, Advanced Organic Chemistry, Part A &B, III Edn, Plenum Press, 1990.
- 3. Charles H. DePuy, **Molecular Reactions and Photochemistry**, Orville L. Chapman, Prentice Hall of India Private Limited, New Delhi, 1988.
- 4. G. Chatwal, **Organic Chemistry of Natural Products**, Vol. I & II, Himalaya Publishing House, 1988.
- 5. Atta Ur Rahman and M.I. Choudhary, New Trends in Natural Product chemistry, Gordon & Breach Science Publishers, I Edn. 1998.

#### **Reference Books:-**

- 1. J.M. Coxon and B. Halton, Organic Photochemistry, Cambridge University press, 1979.
- 2. T.L. Gilchrist and R.C. Storr, Organic Reactions and Orbital symmetry, Cambridge, 1972.
- 3. S.M. Mukerjee and S.P. Singh, Pericyclic reactions, McMillan, 1976.
- 4. R.O. Kan, Organic Photochemistry, McGraw Hill, 1966.
- 5. O.P. Agarwal, Chemistry of Organic Natural Products, Vol I & II, Goel Publishing House, 1988.
- 6. Fisher and Fisher, Steroids, Reinhold, 1959.

#### Elective Paper - IV

#### 08POCZ04 INDUSTRIAL AND MEDICINAL ORGANIC CHEMISTRY [90 Hours]

#### **UNIT – I Petrochemicals**

#### (18 Hours)

Origin of petroleum: Products from fractional distillation; classification; composition of petroleum; fuel gases – knocking, octane number, cetane number; lubricating oils, greases and waxes; cracking, types of cracking – hydrocarbons from petroleum –  $C_2H_4$ ,  $C_2H_2$ ,  $C_6H_6$  and LPG.

Manufacture and uses of acetaldehyde, acetic acid, formaldehyde, ethylene glycol, 1,3-butadiene, styrene; chemical processing of aromatic hydrocarbons.

#### UNIT – II Paints and Dyes

#### (18 Hours)

**Paints :** Compositions – pigments, binders, extender, thinner and surface active agents; functions of the ingredients; Paint formulations; Importance of PVC, alkyds, epoxy and polyurethane resins.

**Dyes:** Colour and chemical constitutions; classification; brightening agents; cyanine dyes; chemistry of colour developer – instant colour processes; synthesis and applications of congo red, crystal violet, malachite green and Rhodamine B.

#### UNIT – III Antibiotics Analgesics and Antiseptics (18 Hours)

Antibiotics – synthesis, assay and structure and uses of penicilline, chloramphenicol and tetracyclines. Sulphonamides – mechanism and action of sulpha drugs, preparation and uses of sulphadiazine, sulphapyridine, sulphathiazole and sulphafurazole.

Narcotic analgesics – isolation, pharmacological action and uses of morphine, heroin and codeine; Synthetic analgesics – pethidine and methodone; Antipyretic analgesics – synthesis and structure and action of methyl salicylate, aspirin, paracetamol and phenacetin; Antiseptics and disinfectants – phenol as disinfectant and phenol coefficient; dyes and organo mercurials and cationic surfactants.

#### UNIT – IV Anaesthetics, Tranquilisers and Antineoplastics (18 Hours)

Anaesthetics – classification as general, local and intravenous anaesthetics, chemistry of anaesthetic ether, nitrous oxide, halothane, chloroform, thiopental sodium methohexitone, cocaine and benzocaine, Alkaloids – detection of alkaloids, colour reagents; Isolation, colour reaction and SAR of quinine; Tranquilisers, hypnotics and sedatives; Antineoplastic and hypoglycemic agents – detection of sugar and serum in

urine; cause and control of diabetes; Oral hypoglycemic agents; causes and control of cancer; Preparation and uses of thiotepa and cyclophosphoramide.

#### UNIT - V Organic Pharmaceutical Aids and Blood Chemistry

#### (18 Hours)

Preservatives and antioxidants, colouring, flavouring and sweetening agents and ointment bases; Blood – blood groups, Rh factor, blood pressure - normal, high and low; control of pressure; Causes and control of anaemia- antianaemic drugs, coagulants and anticoagulants; causes and control of AIDS.

#### **Text Books:-**

- 1. T.C. Daniels and E.C. Jorgensen, **Text book of organic medicinal and** pharmaceutical chemistry, J.B. Lippincott, Philadelphia, 1977.
- 2. Ashutosh Kar, Medicinal Chemistry, New Age International, 1996.
- 3. B.K. Sharma, Industrial Chemistry, Goel Publications, Meerut, 1992.

#### **Reference Books:-**

- 1. M. Gordon, Psychopharmacological agents, Academic press, New York, 1965.
- J.M. Ritchie and P.J. Cohen, The pharmacological basis of therapautics, 5<sup>th</sup> Edn., Macmillan, New York, 1975.
- D. Lednicer and L.A. Mitscher, Organic Chemistry of drug synthesis, John Wiley & Sons, New York, 1959.
- J.E. Hoover, Remington's Pharmaceutical sciences, 15<sup>th</sup> Edn. Mack Publ. Company, Easton, 1975.
- 5. B.N. Chakrabarthy, Industrial Chemistry, Oxford and IBH, New Delhi, 1981.
- M.G. Arora and M. Singh, Industrial Chemistry, Annol Publications, I edition, 1994.
- K.Venkataraman, The Chemistry of synthetic dyes, Part I & II, Academic Press, New York, 1952.
- V.A. Shenai, Introduction to Chemistry of Dyestuffs, Sevak Prakashan Pub., Mumbai, 1991.

#### **Core Practical - IV**

#### 08POCP04 ORGANIC CHEMISTRY PRACTICALS 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. para-Amino benzene sulphonamide from acetanilide
- 6. Anthraquinone from phthalic anhydride.

#### **Reference Books:**

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

#### **Distribution of Marks**

Total	: 60 marks
Record	: 5 marks
Viva-voce in practical	: 10 marks
Organic Preparation	: 20 marks
Organic estimation	: 25 marks

Core Practical - V ORGANIC CHEMISTRY PRACTICALS III

**08POCP05** 

#### 54

- 1) Estimation of the following:
  - 1. Hydroxyl group
  - 2. Amino group
  - 3. Amide group
  - 4. Glycin
  - 5. Ascorbic acid
  - 6. COD
- 2) Multistage preparation involving oxidations and reductions:
  - 1. Preparation of cyclohexanone (Oxidation)
  - 2. Preparation of adipic acid (Oxidation)
  - 3. Preparation of trimethyl acetic acid (Oxidation)
  - 4. Preparation of ethyl benzene (Wolff- Kishner reduction)
  - 5. Preparation of benzhydrol (Reduction)
  - 6. Preparation and stereochemistry of azobenzene (Reduction)

#### **Reference Books:**

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

#### **Distribution of Marks**

Total	: 60 marks
Record	: 5 marks
Viva-Voce in practical	: 10 marks
Preparation	: 20 marks
Estimation	: 25 marks

Core Practical - VI ORGANIC CHEMISTRY PRACTICALS IV

**08POCP06** 

1. Extraction of natural products such as caffeine, embelin, piperine, stigmasterol and  $\beta$  - carotene.

2 Separation and identification of aminoacids and sugars by paper and thin layer chromatography.

- 3 Column chromatographic separation of mixture of organic compounds
  - (a) Purification of anthracene
  - (b) Separation of aminoacids
  - (c) Separation of benzoic acid from benzaldehyde.
- 4. Elucidation of the structure of an organic compound from the spectra provided.

#### **Reference Books:**

- 1. Raj K. Bansal, Laboratory manual of Organic Chemistry, III Edn., New Age International (P) Ltd., 1996.
- B.S. Furniss, A.J. Hannaford., P.W.G. Smith and A.R. Tatchell, Vogel's Practical Organic Chemistry, 5<sup>th</sup> edn. ELBS, 1989.
- 3. Arun Sethi, Lab experiments in organic chemistry, New Age International Publishers.

#### **Distribution of Marks**

Total	: 60 marks
Record	: 5 marks
Viva-Voce in practical	: 10 marks
Spectral interpretation	: 20 marks
Extraction	: 25 marks

Model Question Paper (For the candidate admitted from 2008 – 2009 onwards)

## M.Sc. Degree – Branch – IV D Organic Chemistry Third Semester Core Paper - VI Organic Chemistry - III

**Time : 3 Hours** 

Maximum: 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### Answer all the questions

#### 1. a) $R_2CO + \dots > RCOOR + R'COOH$

Give the name of the reagent that have been used for the above reaction and discuss the mechanism of above reaction.

Or



Indicate the product of the above reaction and give the mechanism of it.



What is the reagent, used for the above condensation and give the name of the condensation and mechanism of it.

Or

- b) Give the importance of Gilman's reagent with some applications.
- 3. a) What is the reagent used for Anti-Markownikoff's reaction? Discuss the mechanism of it.

#### Or

b)  $CH_2 = CH - CH = CH_2 + Br_2$  -----> ?

Predict the products of the above reaction and discuss the mechanism of it

4. a) 
$$( = 0 \longrightarrow ( = CH_2 )$$

Give the reagent used for the above reaction and discuss the mechanism of it indicating the name.

#### Or

- b) Discuss the applications of Strecker synthesis.
- 5. a) Write notes on retro Diels Alder reaction.

#### Or

b) Explain the retro synthesis of olefins.

#### PART - B (5 X 10 = 50 Marks)

#### Answer all questions

- 6. a) i) Discuss the migratory aptitude of the groups with respect to Pinacol Pinacolone rearrangement
  - ii) Discuss the importance of Curtius rearrangement.

#### Or

- b) i) What is Wagner Meerwin rearrangement? Discuss its mechanism
  - ii) Discuss the factors which favours the formation of o- (or) p- isomers in Fries management.

7. a) i) What is Chichibabin reaction? Discuss its mechanism.

ii) Discuss the importance of Grignard reactions.

#### Or

b) i)  $CH_2 = CH_2 \longrightarrow \nabla$ 

Give the reagent that have been used for the above conversion and discuss the mechanism of it and importance of it.

- ii) Discuss the applications of Duff reactions in the field of Chemistry?
- 8. a) Discuss the evidences which favour the mechanisms of addition of halogens to olefins.

#### Or

b) i) What are the reagents that have been used for hydroxylation reaction and discuss the stereochemical aspects of above reactions.

ii) Write short notes on Hydroboration reaction

9. a) i) Discuss the mechanism of Michael addition and catalysts that have been used in it.?

ii)  $C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} ?$ 

Predict the product of above reaction and its mechanism.

#### Or

- b) Suggest a suitable mechanism of the Darzen glycidic ester condensation and Mannich reaction.
- 10. a) i) Write notes on functional group interconversion
  - ii) How do you protect the alcoholic and acid group in organic synthesis?

#### Or

b) Discuss the linear and convergent method in organic synthesis.

Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. Degree – Branch – IV D Organic Chemistry Third Semester Core Paper - VII

#### **ORGANIC CHEMISTRY - IV**

#### **Organic Spectroscopy**

#### Time : 3 Hours

#### Maximum: 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### Answer all the questions

1. a) Explain the various types of electronic transitions.

#### Or

b) What is ORD? Briefly discuss the various types of ORD curves.

2. a) Discuss the factors influencing vibrational frequencies.

#### Or

b) Describe the basic principles of Raman Spectroscopy.

3. a) Discuss the various factors influencing the chemical shift of a proton.

#### Or

b) Explain spin – spin coupling with an example

4. a) Explain nuclear Overhauser effect

#### Or

b) Write a note on zerofield splitting and Kramer's degeneracy.

5. a) By means of mass spectra how will you distinguish between i) Methyl benzoate and phenyl acetate ii) gly – ala and ala – gly peptides.

Or

b) State and explain nitrogen rule with suitable examples.

#### $PART - B \quad (5 X 5 = 25 Marks)$

#### Answer all the questions

6. a) i) Calculate the  $\lambda$ max for the following compounds. (4)



ii) Explain solvent polarity in uv

(6)

#### Or

b) Write short notes on octant rule and axial haloketone rule and explain its application7. a) i) Explain hydrogen bonding stretching frequency and how will you differentiateinter and intra molecular hydrogen bonding in IR (5)

ii) How will you differentiate primary, secondary, and tertiary amine in IR spectrum? (5)

Or

- b) Explain the terms giving illustrations (4)
  - i) Overtone
  - ii) Fermi resonance

c) Discuss the applications of Raman spectroscopy (6)

- 8. a) i) Give an example each for AX and AMX spin system (3)
  - ii) Match the following with the given <sup>1</sup>H NMR chemical shift values ( $\delta$  ppm) (7)

I –OCH <sub>3</sub>	IV –CHO
II $-C_6H_5$	V -COOH
- C - CH <sub>3</sub> III " O	VI >C=CH <sub>2</sub>
(12.0, 8.7, 7.2, 5.2, 3.8, 2.2)	

#### Or

b) i) Explain Diamagnetic anisotropy with an example	(5)
--	-----

ii) Discuss the shielding and de-shielding effects in <sup>1</sup>H NMR spectra. (5)

9. a) i) How does <sup>13</sup>C- nmr differs from <sup>1</sup>H – nmr ? Give the applications of <sup>13</sup>C-nmr and  ${}^{1}$ H – nmr ? (6)

ii) Write notes on coupled and decoupled spectrum in  ${}^{13}C$  NMR. (4)

#### Or

b) i) How is 'g' value of electron in a free radical useful in identification of a	
species?	(5)
ii) Describe the applications of ESR spectroscopy with examples.	(5)
10. a) i) Explain McLafferty rearrangement with examples.	(5)
ii) Write short notes on metastable ions	(5)

Or

b) Three compounds of molecular formula  $C_4H_8O$  have the following <sup>13</sup>C spectra, and the described features in their IR spectra

Compound 1: IR :  $1730 \text{ cm}^{-1}$ 

<sup>13</sup>C NMR : 13.3, 15.7, 45.7, 201.6 ppm

Compound 2 : IR : 3200 (broad)  $\text{cm}^{-1}$ 

<sup>13</sup>C NMR : 36.9, 61.3, 117.2, 134. 7 ppm

Compound 3: IR : no peaks except CH and fingerprint,

<sup>13</sup>C NMR: 25.8 and 67.9 ppm

Suggest a structure for each compound, and then see whether your suggestions are compatible with the following information. Compound 1 reacts with NaBH<sub>4</sub> to give compound 4  $C_4H_{10}O$ , IR 3200 (broad) cm<sup>-1</sup> and <sup>13</sup>C NMR 15.2, 20.3, 36.0, and 62.9 ppm. Compound 2 reacts with hydrogen over a palladium catalyst to give the same product 4, while compound 3 reacts with neither reagent.

Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. Degree – Branch – IV D Organic Chemistry Third Semester

**Core Paper - VIII** 

Organic Chemistry - V

Time : 3 Hours

Maximum: 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### Answer all the questions

1. a) What is nutarotation? Give its mechanism

#### Or

- b) Glucose is a reducing sugar while sucrose is not. Explain
- 2. a) Explain the synthesis of ascorbic acid from D- glucose

#### Or

b) Outline the synthesis of riboflavin

3. a) What are alkaloids ? Write the structure of two of them

#### Or

b) How are alkaloids classified?

4. a) Discuss the mechanism of Allylic Oxidation of olefins.

#### Or

- b) Illustrate the mechanism of Oxidation of alcohols by DMSO DCC
- 5. a) Discuss the mechanism of MPV reduction

#### Or

b) Write a note on Birch reduction

#### **PART – B** (5 X 10 = 50 Marks)

#### Answer all the questions

6. a) Establish the structure of maltose.

#### Or

- b) i) How will you determine the ring size of glucose? (6)
  - ii) Name the two components of starch ? How are they separated. (4)
- 7. a) Establish the structure of Pyridoxine

#### Or

b) Deduce the structure of Thiamine

8. a) Discuss the structure of Morphine alkaloid

#### Or

- b) Elucidate the structure of Quinine alkaloid
- 9. a) i) Discuss the mechanism of Oxidative cleavage of alkenes by ozone (5)

ii) Discuss the oxidation of methylene alpha to a carbonyl group by SeO<sub>2</sub> with the mechanisms (5)

#### Or

Or	
ii) Write a note on Clemmensen reduction	(5)
10. a) i) Discuss the mechanism of Wolff – Kishner reduction	(5)
ii) Write a note on oppenauer oxidation	(4)
b) i) Discuss the mechanism of oxidation of alcohols by $CrO_3$ and DMSO	(6)

b) Write a note on homogeneous and heterogeneous hydrogenation (10)

**Model Question Paper** 

(For the candidate admitted from 2008 – 2009 onwards)

M.Sc. Degree – Branch – IV D Organic Chemistry

#### **Third Semester**

**Elective Paper - III** 

#### **Instrumental methods of Analysis**

Time : 3 Hours

Maximum : 75 Marks

#### $PART - A \quad (5 X 5 = 25 Marks)$

#### Answer all the questions

1. a) Illustrate Beer Lamberts law? Give the principle of nephelometry

#### Or

- b) Write notes on Atomic fluorescence
- 2. a) What is Thermogram? List out the characteristics of thermogram?

#### Or

b) Explain the magnetic behaviour of Lanthanides ?

3. a) What is called as "Zero field spilitting" in EPR? Give example.

#### Or

- b) Explain the importance of shift reagents in NMR
- 4. a) What is polarogram? List out the advantages of DME

#### Or

b) Write notes on Two indicator electrodes

5. a) What is carrier gas? Give the importance of carrier gas with example ?

#### Or

b) Define gradient and isocractic elution?

#### PART - B (5 X 10 = 50 Marks)

#### Answer all the questions

6. a) i) List out the applications of AAS

ii) Discuss the components of the Flame photometer

#### Or

b) i) Discuss the principle of Fluorimetry and give the applications of it

ii) What is photometric titration? Explain with example.

7. a) Give the principle of D.T.A? What are the information that you have obtained from

a D.T.A curve? Discuss the DTA curve of calcium oxalate monohydrate ?

#### Or

b) Explain the Gouy's balance of measuring the magnetic susceptibility? Calculate the spin – only magnetic moment of the following complexes  $[Fe(CN)_6]^{3-}$ ,  $[Fe F_6]^{3-}$  and  $[Co(NO_2)_6]^{3-}$ 

8. a) i) Discuss about the relaxation process in NMR

ii) Give the factors affecting the chemical shift in NMR

#### Or

b) What is hyperfine interaction in ESR? List out some applications of ESR in qualitative analysis

9. a) i) What is kinetic and catalytic currents in Polarography

ii) How do you find out the reversibility of the system using polarographic waves.

#### Or

b) Give the principle of amperometric titrations. Discuss the types of titration curves that have been obtained from it? Explain the successive titration with one example.10. a) i) Explain the solvent delivery system of HPLC

ii) Discuss the electron capture detector of Gas liquid chromatography

#### Or

b) Give the principle of TLC and explain the pumps that have been used in HPLC.

Model Question Paper (For the candidate admitted from 2008 – 2009 onwards) M.Sc. Degree – Branch – IV D Organic Chemistry Fourth Semester Core Paper - IX

#### **Organic Chemistry - VI**

#### Organic Photochemistry, Pericyclic reactions and Steroids

Time : 3 Hours

Maximum: 75 Marks

#### Answer all the questions

 $PART - A \quad (5 X 5 = 25 Marks)$ 

1. a) Explain the interaction between molecular orbitals.

#### Or

b) Write the application of perturbation theory and symmetry to pi system

2. a) Explain the photo chemical reactions of saturated ketones by Norrish Type I reaction.

#### Or

b) Explain Paterno Buchi reaction

3. a) What is Woodward Hofmann rules. Explain with one example.

#### Or

b) Explain cyclo addition and sigmatropic shift reactions with example.

4. a) Explain the structure and stereochemistry of cholesterol

#### Or

b) Explain the structure and stereochemistry of stigmasterol.

5. a) Explain the synthesis of saponics

#### Or

b) Explain the synthesis of Strophanthidin

#### PART - B (5 X 10 = 50 Marks)

- 6. a) Write short notes on i) fluorescence
  - ii) Phosphorescence

#### Or

b) Explain the following

i) Jablonski diagram

ii) Quantum yields and their determination.

7. a) Explain the following:

i) 1, 5 – dienes – sigmatropic rearrangements

ii) Barton reaction

Or

b) Write briefly about i) Photo - Fries rearrangement

ii) Photo rearrangement of 2,5 – cyclo hexadienones

8. a) Explain the comparison of Woodward – Hofmann and Dewar – Zimmermann pericyclic Selection rules.

#### Or

b) Explain the following rearrangements

i) Sommelet

ii) Hauser

iii) Cope and Claisen

9.a) Explain the structure, stereochemistry and synthesis of the cholic acid.

#### Or

b) Explain the Biosynthesis of Sterols

10. a) Write notes on Androsterone and testosterone

#### Or

- b) Write briefly about the following harmones
  - i) Oestrone and Eqilenin
  - ii) Oestradiol and Oestriol

#### Model Question Paper

(For the candidate admitted from 2008 – 2009 onwards)

M.Sc. Degree – Branch – IV D Organic Chemistry

#### **Fourth Semester**

#### **Elective Paper - IV**

#### **Industrial and Medicinal Organic Chemistry**

**Time : 3 Hours** 

Maximum: 75 Marks

#### Answer all the questions

#### $PART - A \quad (5 X 5 = 25 Marks)$

1. a) What is meant by octane number and cetane number?

#### Or

b) Explain cracking and various types of cracking

2. a) Explain thinner? Explain with suitable example

#### Or

b) What is PVC? Explain the importance of PVC.

3. a) Explain the structure and uses of penicilline

#### Or

b) Explain the preparation and uses of sulphapyridine and sulpha furazole

4. a) What is local and intravenous anaesthetics. Explain with example.

#### Or

b) Explain the detection of alkaloids. Give example

5. a) What is flavouring and sweetening agent? Explain it.

#### Or

b) Explain the term Rh factor?

#### **PART – B** (5 X 10 = 50 Marks)

6. a) Explain the manufacture and uses of acetaldehyde and ethylene glycol.

#### Or

b) Explain the chemical processing of aromatic hydrocarbons

7. a) Write briefly about the chemistry of colour developer and instant colour processes.

#### Or

b) Explain the synthesis and application of the following

i) Congo red

- ii) Malachite green
- iii) Rhodamine B
- 8. a) Explain the synthesis and structure and action of the following:
  - i) Methyl Salicylate
  - ii) Aspirin

#### Or

- b) Explain the following:
  - i) Pethidine and methodone
  - ii) Phenol as disinfectant and phenol coefficient
- 9. a) Explain the detection of sugar and serum in urine. What are the causes and control of diabetes.

#### Or

- b) Explain the preparation and uses of thiotepa and cyclophosphoramide
- 10. a) Write short note on blood pressure. How is it controlled?

#### Or

- b) Explain the following terms:
  - i) Causes and control of anaemia antianaemic drugs
  - ii) Coagulants and anticoagulants.