# Annexure – 5

# Periyar University Salem-6.



# Periyar Institute of Distance Education (PRIDE)

M.Sc., DEGREE

**Branch IV (B)** CHEMISTRY

# **REGULATIONS AND SYLLABUS**

[ For the Candidates admitted from the academic year 2007 – 2008 and onwards ]

# Periyar Institute of Distance Education (PRIDE)

# M.Sc., DEGREE Branch IV (B) CHEMISTRY REGULATIONS AND SYLLABUS

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## I. Objectives of the Course

Life has changed more in the past two centuries than in all the previously recorded span of human history. In one way or another, all these changes involve CHEMISTRY, the study of the composition, properties and transformations of matter. Chemistry is deeply involved in both the changes that take place in nature and profound social changes of the past two centuries. In addition, chemistry is central to the current revolution in all sciences. No educated person today can understand the modern world without a basic knowledge of chemistry. An advanced course in chemistry will be a fascinating experience because it helps us understanding and our surroundings.

The major objectives of M.Sc. Chemistry course are:

- To impart knowledge in fundamental aspects of all branches of chemistry
- To acquire deep knowledge in the study of physical, chemical, electrochemical and magnetic properties, structure elucidation using various techniques and applications of various organic and inorganic materials
- To acquire basic knowledge in the specialized areas of chemistry and
- To train the students in various quantitative and qualitative analyses

# **II. Eligibility for Admission**

A candidate who has passed B.Sc., Degree Examination with Branch IV Chemistry as main subject of study of this university or any of the B.Sc., degree examination with specialization such as Industrial chemistry, Applied Chemistry, or any other specialization in Chemistry of some other university accepted by the syndicate as equivalent thereto, subject to such condition as may be prescribed therefore shall be permitted to appear and qualify for the M.Sc. degree in Chemistry of this University after a course of study of two academic years.

#### **III.** Duration of the Course

The course for the degree of Master of Science in Chemistry shall consist of two academic years .

# **IV.** Course of Study

# FIRST YEAR

Code No.	Subject			
	Organic Chemistry I			
	Inorganic Chemistry I			
	Physical Chemistry I			
	Polymer Chemistry			
	Spectroscopy-I			
	Nano materials and Green Chemistry			
	Organic Chemistry Practical I			
	Inorganic Chemistry Practical I			
	Physical Chemistry Practical I			

# SECOND YEAR

Code No.	Subject		
	Organic Chemistry II		
	Inorganic Chemistry II		
	Physical Chemistry II		
	PhotoChemistry		
	Spectroscopy-II		
	Environmental Chemistry		
	Organic Chemistry Practical II		
	Inorganic Chemistry Practical II		
	Physical Chemistry Practical II		

# **V. Examinations**

The examination shall be three hours duration to each paper at the end of each year. The candidate failing in any subject(s) will be permitted to appear for each failed subject(s) in the subsequent examination.

Practical examinations for M.Sc. course in Chemistry should be conducted at the end of each year

# **VI** Scheme of Examinations

# FIRST YEAR

Code No.	Subject	Duration (hours)	Marks
	Paper I-Organic Chemistry I	3	100
	Paper II-Inorganic Chemistry I	3	100
	Paper III - Physical Chemistry I	3	100
	Paper IV-Polymer Chemistry	3	100
	Paper V-Spectroscopy-I	3	100
	Paper VI-Nano materials and Green Chemistry	3	100
	Practical I- Organic Chemistry Practical I	6	100
	Practical II- Inorganic Chemistry Practical I	6	100
	Practical III- Physical Chemistry Practical I	6	100

# SECOND YEAR

Code No.	Subject	Duration (hours)	Marks
	PaperVII-Organic Chemistry I	3	100
	Paper VIII-Inorganic Chemistry I	3	100
	Paper IX -Physical Chemistry I	3	100
	Paper X- PhotoChemistry	3	100
	Paper XI-Spectroscopy-II	3	100
	Paper XII Environmental Chemistry	3	100
	Practical IV- Organic Chemistry Practical II	6	100
	Practical V- Inorganic Chemistry Practical II	6	100
	Practical VI- Physical Chemistry Practical II	6	100
	Total		1800

# **VII.** Question Paper Pattern

Time: 3 Hours

Max.Marks - 100

# **PART-A: 5x5=25**

(Answer all questions) (One question from each unit with internal choice)

# **PAPER-B: 5x15=75**

(Answer all questions) (One question from each unit with internal choice)

Organic Chemistry Practical – I		Organic Chemistry Practical -II	
Qualitative analysis	45 marks	Organic estimation	40 marks
Preparation	25 marks	Preparation	30 marks
Viva – Voce in practical	10 marks	Viva – Voce in practical	10 marks
Record	20 marks	Record	20 marks
Total	100 marks	Total	100 marks

# VIII. Distribution of marks for practical examinations

<b>Inorganic Chemistry Prac</b>	ctical - I	Inorganic Chemistry Practical – II	
Qualitative analysis	30 marks		
Colorimetric analysis	20 marks	Quantitative analysis	50 marks
Preparation	20 marks	Preparation	20 marks
Viva-voce in practical	10 marks	Viva-voce in practical	10 marks
Record	20 marks	Record	20 marks
Total	100 marks	Total	100 marks

Physical Chemistry Practical - I		Physical Chemistry Practical - II	
Experiment	70 marks	Experiment	70 marks
Viva-voce in practical	10 marks	Viva-voce in practical	10 marks
Record	20 marks	Record	20 marks
Total	100 marks	Total	100 marks

# **IX.** Passing Minimum:

The candidate shall be declared to have passed the examination if the candidate secures not less than 50 marks in the University examination in each paper.

For the Practical paper, a minimum of 50% marks in the University examination and the record notebook taken together. There is no passing minimum for the record notebook. However submission of a record notebook is a must.

Candidate who do not obtain the required minimum marks for a pass in a paper shall be required to appear and pass the same at a subsequent appearance.

### X. Classification Of Successful Candidates:

Candidates who secure not less than 60% of the aggregate marks in the whole examination shall be declared to have passed the examination in **First Class.** 

All other successful candidates shall be declared to have passed in the **Second Class**.

Candidates who obtain 75% of the marks in the aggregate shall be deemed to have passed the examination in **First Class with Distinction** provided they pass all the examinations prescribed for the course at the first appearance.

Candidates who pass all the examinations prescribed for the course in the first instance and within a period two academic years from the year of admission to the course only are eligible for **University Ranking**.

## XI. Maximum Duration for the completion of M.Sc. Chemistry Programme:

The maximum duration for completion of the PG Programme shall not exceed four years

#### XII. Commencement of this Regulation:

These regulations shall take effect from the academic year 2007-08.i.e., for students who are to be admitted to the first year of the course during the academic year 2007-08 and thereafter.

#### XIII. Transitory Provision:

Candidates who were admitted to M.Sc. Chemistry course of study before 2007-2008 shall be permitted to appear for the examinations under those regulations for a period of three years i.e., up to and inclusive of the examination of April/May 2010. Thereafter, they will be permitted to appear for the examination only under the regulations then in force.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY FIRST YEAR

# PAPER I- ORGANIC CHEMISTRY - I

# UNIT - I Types of Reactions, Mechanisms and Reaction intermediates

**Types of reactions :** Substitutions, Additions, Eliminations, Rearrangements, Oxidations and Reductions reactions – a general study.

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

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

Long lived and short lived free radicals, methods of generation and detection of free radicals, free radical reactions: Sandmeyer reaction, Gomberg-Bachmann reaction, Pschorr reaction and Ullmann reaction, mechanism of Hunsdiecker reaction.

# **UNIT – II Stereochemistry**

Concept of chirality, recognition of symmetry elements and chiral structures, R - S nomenclature, Fischer, Newman and Sawharse projections of erythro and threo forms of organic molecules and their interconversion. Optical activity in the absence of chiral carbon – biphenyls, allenes and spiranes – R and S notations. Chirality due to helical shape, trans cyclooctene, cyclononene. E - Z isomerism of olefins containing one double bond. Stereochemistry and Conformational Analysis : Stereospecific and stereoselective synthesis with one suitable example, asymmetric synthesis – Crams rule, 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,

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

The  $S_N^2$ ,  $S_N^1$ ,mixed  $S_N^1$  and  $S_N^2$ ,  $S_N^i$  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. Substitution at carbon doubly bonded to oxygen and nitrogen, Williamson reaction, Von-braun reaction, hydrolysis of esters, Claisen and Dieckmann condensation.

#### **UNIT IV Heterocyclic Compounds**

Synthesis and properties of imidazole, oxazole, thiazole and indole. General methods of Synthesising Anthocyanidins, Synthesis and Structural elucidation of Cyanidin Chloride, Synthesis and Structural elucidation of flavones and isoflavones (Daidzein), Synthesis of pyrimidine and its derivativess, Synthesis of purine, uric acid and caffeine).

# **UNIT V** Aromatic electrophilic, nucleophilic substitution reactions and Aromaticity

The arenium ion mechanism, typical reactions like nitration, sulphonation, haloganation, Friedal-Crafts alkylation, acylation and diazonium coupling, electrophilic substitution on monosubstituted benzene, orientation and reactivity-ortho, meta and para directing groups, Gatterman, Gatterman-koch, Vilsmeir, Reimer-Tiemann reaction.

Aromatic nucleophilic substitution reactions, the  $S_NAr$ , mechanism, aromatic nucleophilic substitution of activated halides-Ziegler alkylation, Chichibabin reaction. 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.

### **Text Books**

- Jerry March, Advanced Organic Chemistry- Reactions, Mechanisms and Structure, Fourth Edition, John Wiley & Sons (1992)
- 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.
- Ernest L. Eliel, Stereochemistry of Carbon Compounds, T.M.H Edition, Tata McGraw-Hill Publising Company, 1995.
- P. S. Kalsi, Stereochemistry Conformation and Mechanism, 6<sup>th</sup> Edition, Wiley Eastern Limited, 2005.
- 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.
- D. Nasipuri, Stereochemistry of Organic Compounds, 2<sup>nd</sup> Edition, New Age International Publishers, 1994.
- S.M.Mukherji and S.P.Singh, Reaction Mechanism in Organic Chemistry, 1<sup>st</sup> Edn., Macmillan 1976.
- 5. R.T.Morrison and R.N.Boyd, **Organic Chemistry**, 6<sup>th</sup> Edn., Prentice-Hall,1992.
- 6. R.O.C. Norman, **Principles of Organic Synthesis**, Second Edition, Chapman and Hall, 1978.
- R.M.Acheson, Introduction to Chemistry of Heterocyclic Compounds, 2<sup>nd</sup> Edn., interscience Publishers, 1967.
- J.A. Joule and G.F. Smith, Heterocyclic Chemistry, Van Notrand Reishord Co., London, 1978.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY FIRST YEAR

# PAPER II - INORGANIC CHEMISTRY - I

# UNIT I Structure and Bonding

van der Waals bonding, Hydrogen bonding and applications, Hard and Soft acids and bases-classification, Acid-Base strength, hardness, Symbiosis, Theoretical basis of Hardness and Softness, applications of HSAB.

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

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

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

# UNIT – II Nuclear Chemistry

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 - Cloud chamber, nuclear emulsion, Bubble chamber, 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, synthesis of elements.

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

Radiation Chemistry - Range of alpha and beta radiations, radiation dosimetry, radiolysis of water, the hydrated electron.

**UNIT III Stability and bonding in complexes** 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, chilarity 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 )

# Metal-Ligand Bonding

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 eff

# UNIT IV Electronic Spectra of Complexes

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

# UNIT V Analytical Chemistry

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

Amperometric titrations - Theory, apparatus, types of titration curves, successive titrations and two indicator electrodes; applications; Complexometric titrations - Chelating agents; types of EDTA titration - direct and back titrations; replacement titrations - masking and demasking reagents.

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

High performance liquid chromatography – scope; column efficiency;

instrumentation; pumping systems; columns; column packing; detectors; applications.

# **Text Books :**

- 1. H.J. Emelius and Sharpe, **Modern aspects of Inorganic chemistry**, Universal book Stall, New Delhi, 1989.
- 2. 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.
- 3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern, 5<sup>th</sup> edition, 1988.
- 4. F. Basolo and R.G. Pearson, Mechanism of Inorganic Reactions, Wiley Eastern, 1967.
- 5. S. Glasstone, Source book of Atomic Energy, Van Nonstrand Co., 1969.
- 6. H.J. Arniker, **Essentials of nuclear chemistry**, 2<sup>nd</sup> edition Wiley eastern Co.,1987.
- D.A. Skoog, Principles of Instrumental Analysis, Saunders College Pub.Co, III Edn., 1985.
- 8. J.G. Dick, Analytical Chemistry, McGraw Hill Publishers, 1974.
- A.I Vogel, Text Book of Quantitative Inorganic Analysis, Pearson V Edn., 2001.
- R.C. Kapoor and B.S. Agarwal, **Principles of polarography**, Wiley Eastern Ltd., 1991.

# **Reference Books**

- K.F. Purcell and J.C. Kotz, Inorganic Chemistry, WB Saunders Co. USA 1977.
- 2. G.S. Manku, Inorganic Chemistry, TMH Co., 1984.
- 3. 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 Radiochemistry, Wiley, 1964

1964.

- 5. Willard, Merit, Dean and Settle, **Instrumental Methods of Analysis**, CBS Publishers and Distributors, IV Edn., 1989
- G. D. Christian and J.E.O Reilly, Instrumental Analysis, Allyn and Bacon Inc, II Edn., 1986.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY PAPER III -PHYSICAL CHEMISTRY – I

# **UNIT- I Classical Thermodynamics –I**

Maxwell's relations and thermodynamic equations of state – applications in the evaluation of Cp – Cv for solids and for vanderwaals gases, Cp – Cv interms 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 – Thermodynamic derivation of phase rule – application to three component systems involving solids and liquids

(CH<sub>3</sub> COOH – CHCl<sub>3</sub> – H<sub>2</sub>O, NaCl – Na<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O and NH<sub>4</sub> NO<sub>3</sub> –( NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> -H  $_2$ O).

# UNIT –II Statistical Thermodynamics

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

Maxwell – Bottzmann, Bose – Einstein and Fermi – Dirac statistics – comparison and application.

Partition Functions – evaluation of Translational, Vibrational, Rotational and Electronic partition Function – Thermodynamic Functions in terms of partition Function – Application of Partition Function to monatomic and diatomic gases – Statistical expression for equilibrium Constant – Calculation of Equilibrium Constant from Partition Function – ( isotope exchange equilibrium and dissociation of diatomic molecules) – Heat capacities of Monatomic crystals – Einstein and Debye theory of heat capacities.

# UNIT -III 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 – 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 H2O, CH4, XeF4, SF6 and NH3 – symmetry of Hybrid orbitals in non- linear molecule (BF3, CH4, XeF4, PCl5, and SF6,) – Electronic spectra of formaldehyde – application of group theory.

# **UNIT –V Chemical Kinetics**

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

Transition state theory of reaction rates - Potential energy surface – Partion functions and activated complex – Eyring equation - Comparison of results with Eyring and Arrhenius equations – Estimation of free energy, enthalpy and entropy of activation and their significance.

# **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 New york, 1987.

- 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.

# **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
- 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. I.N.Levine, Quantum chemistry, Allyn and Bacon, Boston, 1983
- 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.
- 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.
- 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

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY PAPER IV -POLYMER CHEMISTRY

# UNIT I Basic Concepts

Monomers, repeat units, degree of Polymerization, Linear, branched and network Polymers.Condensation Polymerization :Mechanism of stepwise polymerisation .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

Kinetics, mono and bimetallic mechanism of co-ordination polymers.. Co-Polymerization : Block and graft co-polymers, Kinetics of copolymerization. Types of co-polymerization. Evaluation of monomer. Reactivity ratio. Rate of Co-Polymerization.

### UNIT III Molecular Weight and Properities

 $\label{eq:polydispersion-average-molecular weight concept, number , weight and viscosity average molecular weights. Measurement of molecular weights. Gel permeation chromatography, viscosity, light scattering, osmotic and ultracentrifugation methods. Polymer structure and physical properities – crystalline melting point T_m. The glass transition temperature. Determination of T_g. Relationship between T_m and T_g.$ 

### UNIT IV Polymer Processing

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

# UNIT V Properties of Commercial Polymers

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

# **Text Books**

- 1. F.W.Billmeyer, **TextBook of Polymer Science**, 3<sup>rd</sup> Edn., J.Wiley, 2003.
- V.R.Gowarker, N.V.Viswanathan and J.Sreedhar, Polymer Science, New Age Int., 1986.

# **Reference Books**

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

2. P.J.Flory, **Principles of Polymer chemistry**, Cornell University press, Newe York, 1953.

3. G.Odian, **Principles of Polymerization**, 2<sup>nd</sup> Edn., John Wiley & Sons, New York,1981.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY FIRST YEAR PAPER V -SPECTROSCOPY – I

# UNIT I Microwave Spectroscopy

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.

# UNIT II IR and Raman Spectra

Theory, principle, instrumentation of IR and Raman Spectra. Characteristic group frequencies of organic molecule, Factors influencing vibrational frequencies, interpretation of IR spectra of organic molecules. Raman spectroscopy – Raman effect – Rotational and vibrational Raman Spectra. Applications of Raman Spectra.

# **UNIT III UV-VIS and Emission Spectra**

Theory, principle, instrumentation of UV – VIS and Emission spectra.

UV-VIS : Woodward – Fieser rules for dienes, enones. Calculation of  $\lambda$ max for organic molecules. Chromophores and effect of conjugation, substituents with unshared electrons and their capability of  $\pi$  - conjugation . Colour in compounds. Applications of UV – VIS and Emission spectra.

# UNIT IV <sup>1</sup>H and <sup>13</sup>C NMR Spectra

NMR spectroscopy : Theory, principle, instrumentation, Chemical shift, factors influencing chemical shift, spin-spin coupling, NMR of simple AX and AMX type organic molecules, calculation of coupling constants, identification of H in various chemical environments to assign structure to the organic molecules using chemical

shift values, resonance coupled and decoupled spectra <sup>13</sup>C NMR, applications of <sup>13</sup>C NMR to find the different carbon functional groups.

# UNIT V Mass spectra

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

# **Text Books**

- Y. R. Sharma, Elimentary Organic Spectroscopy, 1<sup>st</sup> Edn., S. Chand & Company Ltd, New Delhi, 1980.
- J. Dyer, Application of absorption spectroscopy of organic compounds, Prentice Hall of India Pvt. Ltd., New Delhi, 2005
- Raymond chang, Basic principles of Spectroscopy, McGraw Hill Ltd., New York, 1971
- C.N.Banwell, Fundamentals of Molecular spectroscopy, Mc Graw Hill, Newyork, 1966.

### **Reference Books**

- R.M Silverstein, C.G. Bassler and Monsil, Spectrometric identification of organic compounds, 6<sup>th</sup> Edn., John Wiley & sons, New York 2004.
- 2. William Kemp, Organic Spectroscopy, ELBS, New Delhi, 1982.
- S. Kalsi, Spectroscopy of organic compounds, 5<sup>th</sup> Edn., Wiley Eastern Ltd., Madras,

2002.

- C.N.Banwell, Fundamentals of Molecular Spectroscopy, McGraw Hill, New York,1966.
- 5. A.Carrigton and A.D.McLachlan, Introduction to Magnetic Resonance, Harper and Row New York 1967.
- 6. R.Drago, Physical methods in Inorganic chemistry, Reinhold, Ny.1968.

- G.M.Barrow, Introduction to Molecular Spectroscopy, McGrawHill, NewYork,1962.
- 8. W.Kemp, NMR in Chemistry, MacMillan Ltd, 1986.
- 9. G.W.King, Spectroscopy and Molecular structure, Holt, Rienehart and winston 1964.
- C.N.R.Rao, J.R.Ferraro, Spectroscopy in Inorganic Chemistry, Methven Co., London. 1968.

11.Raymond Chang, Basic Principles of Spectroscopy, Mc Graw Hill Ltd., New York,

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY

# FIRST YEAR

# PAPER VI - NANOMATERIAL AND GREEN CHEMISTRY

### UNIT I Introduction to Nanotechnology

Definition, classification, a historical perspective, nanoparticles, nanocrystal, quantum dot, nanometer., new properties of nanomaterials, nanomaterials in medicine, information storage, sensors, new electronic devices, environmental remediation, clean catalysts. Metal nanoparticles, Chemical bonding and properties of bulk metals as well as metal nanoparticals. Gas phase and chemical synthetic methods to metal nanoparticles, nanoelectrons, conductivity of nanoelectrons.

### UNIT II Properties and Applications of Nanocrystals

Nanotubes, Nanocrystal shape, Sequestration of gases, destructive adsorption of environmental toxins, Optical properties, Magnetic properties of nanoscale materials – diamagnetism, paramagnetism, ferromagnetism, and supermagnetism. Size dependent properties such as coercivity (magnetic memory) and saturation magnetization, nanoparticles in polymers, inks, fluids, dyes and catalysis. Nanocrystals as colorants, ultraviolet absorbers, electronics and in biomedical applications.

### UNIT III Green Chemistry Basics

The need for green chemistry and eco-efficiency, environmental protection laws, challenges and green chemistry education, pollution control and pollution prevention – green methods, green products, recycling of waste.

Twelve principles of green chemistry, inception of green chemistry, awards for green chemistry and international organizations promoting green chemistry.

# UNIT IV Solvent Free Organic Synthesis

Solvent free microwave assisted organic synthesis – microwave activation, microwave heating, advantages of microwave exposure and specific effects of microwaves. Organic synthesis under microwaves – benefits, limitations, equipments. Reactions on solid supports, phase transfer catalysis, solvent free esters saponification, reactions without support or catalyst, examples – microwave assisted reactions in water – oxidation of toluene to benzoic acid, microwave assisted reactions in organic solvent Diels Alder reaction.

#### UNIT V Designing Green Synthesis

Designing Green Synthesis – choice of starting materials, choice of reagents, choice of catalysts – bio catalysts, polymer supported catalysts, choice of solvents.

Synthesis involving basic principles of green chemistry – examples – synthesis of adipic acid, methyl methacrylate, paracetamol.

Ultrasound assisted reactions – esterification, reduction, coupling reactions. Strecker synthesis and reformatsky reaction.

### **Text Books**

- Kenneth . Klabunde, Nanoscale Materials in Chemistry, John Wiley & Sons, Inc. 2002
- Rashmi Sanghi, M. M. Srivastava, Green Chemistry, Environment Friendly Alternatives, Narosa Publishing House, 2007
- V. Kumar, An Introduction to Green Chemistry, Vishal Publishing CO. Jalandhar, 2007

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR

# PAPER VII- ORGANIC CHEMISTRY - II

# **UNIT I** Molecular Rearrangements

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

# UNIT II Reagents in Organic Synthesis

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.

# UNIT III Oxidation and Reduction 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 oxidation of olefins, oxidative cleavage of glycols, oxidative cleavage of double bonds by ozonolysis.

Study of the following reduction reactions with mechanism: Reduction of carbonyl compounds by hydrides, selectivity in reduction of 4-ter-butyl cyclohexanone using selectrides, Clemmensen and Wolff Kishner reductions, Birch reduction, MPV reduction.

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# UNIT IV Elimination and Addition Reactions

Elimination Reactions : E1, E2, E1cB mechanisms, Orientation of the double bond - Hofmann and Saytzeff rule, dehydration and dehydrohaloganation reactions, stereochemistry of E2 eliminations in cyclohexane ring systems, mechanism of pyrolytic eliminations, Chugaev reaction and Cope elimination.

Addition *Reactions* : Addition of halogen and nitrosyl chloride to olefins, hydration of olefins and acetylenes, hydroboration, Michael addition, 1,3 dipolar addition, Diels-Alder reaction. Mechanism and reactivity. Mannich, Stobbe, Darzen Glycidic ester condensation, Peterson olefination(Silyl Wittig reaction), Strecker synthesis, Perkin, Thorpe, Ritter, Prins reactions.

# **UNIT V** BioOrganic Chemistry

Proteins, polypeptides and their synthesis (upto a tripeptide), solid phase synthesis (Merrifield synthesis), determination of primary structure of proteins (end group assay), discussion on secondary and tertiary structure of proteins.

Structure and role of (genetic code) DNA and RNA.(Determination of structure is not required) Biosynthesis of amino acids (phenylalanine, tyrosin, 3,4-dopa, praline only) and cholesterol.

Text Books

- Jerry March, Advanced Organic Chemistry- Reactions, Mechanisms and Structure, Fourth Edition, John Wiley & Sons, 1992.
- 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, 2000.
- 4. 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, III Edn. 1984, MacMillan.
- 3. R.T.Morrison and R.N.Boyd, Organic Chemistry, Prentice-Hall, 6<sup>th</sup> Edn., 1992.

- 4. R.O.C. Norman, Principles of Organic Synthesis, Second Edition, Chapman and Hall, 1978.
- 5. Neil Issac, Physical Organic Chemistry, J.Wiley, New York, 1987.
- Paul de Mayo, Molecular Rearrangements, Vol.I, Vol. II, Interscience, NY, 1963.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR PAPER VIII- INORGANIC CHEMISTRY-II

#### UNIT I Boron compounds and Clusters

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

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

Metal clusters - Chemistry of low molecularity metal clusters only-structure of Re<sub>2</sub>Cl<sub>8</sub>; multiple metal-metal bonds.

# UNIT II Solid - State Chemistry

Structure of Solids; comparison of X-ray, neutron and electron diffractions; Structure of NiAs, CdI<sub>2</sub>, Pervoskite, spinels and inverse spinels; defects in solids - point defects, line defects and surface defects; Non-stoichiometric compounds; Use of X-ray powder data in identifying inorganic crystalline solids; details for cubic systems.

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

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

# UNIT III Reaction mechanisms in Complexes

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; Application of electron transfer reactions in synthesis.

Reaction mechanism of coordination compounds - Substitution reactions, Labile and inert complexes; Kinetic application of V.B and C.F.Theories.

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 & Catalysis

Carbon donors - Alkyls 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; dinitrogen complexes; Chain Carbon donors - Olefins, acetylene and allyl complexes - synthesis, structure and bonding; Cyclic Carbon donors - Metallocene - synthesis, structure and bonding (Ferrocene only).

Reactions - Association reaction - Only ligand protonation; substitution - electrophilic and nucleophilic attack on ligands; addition and elimination; carbonylation and decarbonylation; oxidative addition to organometallics; fluxional isomerism.

Hydrogenation of olefins (Wilkinsons 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.

# UNIT – V Bioinorganic Chemistry

Metal ions in biological systems - essential and trace metals,  $Na^+/K^+$  Pump; Biologically important complexes of Iron (transport proteins) - haemoglobin, myoglobin, iron-sulphur proteins, cytochrome-C, Magnesium (chlorophyll), Cobalt (vitamin B<sub>12</sub>), Zinc (carbonic anhydrase, carboxy peptidase); macrocyclic effect; fixation of Nitrogen.

## **Text books**

- 1. 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.
- E.A.V. Ebsworth, D.WH. Rankine and S. Craddock, Structural methods in Inorganic Chemistry, Black well Scientific Publ., 1987.
- 4. R.S. Drago, Physical Methods in Chemistry, Reinhold, New York, 1968.
- 5. Charles A. Depuy and Orville L. Chapman, Molecular reactions and photochemistry, Prentice Hall, 1992.
- A.W. Adamson and P. Fleischauer, Concepts of Inorganic Photochemistry, Wiley, 1975.
- D.A.Skoog and D.M.West, Fundamentals of Analytical Chemistry, Holt Rinehart and Winston Publications, IV Edn, 1982.
- D.A. Skoog, Principles of Instrumental Analysis, Saunders College Pub.Co, III Edn., 1985.
- 9. J.G. Dick, Analytical Chemistry, McGraw Hill Publishers, 1974.
- A.I Vogel, Text Book of Quantitative Inorganic Analysis, Pearson V Edn., 2001.

### **Reference Books**

- 1. E.L. Mutteri, Polyhedral boranes, Acadamic press, NY, 1975.
- 2. N.H. Ray, Inorganic polymers, Academic press, NY, 1975.
- K.F. Purcell and J.C. Kotz, Inorganic Chemistry, WB Saunders Co. USA 1977.
- 4. G.S. Manku, Inorganic Chemistry, TMH Co., 1984.
- N.J. Turro, Modern molecular photochemistry, Benjamin/Cummings, Menlo Park, California, 1978.
- 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.

- 8. Willard, Merit, Dean and Settle, **Instrumental Methods of Analysis**, CBS Publishers and Distributors, IV Edn.,1989
- 9. G. D. Christian and J.E.O Reilly, **Instrumental Analysis**, Allyn and Bacon Inc, II Edn., 1986.
- 10. G.W.Ewing, Instrumental Methods of Chemical Analysis, McGraw Hill Pub, 1975.
- J.H.Knox (Ed), High Performance Liquid Chromatography, Edinburgh University Press, Edinburgh, 1982.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR PAPER IX- PHYSICAL CHEMISTRY – II

# UNIT – I Quantum Chemistry –I

Photoelectric effect – De Broglie equation – Heisenberg uncertainty principle – Compton effect – operators and commutation relations – quantum mechanical postulates – Schordinger equation and its solution to the problem of a particle in one, three dimensionel boxes and harmonic oscillator. Schrodinger equation for the rigid rotator and Hydrogen atom – arriving solution for energy and wave function – the orgin of quantum numbers and their physical significance – Probability distribution of electrons.

#### UNIT –II Quantum Chemistry –II

Born – Oppenheimer approximation, 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. Concept of Hybridisation – sp, sp<sup>2</sup> and sp<sup>3</sup> hybridisation, Huckel Molecular orbital (HMO) theory for conjugated  $\pi$  - system, application to simple systems such as Ethylene, butadiene and benzene, Self consistant field approximation – Hartree's and Hartree- Fock Self Consistent field theory, Slater type orbitals – Slater rules.

#### **UNIT-III** Electrochemistry –I

Ions in solutions – Debye – Huckel theory of strong electrolytes – Debye-Hückelonsager equation – verification and limitation – Debye – Hückel limiting law and its extension. Electrode – Electrolyte interface adsorption at electrified interface – electrical double layers – Electro capillary phenomena – Lippmann capillary equation – structure of double layers – Helmholtz Perrin, Guoy Chappman and Stern models of electrical double layers-electro kinetic Phenomena - Tiscelius method of separation of proteins – membrane potential.

#### UNIT -IV Electrochemistry -II

Mechanism of electrode reactions –the Butler Volmer equation for one step electron transfer reaction – significance of equilibrium exchange current density and symmetry factor – transfer coefficient and its significance – Cyclic voltametry – Principles and applications. Mechanism of Hydrogen and Oxygen evolution reactions. Corrosion and Passivation of metals – construction of Pourbaix and Evans diagrams – Prevention of Corrosion. Electrochemical energy systems – Primary and Secondary batteries – ( dry cells, lead acid – storage batteries, silver - zinc cell, nickel - cadmium battery, mercury cell) – Fuel cells.

# UNIT –V Surface Chemistry and Catalysis

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

Acid – Base catalysis – mechanism – Bronsted catalysis Law – catalysis by enzymes – rate of enzyme catalysed reactions – effect of substrate concentration, pH and temperature on enzyme catalysed reactions – inhibition of enzyme catalyzed reactions.

#### **Text Books**

- 1. Gurudeep raj, Advanced Physical chemistry, Goel Publishing House, Meerut.
- 2. R.K.Prasad, Quantum Chemistry, Wiley Eastern, New Delhi, 1992.
- 3. M.W.Hanna, Quantum Mechanics in Chemistry, W.A.Benjamin Inc, London 1965.
- D.A.McQuarrie, Quantum Chemistry, University Science Books, Mill Valley, California, 1983

5. S. Glasstone, Introduction to Electrochemistry, Affiliated East West press, New Delhi, 1960

6. D.R. Craw, Principles and Applications of Electrochemistry, Chapman and Hall, 1991

- 7. J.Rajaram and J.C.Kuriacose, Kinetics and mechanism of chemical transformation, Macmillan India Ltd., (1993)
- 8. K.J.Laidlar, Chemical kinetics, Harper and Row, New york (1987)

**Reference Books** 

- 1. A.K.Chandra, Introductory Quantum Chemistry, Tata McGraw Hill.
- P.W.Atkins, Molecular Quantum Mechanics, Oxford university press, Oxford, (1983)
- 3. J,N,Murrell, S.F.A.Kettle and J.M.Tedder, The Chemical Bond, Wiley.
- 4. J.O.M.Bockris and A.K.N. Reddy, Electrochemistry, Vols 1 and 2, Plenum, New York 1977.
- 5. C.M.A.Brett and A.M.O.Brett, Electrochemistry, Principles, Methods and application, OUP, Oxford (1993)
- 6. R.H.Rieger, Electrochemistry, Chapmann and Hall, New York (1994)
- 7. P.Delahay, Electrode kinetics and structure of Double layer, Interscience, 1965
- 8. R.G.Frost and Pearson, Kinetics and Mechanism, Wiley New York (1961)
- 9. J.W.Moore and R.G.Pearson, Kinetics and Mechanism (1981)
- 10. C.Capellos and B.H.J.Bielski, Kinetic systems, Willey inter science, New York (1968)
- 11. G.M.Harris, Chemical Kinetics, D.C.Heath and co, (1966)

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR PAPER X- PHOTOCHEMISTRY

# **UNIT - I** Organic Photochemistry

Photochemical reactions: fate of excited molecules, Jablonski diagram, Norrish Type I and Norrish Type II reactions, photoreduction of ketone, photoaddition reactions, Paterno Buchi reaction, di-pi methane rearrangement, photochemistry of arenas, Photooxidation (Formation of peroxy compounds), Photoisomerization ( Cis-trans isomerization ), Photo addition of olefins and amines to aromatic compounds, Photo rearrangements: Photo-Fries rearrangement and Photo rearrangement of 2,5-Cyclohexadienones.

# **UNIT – II Inorganic Photochemistry**

Photosubstitution, Photoredox, photoisomerisation and photo rearrangementreactions in inorganic complexes. Photovoltaic and Photogalvanic cells – Photoelectrochemical cells – photoassisted electrolysis of water – aspects of solar energy conversion. Application of metal complexes in solar energy conversion

### **UNIT – III** Physical Photochemistry

Absorption and emission of radiation – Franck – Condon principle – decay of electronically excited states, spin allowed and spin forbidden transition. – radiative and non –radiative processes - theory of radiationless transition – Internal conversion and intersystem crossing. Radiative processes - Fluorescence and Phosphorescence – Theory of Fluorescence and Phosphorescence – Theory of Fluorescence – Prompt and delayed Fluorescence - Fluorescence and structure. quenching of Fluorescence – static and dynamic quenching – Stern – volmer equation

# UNIT IV Techniques and application of Photochemistry

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

# **UNIT V Pericyclic Reactions**

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

# **Text Books**

- 1. Charles H. DePuy, Orville L. Chapman Molecular Reactions and Photochemistry, , Prentice Hall of India Private Limited, New Delhi, 1988
- 2. K.K.Rohatgi Mukherjee, **Fundamentals of Photochemistry**, Wiley Eastern Ltd., 1978
- N.J.Turro, Modern molecular Photochemistry Benjamin / cummings, Menlo park, California (1978)
- 4. A.W. Adamson and P. Fleischauer, **Concepts of Inorganic Photochemistry**, Wiley, 1975.

## References

- 1. J.C.Calvert and J.N.Pitts, Photochemistry, Wiley, London 1966
- 2. R.P.Wayne, Photochemistry, Butterworths, London 1970
- 3. R.P.Cundell and A.Gilbert, **Photochemistry**, Thomas Nelson, London, 1970

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR PAPER XI- SPECTROSCOPY– II

## **UNIT I Atomic Absorption Spectroscopy**

Atomic absorption spectroscopy – theory, principle, instrumentation. EMR sources – cells, furnaces, detectors; interferences and their corrections; applications of AAS.

# **UNIT – II ESR Spectroscopy**

ESR Spectroscopy : Basic principles, Instrumentation, zero field splitting and Kramer's degeneracy, factors affecting the 'g' value. Isotropic and anisotropic hyperfine coupling constants. Applications of ESR spectroscopy. Electronic Zeeman effect – hyperfine interactions – Spin densities – Mcconnel relationship – selection rules in ESR – bonding parameters from 'g' and coupling constants.

## **UNIT – III Mossbauer Spectroscopy**

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

## **UNIT – IV Photoelectron Spectroscopy**

Photoelectron Spectroscopy - Principle, PES of diatomic molecules and polyatomic molecules (HCl, HBr, HI, CO, NH<sub>3</sub>, H<sub>2</sub>O and N<sub>3</sub><sup>-</sup> ion); Core electron PES; X-ray photoelectron spectroscopy (ESCA) applications.

### UNIT -V ORD-CD

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.

### **Text Books**

- 1. D.A.Skoog and D.M.West, Fundamentals of Analytical Chemistry, Holt Rinehart and Winston Publications, IV Edn, 1982.
- D.A. Skoog, Principles of Instrumental Analysis, Saunders College Pub.Co, III Edn., 1985.
- 3. J.G. Dick, Analytical Chemistry, McGraw Hill Publishers, 1974.
- 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.
- Willard, Merit, Dean and Settle, Instrumental Methods of Analysis, CBS Publishers and Distributors, IV Edn., 1989
- G. D. Christian and J.E.O Reilly, Instrumental Analysis, Allyn and Bacon Inc, II Edn., 1986.
- G.W.Ewing, Instrumental Methods of Chemical Analysis, McGraw Hill Pub, 1975.
- 9. R.S. Drago, Physical Methods in Chemistry, Reinhold, New York, 1968.
- 10. C.Djerassi, Optical rotatory dispersion- application to organic chemistry, McGraw Hill, 1960.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY----SECOND YEAR PAPER XII- ENVIRONMENTAL CHEMISTRY

## **UNIT - I COMPOSITION**

Composition of atmosphere, vertical temperature, heat budget of the earth atmospheric system, vertical stability atmosphere, biogeochemical cycles of C, N, P, S and O. Biodistribution of elements. Soil composition, micro and macro nutrients, pollution – fertilizers, , pesticides, plastics and metals. Waste treatment.

## **UNIT - II HYDROSPHERE**

Aquatic pollution – inorganic, organic, pesticides, agricultural, industrial and sewage, detergents, oil spills and oil pollutants. Water quality parameters – dissolved oxygen, biochemical oxygen demand, solids, metals, content of chloride, sulphate, phosphate, nitrate and micro organisms, water quality standards.

## UNIT - III ATMOSPHERE

Chemical composition of atmosphere – particles, ions and radicals and their formation, chemical and photochemical reactions in atmosphere, smog formation, oxides of N, C, S, O and their effect, pollution by chemicals, petroleum, minerals, chlorofluorohydrocarbons. Air pollution control and their chemistry.

### **UNIT - IV INDUSTRIAL POLLUTION**

Cement, sugar, distillery, drug, paper and pulp, thermal power plants, nuclear power plants, metallurgy, polymers and drugs. Radionuclide analysis, Disposal of wastes and their management.

## UNIT - V ENVIRONMENTAL TOXICOLOGY

Chemical solutions to environmental problems, biodegradability, principles of decomposition, better industrial processes. Bhopal gas tragety, Chernobyl, Three miles island, Sewozo and Minamata disasters.

# **TEXT BOOKS**

- Ed.J. Rose, Environmental Toxicology, Gordon and Breach Science Publication.
- 2. Ed.S.Landsberger and M.Creatchman, Elemental Analysis of Airborne Particles, Gordon and Breach Science Publication.
- 3. S.E. Manahan, Environmental Chemistry Lewis Publishers.
- 4. Sharma & Kaur, Environmental Chemistry Krishna Publishers.
- 5. A.K.DE., Environmental Chemistry, Wiley Eastern.
- 6. S.M. Khopkar, Environmental Pollution Analysis, Wiley Eastern.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY FIRST YEAR

## PRACTICAL- I -ORGANIC CHEMISTRY PRACTICAL - I

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 methl 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-Nitroanilline from meta dinitrobenzene
- 8. Methyl orange from sulphanillic acid
- 9. Anthraquinone from antracene
- 10. Benzhydrol from benophenone

Reference: Laboratory manual of organic chemistry – B. B. Dey, M. V. Sitaraman

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY FIRST YEAR

# PRACTICAL - II- INORGANIC CHEMISTRY PRACTICAL - I

## Part – I

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

## Part – II

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

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY FIRST YEAR

# PRACTICAL - III-- PHYSICAL CHEMISTRY PRACTICAL - I

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

#### **DETAILED LIST OF EXPERIMENTS**

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

- 1. Study the kinetics of acid hydrolysis of an ester, determination of the temperature coefficient of the reaction and determination of the activation energy of the hydrolysis of ethylacetate.
- Study the kinetics of the reaction between acetone and iodine in acidic medium by half life method and determine the order with respect to iodine and acetone.
- 3. Study of the saponification of ethylacetate by sodium hydroxide conductometrically and determine the order of the reaction.
- 4. Determination of association of ethylacetate by sodium hydroxide conductomertically and determine the order of the reaction.
- 5. Study the phase diagram for m-toluidine and glycerine system.
- 6. Construction of phase diagram for a simple binary system (naphthalenephenanthrene and benzophenone-diphenylamine).

- Construction of the phase diagram of the three component of partially immiscible liquid systems (DMSO-Water-Benzene; Water-Benzene-Acetic acid; Ethyl alcohol-Benzene-Water; Acetone-Chloroform-Water; Chloroform-Acetic acid-Water).
- 8. Determination of the equilibrium constant of the reaction between Iodine and KI by partition method.
- 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.
- 10. 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.
- **11.** Conductometric titrations of a mixture of HCL and CH<sub>3</sub>COOH against Sodium hydroxide
- **12.** Compare the relative strength of acetic acid and monochloroacetic acid by conductivity method.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR

# PRACTICAL – IV-- ORGANIC CHEMISTRY PRACTICAL – II

# I. Organic Estimation

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

# **II** Organic Preparation, Involving Two Stages

- 1. Sym-tribromobenzene from aniline.
- 2. m-Nitrobenzoic acid from methyl benzoate
- 3. para -Nitroaniline from acetanilide.
- 4. Benzanilide from benzophenone.
- 5. para Amino benzene sulphanamide from acetanilide
- 6. Anthraquinone from phthalic anhydride.

## **III. Extraction of Natural Products:**

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

## **IV Chromatographic Separations**

- 1. Column chromatography : separation of a mixture of ortho and para-Nitroanilines.
- 2. Thin layer Chromatography : separation of a mixture of ortho and para Nitroanilines.
- 3. Paper chromatography identification of natural alpha amino acids.
- Ref: 1. Vogel's Practical organic chemistry
  - 2. Laboratory manual of organic chemistry B.B.Dey and M.V.Sitaraman

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR

# PRACTICAL -V-- INORGANIC CHEMISTRY PRACTICAL II

## Part I Quantitative analysis of complex materials

A) Quantitative analysis :

Quantitative analysis of mixture of iron and magnesium; iron and nickel, copper and nickel and copper and zinc.

B) Analysis of Ores

- 1. Determination of percentage of calcium and magnesium in dolomite.
- 2. Determination of percentage of MnO<sub>2</sub> in pyrolusite
- 3. Determination of percentage of lead in galena.

C) Analysis of Alloys

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

#### Part II : Preparations of the following :

- 1. Sodium hexanitrocobaltate (III)
- 2. Tris (ethyleneamine) Cobalt (III) chloride
- 3. Chloropentammine Cobalt (III) chloride
- 4. Bis (acetylacetanato) Copper (II)
- 5. Hexamminecobalt (III) chloride
- 6. Hexamminenickel (II) chloride.

Reference Books for Inorganic Chemistry Practicals I and II

- 1. Vogel's **Qualitative Inorganic analysis** Revised by G.Svehla, VI Edition, orient Longmax (1987).
- 2. V.V.Ramanujam, **Inorganic Semimicro Qualitative analysis**, National Publishing co.1971.
- 3. J.Basset, R.C.Denney, G.H.Jeffery and J.Mendham Vogel's **Text book of** quantitative

inorganic analysis, ELBS, IV Edition(1985).

4. W.G.Palmer, **Experimental Inorganic Chemistry**, Van Nostrand Reinhold Co.,London

1972.

4. D.N.Grindley, An advanced course in practical Inorganic Chemistry, Butterworths 1964.

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY SECOND YEAR

# PRACTICAL – VI-- PHYSICAL CHEMISTRY PRACTICAL – II

Experiments in electro chemistry, Polarography and Chemical Kinetics.

## **EMF Measurements**

Determination of standard potentials (Cu and Ag)

Determination in thermodynamic quantities from EMF measurements, Potentiometric titrations

Determination of  $p_{H}$  and calculation of  $p_{a.}^{K}$ 

Determination of stability constant of complex.

Determination of solubility product of a sparingly soluble salt, Redox titrations.

Precipitation titration of mixture of halides by emf measurements.

## **DETAILED LIST OF EXPERIMENTS**

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

- 1. Determination of the activity coefficient of an electrolyte at different molalities by emf measurements.
- 2. Determination of the dissociation constant of acetic acid by titrating it with sodium hydroxide using quinhydrone as an indicator electrode and calomel as a reference electrode.
- 3. Determination of the strength of a given solution of KCl using differential potentiometric titration technique.
- 4. Determination of the P<sup>H</sup> of the given solutions with the help of the indicators using buffer solutions and by colorimetric method.
- 5. Determination of the P<sup>H</sup> of a given solution by emf method using hydrogen electrode and quinhydrone electrode.

- 6. Determination of the composition and instability constant of a complex by mole ratio method.
- 7. Calculation of the thermodynamic parameters for the reaction  $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$  by emf method.
- 8. Determination of the formation constant of silver ammonia complex and stoichiometry of the complex potentiometrically.
- 9. Solubility and Solubility products by emf method.
- 10. Determination of the activity coefficient of Zinc ions in the solution of 0.002 M Zinc sulphate using Debye Huckel Limiting law.
- 11. Determination of solubility product of Silver bromide and calculate its solubility in water and 0.01 M and 0.01 M KbrO<sub>3</sub> using Debye Huckel limiting law.
- 12. Determinations of the electrode potentials of Zn and Ag electrodes in 0.1 M and 0.001 M solutions at 298 K and find the standard potentials for these electrodes and test the validity of Nernst equations.
- 13. Study the inversion of cane sugar in presence of acid using polarimeter.
- 14. Determination of the rate constant and order of reaction between potassium persulphate and potassium iodide and determine the temperature coefficient and energy of activation of the reaction.
- 15. Study the primary salt effect on the kinetics of ionic reactions and test the Bronsted relationship (iodine ion is oxidized by persulphate ion).
- 16. Determination of the viscosities of mixtures of different compositions of liquids and find the composition of a given mixture.
- 17. Determination of the partial molar volume of the glycine/methanol/formic acid/sulphuric acid by graphical method and by determining the densities of the solutions of different comparisons.
- 18. Study the surface tension concentration relationship for solutions (Gibb's equation)

#### M.Sc CHEMISTRY

# Model Question Paper (For the candidate admitted from 2006-2007 onwards) M.Sc., Degree-Branch-IV Chemistry First Semester Paper I--Organic Chemistry- I

Time: Three Hours

Maximum:100 Marks

# Part-A (5x5=25 marks) Answer All Questions All questions carry equal marks

1 a) Write the mechanism of Sandmeyer reaction with a suitable example.

Or

b) Write two methods of generation of free radicals in detail.

2 a) Explain Hammonds postulate with Potential energy diagram.

Or

b) Explain the effect of resonance and fields effects on reactivity with suitable example

3 a) Explain Chirality due to helical shape of trans cyclooctene and cyclononene.

#### Or

b) Write five examples for erythro and threo compounds.

4 a) Write the mechanism of Dieckmann condensation.

Or

b) Discuss the nucleophilic substitution at an allylic carbon.

5 a) Write short notes on Vilsmeir Hack reaction

## Or

b) Explain Ziegler alkylation reaction

## Part -B ( 5 X 15 = 75 marks)

#### Answer all questions

6 a) i) Explain the Formation, stability and structure of carbonium ions, and carbanions. (3

+3)

ii) Explain rearrangement reaction with an example.

(4)

iii) Discuss Ullmann reaction.

(5)

#### Or

b) i) Discuss the heterolytic, homolytic and pericyclic mechanisms. (3+3+3)ii) Discuss the mechanism of Hunsdiecker reaction.

(6)

7 a) i) Explain : Microscopic reversibility and Marcus theory (3+3)

ii) Discuss : thermodynamic and kinetic control re	actions with suitable
example.	(3+3)
iii) Write notes on Taft equation	(3)

Or

b) i) Discuss the identification of products and determination of the presence

of an intermediate by isotopic labeling method. (8)ii) Discuss the Hammett equation and linear free energy relationship,

- explain the effect of substituent and reaction constant. (7)
- 8 a) i) Explain the optical activity of biphenyls, allenes and spiranes with one example for each. (3+3+3)

ii) Explain the E - Z isomerism of olefins containing one double bond and more than one double bond with two examples for each. (3+3)

Or

b) i) Write the Fischer, Newman and Sawharse projection formula of erythro and threo forms of 3-bromo- 2- butanol. (6)

ii) What are homotopic, enantiotopic, diastereotopic H atoms.	Give two
example for each.	(9)
9 a) i) Discuss the $S_N^{i}$ and SET mechanisms	(3 + 3)
ii) Explain anchimeric assistance	(3)
iii) Discuss Von-braun reaction with the mechanism.	(6)
Or	
b) i) Write notes on :	
Neighbouring group participation by $\pi$ and $\sigma$ bonds,	
Nucleophilic substitution at vinylic carbon and	
Ambident nucleophile	(3 +3 +3)
ii) Discuss the Claisen and Williamson reactions	(3 + 3)
10 a) Explain Arenium ion mechanism with one evidence	(7)
( b) Discuss $S_NAr$ mechanism with evidences	(8)
or	
(a) Define aromatic, non aromatic and anti aromatic	
(b) compounds with examples.	(7)
(c) (b) Write notes on : i. Chichibabin reaction	
ii. Gattermann reaction	(8)

#### M.Sc CHEMISTRY

# Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry First year Paper II --Inorganic Chemistry-I

Time: Three Hours

Maximum:100 Marks

Part -A (5x5=25 marks)

### **Answer All Questions**

## All questions carry equal marks

1. Explain the important empirical rules as given by Pauling to elucidate the structure of a silicate.

#### Or

.Explain the Craig / Peddock model and Dewar model of Phosphazenes

2..Compare the liquid drop and shell models of the nucleus

Or

Give an account of the applications of radioisotopes in the field of medicines.

3. What are the evidences for metal-ligand orbital overlap?

Or

Discuss any two factors affecting the stability of complexes.

4.(a).State Hund's rules for determining the ground term symbol of an atom.Explain with an example.

(or)

(b).The charge transfer spectra of  $[Ir Cl_6]^{3-}$  and  $[Ir Cl_6]^{2-}$  shows one and two spectral transitions respectively. Explain.

5.Discuss the advantages and drawbacks of DME.

Or

Write a note on metal ion indicators with two examples.

## PART-B - (5 X 15 = 75 marks)

# Answer ALL the questions

6.a .Discuss the structure of 12-heteropolyacids	(5)
b. Mention any two applications of Hydrogen bonding	(3)
c.Write a note on Molecular sieves	(3)
d.How do you account for the conductivity of polymeric sulphur nitride	(4)

#### Or

a..Explain Keesam, Debye and London forces of attraction (4)

b. What are hard and soft acids and bases ? Explain HSAB Principle.Mention any two applications of it (5)
c.Give examples and discuss the structural similarities and differences between the polyacids of tungsten and molybdenum (6)
7.a.Describe the construction and working principle of a Geiger-Muller counter for detecting ionizing radiations.

(5)

b.Write a note on nuclear fission taking <sup>235</sup>U as an example. Explain the energy released in a controlled chain reaction.

(2+3)

c.Calculate the Q-value for

 $_{4}\text{Be}^{9}+_{1}\text{H}^{1}- \rightarrow _{4}\text{Be}^{8}+_{1}\text{H}^{2}+\text{Q}$ 

Given that the masses are:

 $_{4}\text{Be}^{9}$ = 9.0150 a.m.u,  $_{1}\text{H}^{1}$ =1.0081 a.m.u,  $_{4}\text{Be}^{8}$ =8.0078 a.m.u and  $_{1}\text{H}^{2}$ =2.0147 a.m.u

(5)

Or

a.What are the different types of isotopic dilution analysis?Explain.What are its applications.

## (5)

b.Write notes on : Radiolysis of water	(5)

c.Highlight the salient features involved in radiation protection. (5)

8.a.Briefly discuss the photometric method of determination of stability constants.

(5)

b.The  $\Delta H$  values of the complexes formed between metal ions and oxalate ions are positive. Yet the complexes are stable. Explain on the basis of thermodynamic concepts.

(5)

c.What is meant by Bjerrum formation function ?

Derive an expression that relates formation function to formation constants. (5)

#### Or

a.What is meant by Spectrochemical series ?How it is quantified by Jorgensen? (5)b.Explain the formation of an octahedral complex by molecular orbital theory with a suitable example.

(5)

c.Explain through orbital splitting why Cu(II) is stable and Au(II) is not stable. (5) 9. (a) i) Explain the electronic spectrum of  $d^3$  ion in Td and Oh field with Orgel diagram.

ii) In the electronic spectrum of  $[Mn(H_2O)_6]^{2+}$ , all the bands are weak. Why?

iii) Interpret the following observation with suitable energy diagram.

 $[CoF_6]^{3-}$  gives a single absorption peak at 13,000 cm<sup>-1</sup>, but  $[Co(en)_3]^{3+}$  gives two absorption peaks at 21400 cm<sup>-1</sup> and 29400 cm<sup>-1</sup>

(4+3+8)

(or)

(b) i) Compare Tanabe-Sugano diagram and Orgel diagram.

ii)[Ni  $(H_2O)_6$ ]<sup>2+</sup> ion shows optical absorption bands at 8,000, 15400 and 26,000 cm<sup>-1.</sup> Assign the transitions using Orgel diagram and estimate Dq and  $\beta$  values. B for Ni <sup>2+</sup> free ion is1050 cm<sup>-1</sup>.

(8+7)

10..a.Discuss the ranks of a polarographic plot of diffusion current vs applied potential

(5)

b.Discuss different types of amperometric titrations. (5)

c.How could you determine Cu(II) ,Zn(II) and Cd(II) ions in a mixture by EDTA titrations

(5)

# Or

a.Write notes on (i) the role of KCl in polarograpic titrations	
(ii) oxygen wave and its elimination	
(iii) Differentiate migration current from diffusion current	(
3x3=9)	
b.Discuss the applications of complexometric titrations	(6)

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY

# M.Sc., Degree Examination

# <u>First Year</u>

## Paper III-- Physical Chemistry- I

Time :Three hours

Maximum : 100 marks

#### **PART A** $(5 \times 5 = 25)$

# Answer all questions

1. a) Write notes on thermodynamic equation of state

(or)

- b) Define the terms
  - i) molar heat capacity at constant pressure
  - ii) molar heat capacity at constant volume
  - ii) and obtain the relation between them.

2. a) Define and explain Thermodynamic and statistical probability

(or)

b) Derive an expression for Fermi-Dirac statistics.

3. a) Define and explain Compton effect.

- (or)
- b) Derive de- Brogile equation. How was it verified?

4. a) Explain the symmetry selection rule for vibrational and electronic spectra

(or)

b) Define and explain mutual exclusion principle

5. a) The rotational constant for  $H^{35}Cl$  is observed to be 10.5909 cm<sup>-1</sup>. What are the

values of B for H<sup>37</sup>Cl and for <sup>2</sup>D <sup>35</sup>Cl ?

```
(or)
```

(b) What are overtones ? How do they arise ?

# <u>**PART-B**</u> (5 X 15 = 75)

6 (a). (i) Discuss the variation of chemical potential with temperature		
and pressure. (	8)	
(ii) Derive phase rule thermodynamically (7)	)	
(or)		
(b) (i) Derive an expression for Cp- Cv for vander Waals gas	(8)	
(iii) Prove that		
$(\delta E / \delta V) T = 0$ for an ideal gas		
and $(\delta E / \delta V) T = \underline{a} V^2$ for van der Waals gas	(7)	
7.a (i).Define Debye theory of heat capacity(10)	)	

#### (or)

(5)

b (i) Derive an expression for equilibrium constant for the dissociation of diatomic molecule (10)

(ii) Define and explain the following terms

(ii)..Evaluate Translational partition function

a.Bosons

Fermism

c.Maxwellars

8..a. (i) If A and B are two operators such that [A,B] = 1, show that

 $[A,B^{2}] = 2B$  (4) (ii) Show that the commutator [x, d/dx] = -1 (4)

(iii) State and explain the important poslulates of quantum mechanics(7)

## (or)

b.(i) Set up the Schordinger equation for the simple harmonic oscillator in one dimension and obtain its eigen value and eigen function. (10)

(ii) Explain the zero point energy associated with a harmonic oscillator. (5)

9. a.(i) Discuss Great orthogonality theorem in detail.

(8)	
(iii) Construct the character table for C2v point group.	(7)
(or)	
b.(i) Assign the point group for the $C_2$ H <sub>2</sub> molecules.	(3)
(ii) Prove that all operations in C2v point group	
commute with each other	(5)
(iii) Deduce the following advible representation	( <b>7</b> )

(iii) Reduce the following reducible representation (7)

Given data

$C_{2v} \\$	E	$C_2$	$\sigma_{v}$	$\sigma_{v}$ ,
A1	1	1	1	1
A2	1	1	-1	-1
B1	1	-1	1	-1
B2	1	-1	-1	1

10.a (i) Explain the influence of isotopic substitution on the rotational energy of a diatomic molecule. (8)

(ii) Explain Fermi resonance. Discuss its influence on the intensity of spectral lines.(7)

(or)

b(i) Discuss the rotational – vibrational Raman spectrum of a diatomic molecules. (8)

(ii) Calculate the force constant for  $H^{35}$ cl from the fact that its fundamental vibrational frequency is 8.667 X  $10^{13}$  sec<sup>-1</sup>. (7)

#### M.Sc CHEMISTRY

# Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry First year Paper IV-- Polymer Chemistry

Time: Three Hours

Maximum:100 Marks

#### Part -A (5x5=25 marks)

## **Answer All Questions**

### All questions carry equal marks

1.a)Write down the structures of the following monomers and repeat units neatly.i) Acrylic acid ii) Methyl methacrylate iii) Styrene iv) Acrylonitrile v) Propene

or

b) Discuss bulk polymerisation

2.a) Discuss block and graft co-polymers with one example for each type.

or

b) What are co-ordination polymerisation catalysts? Give three examples

3.a) Explain "polydispersion" and average molecular weight concept.

or

b) Explain glass transition temperature and write the relationship between  $T_g$  and  $T_m$  4.a) Explain What are plastics, elastomers and fibres

or

b) Discuss about Film casting

5.a) Discuss the properties of polyethylene

or

b) Discuss about electrically conducting po;lymers

#### **PART-B** – (5 X 15 = 75 marks)

#### Answer ALL the questions

6.a) Discuss the mechanism and kinetics of free radical addition polymerization of

vinyl monomers

or

b) Discuss about the heterogeneous polymerisation systems

7.a) Discuss about the mono metallic and bimetallic mechanism of co-ordination

polymerisation reactions

or

b)Discuss the kinetics of co-polymerisation and arrive at the copolymer composition equation.

8.a) Explain how are the following methods used for the determination of molecular weight of the polymers i) light scattering and ii) gel permeation chromatography or

b) Derive the formula for number average and weight average molecular weights and explain the determination of Tg

9. a) Explain the compounding process in polymer processing and discuss about the calendering processing technique.

or

b)Discuss i) injection moulding ii) thermoforming and iii) fibre spinning

10.a) Discuss about i) Phenolic resins ii) epoxy resins iii) polyesters

or

b) Discuss about the biomedical polymers used as contact lens ,dental polymers, artificial heart, skin and blood cells

# Periyar Institute of Distance Education [PRIDE], Salem - 11 M.Sc CHEMISTRY Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry First year

## Paper V--SPECTROSCOPY-I

Time :3 hours

Max Marks:100

#### Part -A (5x5=25 marks)

#### **Answer All Questions**

#### All questions carry equal marks

1.Explain the Einstein's theory of transition probability (OR) How to account for the intensity of spectral lines in rotational spectra

2.Write about the fundamental theory and instrumentation of IR spectroscopy (OR)

Explain with suitable examples about the different group frequencies of organic molecules

3.Explain with examples about Woodward-fisher rules for dienes and enones (OR)

Discus in detail about the various applications of UV-Vis spectroscopy

4.Write about the NMR spectra of AX and AMX type of coupling in organic compounds

(OR) Explain how to apply C<sup>13</sup> NMR spectra to identify the structure of organic compounds

5. Explain the instrumentation involved in Mass spectroscopy (OR)

Explain about the various applications of Mass spectroscopy

# **PART-B** – $(5 \times 15 = 75 \text{ marks})$

## Answer ALL the questions

6.Explain the fundamental principles involved in rotational spectroscopy and about the molecular parameters from rotation spectra

## (OR)

Explain with suitable examples about the effect of isotopic substitution in rotational spectroscopy

7. Explain about the factors that influences the vibrational spectral frequencies

(OR)

Write in detail about the various applications of Raman spectra

8. State and explain the theory, principle and instrumentation of UV-VIS spectroscopy

(OR)

Explain the following

- (i) Chromophores
- (ii) Effect of conjucation in UV spectra
- (iii) Colour in compounds

9. Explain about the spin-spin coupling and factors influencing the chemical shift in NMR spectroscopy

(OR)

Explain the following with examples

- (i) calculation of coupling constants
- (ii) Resonance coupling and decoupling spectra

10. Write about Examples of mass spectral fragmentation of organic compounds with respect to their structure determination

## (OR)

Explain withj suitable examples about McLafferty rearrangement.

## M.Sc CHEMISTRY

Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry Second year Paper VII- Organic Chemistry-II

Time: Three Hours

Maximum:100 Marks

## Part -A (5x5=25 marks) Answer All Questions All questions carry equal marks

1.(a) Show that Hofmann's rearrangement proceeds thro' electron deficient nitrogen

or

(b). Show that Wolff rearrangement is a best method to increase the carbon chain by one.

2..(a) Explain alkylation reactions in enamines

or

(b) Write the synthetic uses of D.C.C

3.(a) Write notes on Wolff-Kishner reduction

or

(b). Suggest a mechanism for the oxidation reaction

$$R-CH_2OT_S + DMSO \rightarrow RCHO + (CH_3)_2S$$

4.(a) Explain Hydroborarion with an example.

Or

(b). Explain the addition of nitrosyl Chloride to Olefins

5.(a) Explain solid phase synthesis and mention the advantages.

Or

(b) Discuss end group analysis

## PART-B – (5 X 15 = 75 marks ) Answer ALL the questions

6.(a). Write down the mechanism of Hofmann rearrangement.Explain why N-Methylacetamide do not undergo this reaction

(5)

(b) Write notes on:

(i) Stevens rearrangement

(ii) Von-Richtr rearranement

(10)

or

( c) Write notes on:

(i).Beckmann rearrangement

(ii) Lossen rearrangement

(iii) Curtius rearrangement

(15)

7.(a) What is an Umpolung.What are the uses of 1,3-dithiane in synthetic organic chemistry (8)

(b) Write a note on Sulphur ylides.

(7)

or

(c) How will you protect and deprotect the following groups

-COOH, -OH

(10)

(d) Explain the Robinson annulation reaction with mechanism

(5)

8. (a) Describe Clemmensen reduction. What are its limitations?

(7)

(b) Explain the stereochemistry of reductions of

(i) 4-t-butylcyclohexanone and

(ii) cis-3-methyl-4-t-butylcyclohexanone with LiAlH<sub>4</sub>

(8)

or

(c) Describe Etard reaction

(5)

(d) Write notes on Ozonolysis

(5)

(e) Explain the utility of NaBH<sub>4</sub> in the reduction reactions.

(5)

9.	Give one	reaction	exemp	lifying	each	of the	following
				10			0

(a) cis addition	(5)
(b) 1,4-addition	(5)
(c) Epoxidation	(5)

or

(d) Why are additions to carbon-carbon double bond mostly electrophile? Under what conditions can you carry out a nucleophilic addition? (5)

(e) Explain the fact that the Diels-Alder addition of maleic anhydride to 2cyclohexenone is faster than that to para-benzoquinone. (5)

(f) How do the carbenes react with an alkene in their singlet and triplet state?(5)

10. (a) Mention the biosynthesis of

I.Phenyl alanine & ii. Proline.	(10)
(b) Give the conversion of Squalene to Cholesterol	(5)
or	

(c) Discuss  $2^0$  and  $3^0$  structure of proteins (15)

#### M.Sc CHEMISTRY

## Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry Second year Paper VIII --Inorganic Chemistry-II

Time: Three Hours

Maximum:100 Marks

# Part -A (5x5=25 marks) Answer All Questions

# All questions carry equal marks

1.a. Give molecular formulae and structures of nido boranes and arachno boranes

(or)

b.What are metal clusters? Give one example.A metal ion in a low oxidation state can adopt one

of the two strategies in forming metal cluster.Explain this statement with reference to Molybdenum

metal clusters

2. a.Compare X-ray, neutron and electron diffraction studies or

b. What are super conductors and LASERS?

3.(a).What are inert and labile complexes ? How C.F.T. explain the labile and inert nature of complexes.

(or)

(b).How is thiourea used to distinguish between the isomeric forms of square planar complexes.? Name the other reagent that can be used for this purpose.

4.(a).Illustrate with one suitable example the oxidative addition and reductive eliminations

inacions

(or)

(b).Propose a mechanism for the polymerization of propene to polypropene by Zeigler- Natta catalyst.

5.(a).Explain  $Na^+/K^+$  pump.

(or)

(b).Write briefly about In Vitro Nitrogen fixation.

## Part-B (5x15=75 Marks) Answer All Questions

6.(a) Discuss the applicability of Wade's rule in the elucidation of structures of metalocarboranes

(b) Give the IUPAC nomenclature and structures of the boranes :  $B_5H_9$ ,  $B_5H_{11}$  and  $C_2B_{10}H_{12}$ .Explain the usefulness of nmr in the elucidation of the structures of boranes(5+10)

(c)Write an essay of nido and closo carboranes with respect to their preparation, structure and uses.

(d)Discuss the structural features of  $\text{Re}_2\text{Cl8}^{2-}$  (5+10)

7. (a) Explain spinel and inverse spinel structures with examples (6)

(b) Describe "Hall effect" and its significance in identification of "n-type" and " p-type" semi-conduction (6)

c. Write a note on : ferro and ferrimagnetism (3)

or

or

(d) Describe the band theory of solids in relation to the properties of insulators, conductors and semi-conductors. (6)

(e) How does nickel Arsenide differ from cadmium Iodode structure?(f) Explain briefly on Ga-As phosphors or garnets and ferrites(4)

8.(a) i) What is meant by Chemical activation? When do outer sphere electron transfer reactions require chemical activation? Illustrate with an example.

ii) What are complementary and non-complementary reactions? Illustrate the mechanism of non-complementary redox reactions.

iii) Distinguish between cross reaction and exchange reaction in redoxreactions. (6+6+3)

(or)

(b) i) Outline Marcus Hush theory and describe its utility in the prediction of rection rates.

ii) The rate of inner sphere electron transfer reaction depends on the nature of the oxidant, the reductant and the bridging ligands..Illustrate with one example for each of the above factors. (6+9)

9. (a) i) Discuss the fluxional isomerism encountered in  $(CH_2=CH-CH_2)_4$  Zr. How is <sup>1</sup>H NMR useful in the study of fluxional isomerism in the complex.

ii) Outline M.O. scheme for Ferrocene. With its help arrange the following in the order of increasing stability ;ferrocene, cobalocene ,nickelocene. (8+7)

(or)

. (a) i) Explain how olefins are oxidized to aldehydes and ketones in Wacker process

ii) Illustrate the detailed mechanism of hydrogenation of ethylene using Wilkinson's catalyst.

Write down the Tolman catalytic loop depiction for the above mechanism.

(7+8)

10. (a). i) Name the important complex containing corrin ring. What is the metal atom present in it.?

Discuss its importance.

ii) Describe the structural features of haemoglobin and its function of oxygen transport.

iii) Explain the biological importance of Mg complexes. (5+5+5)

(or)

(b) i) How is carboxypeptidase-A important in the hydrolysis of proteins and peptides.

ii) Describe briefly on the role played by iron-sulphur proteins in biological process.

iii) Why free heme is useless for oxygen transport ? (6+6+3)

#### M.Sc CHEMISTRY

# Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry Second year Paper IX-- Physical Chemistry-II

Time: Three Hours

Maximum:100 Marks

## Part -A (5x5=25 marks) Answer All Questions All questions carry equal marks

- 1. a) Derive de-Broglie equation. How was it verified (or)
  - b) Define and explain Compton effect.
- 2. a) What are approximation methods? Explain the need for an approximation method.
  - (or) b) State and explain Born-Oppenheimer approximation.
- 3. a) Explain Debye-Huckel theory of strong electrolytes. (or)
  b) Explain Stern model of electrical double layer.
- 4. a) Explain the principle and application of cyclic voltametry (or)b) Write notes on corrosion
- 5. a) Distinguish between physical adsorption and chemical adsorption (or)
  b) Derive kinetic expression for Langmuir adsorption isotherm

## **PART-B** (5x15=75) **Answer All Questions**

6.	Ι	a) Set up Schrodinger equation for a particle in one dimensional	box and
		obtain its eigen value and eigen function	(10)
		b) State and Explain Heisenberg uncertainty principle	(5)

(or)

II a) State and explain the important postulates of quantum mechanics (5)

b) Write Schrodinger equation for rigid rotator and arrive an	expression	
for energy and wave function	(10)	
7. I a) State and Explain variation principle	(5)	
b) Appling HMO theory to ethylene molecule arrive an expression for		
energy and wave function	(10)	
(or) II a) Explain Hartree-Fock self consistent Field theory	(10)	
b) What are Slater rules? Explain its significance	(5)	
8. I a) Explain the Tincelius method of separation of proteins	(10)	
b) Explain electrode-electrolyte interface adsorption	(5)	
(or)		
II a) Explain Helmholtz Perrin theory of electrical double lay	er (10)	
b) Explain the term "membrane potential"	(5)	
9. I a) Derive Butler-Volmer equation for one electron transfer reaction(10)		
b) Write mechanism for $H_2$ - $O_2$ evolution reaction	(5)	
(or)		
II Write notes on the following	(3×5)	
a) Construction of Pourbaix and Evans diagram		
b) Primary and Secondary batteries		
c) Fuel cells		
10. I a) Explain the B.E.T theory of multilayer adsorption	(10)	
b) Explain Bronsted catalysis law	(5)	
(or)		
II a) Derive an expression for Michelis-Menton equation	(10)	
b) Explain the effect of $P^{H}$ and Temperature on enzyme catalyzed		
reaction	(5)	

M.Sc CHEMISTRY

Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry Second year Paper XI-Spectroscopy-II

Time: Three Hours

Maximum:100 Marks

## Part -A (5x5=25 marks) Answer All Questions All questions carry equal marks

1.Explain the basic principles involved in atomic absorption spectroscopy. (OR) Describe the applications of atomic absorption spectroscopy.

2. Predict the number of lines in the ESR spectrum of  $(SO_3)_2NO^{2-}$ . The natural abundance of N<sup>14</sup> (*I*=1) is 99.635 percent and of N<sup>15</sup> (*I*=1/2) is 0.363 percent. Also calculate the relative intensity of ESR lines. (OR)

Explain anisotropic hyperfine interaction in ESR spectrum

3. Explain the theory and principle of Mossbauer spectoscopy.

(OR)

Discuss about the electron-neutron hyperfine interactions in Mossbauer spectroscopy.

4. What are the requirements of a specimen to be suitable for the analysis in a photoelectron spectroscope?

(OR)

How will you obtain a photoelectron spectrum? Find binding energy of an electron.

5. Discus the use of Cotton effect.

(OR)

How can you predict a compound by axial haloketon rule.

## PART-B (5x15=75) Answer All Questions

6. i. Explain the theory and instrumentation of atomic absorption spectroscopy

ii. Define the following terms:

1. Chemical interference

2. Doppler broadening

(OR)

Describe how a deuterium lamp can be employed to provide a background correction

for an atomic absorption spectrum.

7. i. Define g-value. Explain the various factors affecting the g-value.

ii. How many lines are expected in the spectrum of free radical p-

benzosemiquinone

and what would be the relative intensities of these?

(OR)

Explain the following

- (iv) Zero-Field splitting
- (v) Kramer's Degeneracy
- (vi) Electronic Zeeman effect

8. State and explain the Quadrupole interactions and magnetic interactions in Massbauer

spectroscopy

## (OR)

- (a). Discus the application of Massbauer spectroscopy to characterize iron and tin compounds
- (b) Explain the following
  - (i) Doppler effect
  - (ii) Isomer effect

9. Discus the general character of the photoelectron spectra of CO and NH<sub>3</sub>.

(OR)

- (i) Explain the principle of photoelectron spectroscopy.
- (ii) Discus the application of X-ray photoelectron spectroscopy.
- 10. State and explain the octant rule and discus its application for R-(+) Methylcyclo hexanone.

# (OR)

Discus the applications of CD and ORD curves in structural determination of compounds.

#### M.Sc CHEMISTRY

## Model Question Paper (For the candidate admitted from 2007-2008 onwards) M.Sc., Degree-Branch-IV Chemistry Second year Paper XII -Environmental Chemistry

Time: Three Hours

Maximum:100

Marks

# Part -A (5x5=25 marks) Answer All Questions All questions carry equal marks

1.(a) Sketch and explain the biogeochemical cycle of carbon.

Or

- (b)Write a note on: green house effect.
- 2.(a) What is biological oxygen demand? Explain.

Or

- (b) Discuss the detrimental effects of inorganic pollutants in water.
- 3.(a) What are the harmful effects of chlorofluorohydrocarbons?

Or

- (b) Give the various control measures for air pollution.
- 4.(a) Write briefly on : Waste Management.

Or

- (b) Explain how thermal pollutants affect our eco system.
- 5.(a) What are effects caused by biodegradable compounds?

Or

(b)Briefly explain the Chernobyl disaster.

# Part -B (5x15=75 marks) Answer All Questions All questions carry equal marks

- 6.(a) Graphically represent the variation of air temperature with altitude. Explain. (8)
  - (b) Write down the various micro and macro nutrients in the soil. What are the roles played by them? (7)

Or (c). How can we treat the waste materials before they pollute the soil? (8)

(d). Sketch and explain the biogeochemical cycle of nitrogen. (7)

7.(a) What are the roles of metal ions and microorganisms in water?	(10)	
(b) Explain how detergents cause water pollution. Or	(5)	
<ul><li>(c) Industrial effluents and sewage waste pollute the water to a very great extent. Justify. (10)</li></ul>		
(d) Write down the parameters that determine the quality of water.	(5)	
8.(a).Discuss the pollution effects caused by NOx and SOx.	(8)	
(b) Write the various photochemical reactions occuring in the atmosphere.	(7)	
Or		
(c) How are ions and free radicals formed in the atmosphere? Explain.	(8)	
(d) Explain how chemicals cause air pollution.		
9.(a) How can we prevent and control the pollution from nuclear power plants?	(10)	
(b) Write a note on:		
Radionuclueide analysis.	(5)	
Or		
<ul><li>(c) Discuss the nature, effect and breakment of waste from paper pulp indus (10)</li></ul>	tries.	
(d) Explain the pollution effects caused by distillery effluents.	(5)	
10.(a) Write a note on:		
<ul><li>(i) Bhopal gas tragedy.</li><li>(ii) Minameter disaster.</li></ul>	(8) (7)	

Or

(b) Discuss the industrial processes that can be carried out for better environment. (10)

- (d) Write the various principles involved in the
- (e) decomposition of materials. (5)