

# FACULTY OF SCIENCES

## SYLLABUS

FOR

### M.Sc. Chemistry

(Semester I-IV)

(For Colleges)

Session: 2013-14



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## GURU NANAK DEV UNIVERSITY AMRITSAR

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## Scheme of Courses

**Eligibility:-** The candidate having passed B.Sc. degree (10+2+3 system of education) with Chemistry as one of the elective subject with at least 50% marks from Guru Nanak Dev University or any other examination recognized equivalent there to by the University.

**Note:-** Detailed ordinances relating to examinations for this class are contained in the Guru Nanak Dev University Calendar Vol II. Read with Syndicate decisions / amendments made from time to time.

		Max. Marks	Hrs.
<b>Semester- I</b>			
Course-I	Ligand Field Theory	50	45
Course-II	Organic Reaction Mechanism-I	50	45
Course-III	Physical Chemistry – Thermodynamics	50	45
Course-IV	Spectroscopy A: Techniques for Structure Elucidation of Organic Compounds	75	60
Course-V	Computer for Chemists – Theory Computer for Chemists - Practical	50 25	45 30
Course-VI	Inorganic Chemistry Practical (Quantitative Analysis)	75	60
Course-VII	Organic Chemistry Practical	75	60
<b>Total:</b>		<b>450</b>	<b>390</b>

## M.Sc. (Chemistry) (Semester I-IV) (Only For Colleges)

**Semester-II**

Course-VIII	Organometallic Chemistry	50	45
Course-IX	Organic Reaction Mechanism -II	50	45
Course-X	Physical Chemistry – Quantum Chemistry	50	45
Course-XI	Reaction Mechanisms and Metal clusters	50	45
Course-XII	Spectroscopy B: Techniques for Structure Elucidation of Inorganic Compounds	75	60
Course-XIII	Mathematics for Chemists or Biology for Chemists	25	30
Course-XIV	Organic Chemistry Practical	75	60
Course-XXV	Physical Chemistry Practical	75	60
	<b>Total:</b>	<b>450</b>	<b>390</b>

**Semester-III**

Course-XVI	Inorganic Chemistry-II	50	45
Course-XVII	Organic Synthesis	50	45
Course-XVIII	Surface and Polymer Chemistry	50	45
Course-XIX	Electrochemistry and Chemical Dynamics	50	45
Course-XX	Photochemistry and Pericyclic reactions	50	45
Course-XXI	Inorganic Chemistry Practical (Preparations)	75	60
Course-XXII	Physical Chemistry Practical	75	60
	<b>Total:</b>	<b>400</b>	<b>345</b>

**Semester-IV**

Course-XXIII	Advanced Inorganic Chemistry	75	60
Course-XXIV	Natural Products	75	60
Course-XXV	Chemistry of Materials	75	60
Course-XXVI	Advanced Practical		
	- Organic Synthesis	50	90
	- Inorganic Synthesis	50	90
	- Physical Chemistry	50	90
	<b>Total:</b>	<b>375</b>	<b>450</b>

**Course I**  
**LIGAND FIELD THEORY**

**45 Hrs.****Max. Marks: 50****Time: 3 Hrs.****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**1. Symmetry (10Hrs.)**

Symmetry elements, symmetry operations and their matrix representation, group postulates and types, multiplication tables, point group determination, determination of reducible and irreducible representations, character tables, construction of character tables for  $C_{2v}$ ,  $C_{3v}$  (non-abelian group), use of symmetry in obtaining symmetry of orbitals in molecules, use of character table to determine which metal orbitals are used in  $\pi$  and  $\sigma$  bond formation in octahedral, tetrahedral and square planar transition metal complexes, qualitative splitting of s, p, d, f orbitals in octahedral, tetrahedral and square planar fields using character tables and without the use of character tables.

**2. Molecular Orbital Theory for Metal Complexes (5 Hrs.):**

Recapitulaltions, ligands symmetry orbitals and metal orbitals involved in molecular orbitals formation in octahedral complexes, MOEL diagrams for octahedral tetrahedral and square planar complexes showing  $\pi$  and  $\sigma$  bonding in transition metal complexes.

**3. Interelectronic Repulsions (5 Hrs.):**

Spin-spin, orbital-orbital and spin orbital coupling, LS and jj coupling schemes, determination of all the spectroscopic terms of  $p^n$ ,  $d^n$  ions, determination of the ground state terms for  $p^n$ ,  $d^n$ ,  $f^n$  ions using L.S. scheme, determination of total degeneracy of terms, order of interelectronic repulsions and crystal field strength in various fields, two type of electron repulsion parameters, spin orbit coupling parameters ( $\zeta$ ) energy separation between different j states, The effect of octahedral and tetrahedral fields on S, P, D and F terms (with help of the character table), splitting patterns of and G, H and I terms.

**4. Free Ions in Medium and Strong Crystal Fields (5 Hrs.):**

Strong field configurations, transition from weak to strong crystal fields, evaluation of strong crystal field terms of  $d^2$  configuration in octahedral and tetrahedral crystal fields (using group theory), construction of the correlation energy level diagrams of  $d^2$  configuration in octahedral field, study of energy level diagrams for higher configurations, selection rules of electronic transitions in transition metal complexes, their proof using group theory, relaxation of the selection rule in centrosymmetric and non-centrosymmetric molecules, Orgel diagrams, Tanabe Sugano diagrams

**5. Electronic Spectra of Transition Metal Complexes (13 Hrs.):**

Variation of the Racah parameter, nephelauxetic effect -central field covalency, symmetry restricted covalency, differential radial expansion, spectrochemical series, band intensities, factors influencing band widths, discussion of electronic spectra of octahedral and tetrahedral  $d^1$  -  $d^9$  metal ions, calculation of  $10Dq$  and  $B$  with use of Orgel and Tanabe Sugano diagrams, low spin complexes of  $Mn^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{3+}$ ,  $Fe^{2+}$ , comment on the spectra of second and third transition series, spectra of  $K_3MoCl_6$  and  $[Rh(NH_3)_6]^{3+}$ , spectra of cis and trans $[Co(en)_2X_2]^+$ ,  $[Mn(H_2O)_6]^{2+}$ ,  $CuSO_4 \cdot 5H_2O$  and its anhydrous complex, comparison of d-d band with f-f bands. Introduction to Charge Transfer Spectra.

**6. Magnetic Properties (7 Hrs.):**

Van Vlecks formula for susceptibility, first order Zeeman effect, second order Zeeman effect, KT states, quenching of orbitals angular momentum by ligand field, the magnetic properties of A and E terms, the magnetic properties of T terms, electronic delocalization, magnetic properties of  $d^n$  and  $f^n$  metal ions.

**Recommended Books:**

1. F.A. Cotton, Chemical Application of Group Theory, Wiley Eastern.
2. G. L. Miessler, D. A. Tarr, Inorganic Chemistry, 3<sup>rd</sup> edition, Pearson Education.
3. B.N. Figgis, Introduction to Ligand Field, Wiley Eastern.
4. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier.
5. A. Earnshaw, Introduction to Magnetochemistry, Academic Press.
6. J.E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, Harper Interscience.
7. R.S. Drago, Physical Method in Chemistry, W.B. Saunders Company.
8. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Inter-science.

**COURSE II**  
**Organic Reaction Mechanism- I**

**45 Hrs****Max. Marks: 50****Time: 3 hrs.****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about 1/3<sup>rd</sup> of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**1. Nature of Bonding in Organic Reactions: (4 Hrs.)**

Aromaticity in Benzenoid and non-benzenoid compounds. Huckel' Rule, Alternant and non-alternant hydrocarbons. Energy levels of (pi) molecular orbitals in simple systems. Annulenes, Antiaromaticity, Homoaromaticity, PMO approach.

**2. Stereochemistry : (8 Hrs)**

Elements of symmetry, chirality, molecules with more than one chiral center. Threo and erythro isomers, methods of resolution, optical purity. Prochirality – enantiotopic and diastereotopic atoms, groups and faces. Stereospecific and stereoselective synthesis. Asymmetric synthesis. Optical activity in absence of chiral carbon (Biphenyls, Allenes, Spiranes). Chirality due to helical shape.

**3. Reaction Mechanism, Structure and Reactivity: (8 Hrs)**

Types of mechanisms, types of reactions, thermodynamic and kinetic requirements, Kinetic and thermodynamic control in product formation. Transition states and reaction intermediates, Isotope effects, Hard and Soft Acid Base concept, Study of reactive intermediates – Types of intermediates, isolation and detection of intermediates (including use of spectral techniques), trapping of intermediates.

**4. Aliphatic Nucleophilic Substitution: (10 Hrs)**

The SN<sub>2</sub>, SN<sub>1</sub> and SN<sub>i</sub> mechanisms, mixed SN<sub>1</sub> & SN<sub>2</sub> mechanism SET mechanism. The neighbouring group mechanism (anchimeric assistance). Neighbouring group participation by pi and sigma bonds, Classical non-classical & phenonium cations, Rearrangements in carbocations (general survey). Ester hydrolysis. Nucleophilic substitution at allylic, aliphatic trigonal and vinylic carbon. Effect on the reactivity due to – substrate structure, attacking nucleophile, leaving group and reaction medium. Ambident nucleophiles and substrates, regioselectivity. Meyer's synthesis of aldehydes, ketones, acids and esters. Alkylation by organoboranes.

**5. Aliphatic Electrophilic Substitution: (5 Hrs)**

Bimolecular mechanism – SE<sub>2</sub> and SE<sub>i</sub>. The SE<sub>1</sub> mechanism, Hydrogen exchange, electrophilic substitution accompanied by double bond shifts, diazo-transfer reaction, formation of sulphur ylides, effect of substrates, leaving group and solvent polarity on the reactivity.

**6. Aromatic Electrophilic Substitution: (5 Hrs)**

The arenium ion mechanism, orientation and reactivity in mono substituted and di substituted aromatics. Energy profile diagrams. The ortho/para ratio, ipso attack, orientation in other ring systems. Quantitative treatment of reactivity in substrates and electrophiles. Diazo coupling, Vilsmeier reaction, Gattermann-Koch reaction, Pechmann reaction, Houben – Hoesch reaction, Fries rearrangement.

**7. Aromatic Nucleophilic Substitution: (5 Hrs)**

S<sub>N</sub>Ar, S<sub>N</sub>1, benzyne and S<sub>RN</sub>1 mechanisms. Reactivity effect of substrate structure, leaving group and nucleophile. The von Richter, Sommelet-Hauser, and Smiles rearrangements.

**Books Recommended:**

1. Stereochemistry - Eliel
2. Advanced Organic Chemistry – Jerry March.
3. Advanced Organic Chemistry, F. A. Carey, R. J. Sundberg, Volume I and II
4. Highlights of Organic Chemistry, W.J. L. Nobel; An Advanced Text Book.
5. Stereochemistry conformation and Mechanism – P. S. Kalsi

**COURSE III**  
**Physical Chemistry – Thermodynamics**

**45 hrs.**  
**Time: 3 Hrs.**

**Max. Marks: 50**

**Note: The students are allowed to use Non-Programmable Calculator.**

**Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**1. Classical Thermodynamics (Hrs 20)**

Brief resume of concepts of thermodynamics, free energy, chemical potential and entropy. Partial molar properties, partial molar free energy, partial molar volume and partial molar heat content and their significances. Determination of these quantities. Concept of fugacity and determination of fugacity.

Non-ideal systems: Excess functions for non-ideal solutions. Activity, activity coefficients, Debye-Huckel theory for activity coefficient of electrolytic solutions, determination of activity and activity coefficients, ionic strength. Application of phase rule to three component system, second order phase transitions.

**2. Statistical Thermodynamics: (Hrs 15)**

Concept of distribution law, thermodynamic probability and most probable distribution, Ensemble averaging, postulates of ensemble averaging. Canonical, grand canonical and microcanonical ensembles, corresponding distribution laws (using Lagrange's method of undetermined multipliers).

Partition functions: Translational, rotational, vibrational and electronic partition function, calculation of thermodynamic properties in terms of partition functions. Application of partition functions.

Heat capacity behavior of solids-chemical equilibria and equilibrium constants in terms of partition functions, Fermi-Dirac statistics, distribution laws, and application to metals. Bose-Einstein statistics- distribution law and application to helium.

**3. Non Equilibrium Thermodynamics: (Hrs 10)**

Thermodynamic criteria for non-equilibrium states, entropy production and entropy flow, entropy balance equations for different irreversible processes (e.g., heat flow, chemical reaction etc.) transformations of generalized fluxes and forces, non-equilibrium stationary states, phenomenological equations, microscopic reversibility and Onsager's reciprocity relations, electro kinetic phenomena, diffusion, electric conduction, irreversible thermodynamics for biological systems, coupled reactions.

**Books Suggested:**

1. I F Nash: Elements of classical and statistical thermodynamics
2. Pitts: Non equilibrium thermodynamics
3. I Prigogine: Introduction to thermodynamics of irreversible processes
4. T L Hill: Introduction to statistical thermodynamics.

**COURSE IV****SPECTROSCOPY – A: Techniques in Structure Elucidation of Organic Compounds****60 hrs.****Max. Marks: 75****Time: 3 hrs.****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about 1/3<sup>rd</sup> of a page. All questions are compulsory. In paper having 75 marks, each question will be of 1½ marks, total weightage being 15 marks.

**Section-B:** Twelve short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In paper having 75 marks, each question will be of 4½ marks, total weightage being 36 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In paper having 75 marks, each question will be of 12 marks, total weightage being 24 marks.

**1. Nuclear Magnetic Resonance (15 Hrs.)**

The Nuclear spin, Larmor frequency, the NMR isotopes, population of nuclear spin level, spin and spin lattice relaxation. Measurement techniques (CW & FT method), solvent used. Chemical shift, reference compounds, shielding constant, range of typical chemical shifts simple application of chemical shifts, ring current and aromaticity. Shifts for H and <sup>13</sup>C. - Spin-spin interactions, Low and High resolution spectra with various examples, Correlation of H bound to carbon, H bound to other nuclei such as nitrogen, oxygen, sulphur, Complex spin-spin interaction, between two or more nuclei. Effect of chemical exchange, fluxional molecules, Hindered rotation on NMR spectrum Karplus relationship, nuclear magnetic double resonance, chemically induced dynamic nuclear polarization. Brief introduction to multipulse NMR spectroscopy, Application of structure elucidation of simple organic molecules Lanthanide shift.

**2. Mass Spectroscopy (10 Hrs.)**

Elementary theory - Measurement techniques (EI, CI, FD, FAB), Resolution, exact masses of nuclides, Molecular ions, isotope ions, fragment ions of odd and even electron types, rearrangement ions, Factors affecting cleavage patterns, simple cleavage, cleavages at a hetero atom, multicentre fragmentations rearrangements, Retroiels – Alder fragmentation. Cleavage associated with common functional groups (Aldehydes, ketones cyclic and acyclic esters, alcohols, alkenes, aromatic compounds amines). - Special methods of GCMS, high resolution MS, Introduction to radical anion mass spectroscopy. Interpretation of the spectrum of an unknown.

**3. Ultraviolet and Visible Spectroscopy (10 Hrs.)**

The energy of electronic excitation, measurement techniques, Beer-Lambert Law, Molar extinction coefficient. The Frank Condon Principle. Different types of transition noticed in UV spectrum of organic functional groups and their relative energies. Chromophore, auxochromes, factors affecting max, Effect of steric hindrance to coplanarity, Solvent Effects. Applications of U.V. spectroscopy.

**4. Infrared Spectroscopy (10 Hrs.)**

Vibrational Energy Levels, Selection Rules, Force Constant, Fundamental Vibration Frequencies, Factors influencing Vibrational Frequencies (Vibrational Coupling, Hydrogen Bonding, Electronic effect, Bond Angles, Field Effect). Sampling Techniques, Absorption of Common functional Groups, Interpretation, Finger print Regions.

**Applications in Organic Chemistry**

- (a) Determining purity and quantitative analysis.
- (b) Studying reaction kinetics.
- (c) Determining purity and quantitative analysis.
- (d) Studying hydrogen bonding.
- (e) Studying molecular geometry & conformational analysis.
- (f) Studying reactive species

**5. Solution of Structural Problems by Combined Use of the following Spectroscopic Techniques: (15 Hrs.)**

- (a) Electronic spectra
- (b) Vibrational spectroscopy
- (c) NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectroscopy
- (d) Mass Spectroscopy

**Books Recommended:**

1. W. Kemp. Organic Spectroscopy.
2. W. Kemp. N.M.R. Spectroscopy.
3. D.H. Williams and I. Fleming. Spectroscopic Methods in Organic Chemistry.
4. R.M. Silverstein & G.C. Bassler, Spectrometric Identification of Organic Compounds.
5. R.C. Banks, E.R. Matjeha and G. Mercer, Introductory Problems in Spectroscopy.
6. Introduction to Spectroscopy - Pavia

**Course –V**  
**Computer for Chemists**

**75 Hrs.**  
**Time: 3 hrs.**

**Total Marks: 75**  
**Theory Marks: 50**  
**Practical Marks: 25**

**Instructions for the Paper Setters:**

The paper will consist of 45 Hours of teaching in class room and 15 sessions of 2 hours of practical training on computers. The theory will be of 50 marks and practical would be of 25 marks. The students would prepare a record of the programs written by them along with the outputs.

**1. Computer Programming in C language 30 Hrs.**

Principles of programming, algorithms and flowcharts.

Elementary programming, a typical C program, printf function.

Introduction of declarations, assignments and variables: concept of an integer, concept of a variable, rules for naming variables, assignment statement, arithmetic operators.

Integer arithmetic expressions, truncation effects, relative priority of arithmetic operators, use of parenthesis, modulus operator.

Floating point numbers, scientific notation, converting integers to floating point and vice versa , coercion and cast operator, type char.

Decision making in C, scanf function, relational operators, logical operators, if statement, if else statement, nesting of if statement.

The while loop, do while loop, for loop, nesting of for loop.

Type char and ASCII code, character strings and how to print them, octal and hexadecimal notation.

User defined functions, returning value from a function, functions with more than one parameters.

Arrays, declaring an array, initializing an array, break statement, strings and character arrays, sorting an array, finding maximum and minimum in an array, multidimensional arrays.

Input and output.

**2. Computer programs in Chemistry (15Hrs. Theory + 30 hrs Practical)****(these are also be done in the practical class):**

Development of small computer codes involving simple formulae in chemistry:

1. Calculation of mean, median, mode.
2. Solution of a quadratic equation.
3. Calculation of linear regression.
4. Calculation of curve linear regression.
5. Calculation of Bohr orbit from de Broglie Lambda for electron.
6. Calculation of wave number and frequency from value of wave length.
7. Calculation of van der Waals radii.
8. Radioactive decay.
9. Rate constant of a 1st order reaction, 2nd order reaction.
10. Determination
11. Calculation of lattice energy using Born Lande equation.
12. Addition, multiplication and solution of inverse of 3 X 3 matrix.
13. Calculation of average molecular weight of a polymer containing n1 molecules of molecular weight m1, n2 molecules of molecular weight M2 and so on.
14. Program for calculation of molecular weight of organic compound containing C, H, N, O and S.
15. Calculation of reduced mass of diatomic molecule.
16. Calculate the RMS and most probable velocity of a gas.
17. Calculate the ionic mobility from ionic conductance values.
18. Determine the thermodynamic parameters for isothermal expansion of monoatomic ideal gas.
19. Calculation of value of g- factor from value of J and S.
20. Calculate the bond length and bond angles using crystal structure data.

**Recommended Books:**

1. K.V. Raman, Computers in Chemistry, Tata McGraw Hill.
2. Mullish Cooper, The spirit of c, An Introduction to Modern Programming.

**COURSE - VI**  
**INORGANIC CHEMISTRY (PRACTICAL)**  
**(Quantitative Analysis)**

60 hrs.

M. Marks: 75

**I. Oxidation-Reduction Titrations**

1. Standardization with sodium oxalate of  $\text{KMnO}_4$  and determination of  $\text{Ca}^{2+}$  ion.
2. Standardization of ceric sulphate with Mohr's salt and determination of  $\text{Cu}^{2+}$ ,  $\text{NO}_3^{-1}$  and  $\text{C}_2\text{O}_4^{-2}$  ions.
3. Standardization of  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{Fe}^{2+}$  and determination of  $\text{Fe}^{3+}$  (Ferric alum)
4. Standardization of hypo solution with potassium iodate /  $\text{K}_2\text{Cr}_2\text{O}_7$  and determination of available  $\text{Cl}_2$  in bleaching powder,  $\text{Sb}^{3+}$  and  $\text{Cu}^{2+}$ .
5. Determination of hydrazine with  $\text{KIO}_3$  titration.

**II. Precipitation Titrations**

1.  $\text{AgNO}_3$  standardization by Mohr's method by using adsorption indicator.
2. Volhard's method for  $\text{Cl}^-$  determination.
3. Determination of ammonium / potassium thiocyanate.

**III. Complexometric Titrations**

1. Determination of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by using masking reagent by EDTA titration.
2. Determination of  $\text{Ni}^{2+}$  (back titration).
3. Determination of  $\text{Ca}^{2+}$  (by substitution method).

**IV. Gravimetric Analysis**

1. Determination of  $\text{Ba}^{2+}$  as its chromate.
2. Estimation of lead as its lead molybdate.
3. Estimation of chromium (III) as its lead chromate.
4. Estimation of  $\text{Cu}^{2+}$  using Ammonium/ Sodium thiocyanate.

**Book:** Vogel's book on Inorganic Quantitative Analysis.

**COURSE-VII**  
**ORGANIC CHEMISTRY (PRACTICAL)**

Labs Hrs.: 60

Max. Marks: 75

**Unit – I**

1. **Purification and Characterization of Organic Compounds**, the student is expected to carry out the experiments of purification (fractional crystallization, fractional distillation, chromatography) separation, purification and identification of the compounds of binary organic mixture (liquid-liquid, liquid-solid and solid-solid), using chemical analysis and IR and PMR spectral data. The student should also check the purity of the separated components on TLC plates.
2. To carry out the analysis of common analgesic drugs by **thin layer chromatography**, Acetaminophen, Aspirin, caffeine, phenacetin, salicylamide. (Learn to check purity of the given samples and completion of the chemical reactions).

**Unit – 2**

**Organic Synthesis and Extraction of Organic Compounds from Natural Sources.** The student is expected to carry out 4 to 6 organic preparations (usually involving not more than two steps), some of the illustrative experiments are listed below:-

1. *Extraction of Caffeine from tea leaves*  
(Ref. Experiment Organic Chemistry, (H. Dupont Durst, George W. Gokel, P 464 McGraw Hill Book Co., New York).  
Student would be asked to purify crude sample, check the purity on a TLC single spot and get the NMR scanned and interpret (Three methyl singlets and I methane singlet).
2. *Isolation of casein from milk* (try some typical colour reactions proteins).
3. *Synthesis of 2-phenylindole-Fischer Indole Synthesis.* Book 1, p. 852  
**Aim:** To Study condensation and cyclization reactions.
4. *Synthesis of 3-nitrobenzoic from benzoic acid* (Rf. Ibid., p.245-247 and 443-448).  
**Aim:** To demonstrate the process of meta nitration, esterification and saponification of an ester. Make a comparative study of IR and PMR spectra of benzoic acid, methyl benzoate, methyl 3-nitrobenzoate.
5. *Cannizaro's reaction of 4-chlorobenzaldehyde.* Book 1, p 760  
**Aim:** To demonstrate technique of isolation of two products from the reaction mixture and the procedure of intermolecular hydride transfer.  
Make a comparative study of IR and PMR spectra of 4 chlorobenzaldehyde, 4-chlorobenzoic acid 4-chlorobenzyl alcohol.
6. *Synthesis of 1,3,5-Tribromobenzene from aniline.*  
**Aim:** To demonstrate: Bromination, Diazotization and Reduction.

**Book:** Vogel's Text book of practical organic chemistry, 5<sup>th</sup> edition.

**45 Hrs.****Time: 3 Hrs.****Max. Marks: 50****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**Organometallics (25 Hrs.)**

Energy polarity and reactivity of M-C bond, Stability of Main group organometallics: Methods of preparation in perspective-organolithium compounds: structure and bonding & reaction-carbolithiatic organometallics of group 2 and 12 e.g. Mg and Zn, Cd and Hg: Preparation and structure of organoaluminium compounds, Technical applications of Tris (alkyl) aluminium compounds.  $\eta^2$ - ligands: olefinic and acetylenic complexes, chelating olefinic ligands – synthesis and structure.  $\eta^2$  – ligands: Allylic and  $\eta^4$ - complexes of cyclopentadiene. Synthesis and structure.  $\eta^4$  –ligands: Butadiene, cyclobutadiene,  $\eta^2$  – complexes of cyclopentadiene, fullvalene, heterocyclic pentadiene, cyclic dienes and polymers (e.g. eynes hexadiences, 1,3-cycloheptadienes, Boron containing ligands).  $\eta^5$ - Hexadienyl, cyclopentadienyls, carboranes, metallo carboranes – synthesis and structure, MO treatment of ferrocene.  $\eta^6$  – ligands: Benzene and its derivatives, MO treatment of  $\eta^6$  – complex of cycloheptadiene and cyclooctadiene. Multidecker sandwich compounds. Homogeneous hydrogenation of unsaturated compounds, reversible cis-dihydrocatalysis, monohydrido compounds, asymmetrical hydrogenation, hydrosilation of unsaturated compounds, hydrocyanation of alkenes, alkane metathesis, Ziegler-Natta polymerization of ethylene and propylene, water gas shift reaction, acetic acid synthesis by carbonyls, Oxopalladation reactions

**Reaction at Coordinated ligands (5 Hrs):-**

The role of metal ions in the hydrolysis of amino acid esters, peptides, and amides Molecular orbital concept of role of metal ions participation, Modified aldol condensation, Imine formation, Template and Macrocyclic effect in detail.

***f*-acid ligands (15 Hrs.)**

$\pi$ - acceptor character of CO, O<sub>2</sub>, N<sub>2</sub>, NO, PH<sub>3</sub> molecules in terms of MOEL diagram, Metal carbonyls; structure and bonding; vibration spectra of metal carbonyls for bonding and structural elucidation, important reactions of metal carbonyls; preparation, bonding structure and important reactions of transition metal nitrosyl, dinitrogen and dioxygen complexes; tertiary phosphine as ligand.

**Books Recommended:**

1. C. Elschenbroich and A. Salzer, Organometallics: A Concise Introduction, 2<sup>nd</sup> Ed., VCH 1992.
2. J.E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, Harper Interscience.
3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Ed. V & VI. Wiley Inter-science.
4. G. L. Miessler, D. A. Tarr, Inorganic Chemistry, 3<sup>rd</sup> edition, Pearson Education

**COURSE-IX**  
**Organic Reaction Mechanism - II**

**45 hrs.****Max. Marks: 50****Time: 3 hrs.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**1. Free Radical Reactions (6 Hrs)**

Types of free radical reactions, free radical substitution mechanism. Mechanism at an aromatic substrate, neighbouring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. Reactivity in the attacking radicals. Effect of solvents on reactivity. Allylic halogenation (NBS), oxidation of aldehydes to acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts. Sandmeyer reaction, Free radical rearrangement, Hunsdiecker reaction, Kolbe reaction, Hydroxylation of aromatics by Fenton's reagent.

**2 Elimination Reactions (5 Hrs)**

The E2, E1, E1cB mechanisms. Orientation of the double bond. Effects of substrate structure, attacking base, leaving group and medium on reactivity. Mechanism and orientation in pyrolytic eliminations.

**3. Addition to Carbon – Carbon Multiple Bonds (8 Hrs)**

Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regio and chemoselectivity, orientation and reactivity. Addition to cyclopropane ring. Hydroboration, Michael reaction. Sharpless asymmetric epoxidation, Hydrogenation of double and triple bonds. Hydrogenation of aromatic rings.

**4. Addition to Carbon – Hetero Multiple Bonds (8 Hrs)**

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Wittig reaction. Mechanism of condensation reactions involving enolates – Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions, Reformatski reaction.

**5. Formation of Carbon-carbon Bond (8 Hrs)**

Principle, disconnections and synthons, electrophilic and nucleophilic carbon species. Base-catalyzed condensations; Aldol condensation, Claisen reaction, Perkin reaction, Stobbe condensation, Darzen condensation, Knoevengal reaction, Use of malonic, acetoacetic and cyanoacetic esters, Micheal addition, Wittig reactions. Use of acetylides, Acid-catalyzed condensation – self condensation of olefins, Friedal-Craft's reactions, Fries reactions, Mannich reaction, Mannich bases as intermediates in organic synthesis. Four centre reactions. Diels-Alder reaction, 1-3 Dipolar additions.

**6. Oxidation (5 Hrs)**

Introduction. Different oxidative processes. Hydrocarbons - alkenes, aromatic rings, saturated C-H groups (activated and unactivated). Alcohols, diols, aldehydes, ketones, ketals and carboxylic acids. Amines, hydrazines, and sulphides. Oxidations with ruthenium tetroxide, iodobenzene diacetate and thallium(III) nitrate.

**7. Reduction (5 Hrs)**

Introduction . Different reductive processes. Hydrocarbons - alkanes, alkenes, alkynes and aromatic rings. Carbonyl compounds – aldehydes, ketones, acids and their derivatives. Epoxides. Nitro, nitroso, azo and oxime groups. Hydrogenolysis.

**Books Recommended:**

1. Principles of Organic Synthesis – Norman and Coxon
2. Advanced Organic Chemistry – Jerry March.
3. Advanced Organic Chemistry, F.A. Carey, R.J. Sunberg.
4. Highlights of Organic Chemistry, W, J.L. Nobel; An Advanced Text Book.
5. Hand Book of Reagents for Organic Synthesis - Oxidizing and Reducing Reagents. S. D. Burke and R. L. Danheiser (John Wiley and Sons)
6. Organic Synthetic reactions by William Carruthers

**COURSE-X**  
**Physical Chemistry – Quantum Chemistry**

**45 hrs.****Max. Marks: 50****Time: 3 hrs.****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**1. Quantum Theory: Introduction and Principles (18 Hrs):**

Black body radiations, Planck's radiation law, photoelectric effect, Compton effect, De-Broglie hypothesis, the Heisenberg's uncertainty principle, Rydberg relation for explaining atomic spectrum of hydrogen. Bohr's Theory and its limitation solution of classical wave equation by separation of variables method, operators and observations, normal and orthogonal functions, hermitian and unitary operators, introduction to differentiation and integration, Eigen value equation. Hamiltonian operator, interpretation of wave function, postulates of quantum mechanics.

**2. Applications of Quantum Postulates (8 Hrs.)**

Solution of particle in one and three dimensional box, degeneracy, the linear harmonic oscillator, rigid rotators, quantization of vibrational and rotational energy levels, hydrogen and hydrogen like atoms.

**3. Angular Momentum (5 Hrs.)**

Commutative laws, need of polar coordinates, transformation of Cartesian coordinate into polar coordinate, angular momentum of one particle system, orbital angular momentum, the ladder operator method for angular momentum, spin angular momentum and their relations

**4. General Orbital Theory of Conjugated Systems (8 Hrs.)**

Chemical bonding, linear combination of atomic orbital, overlap integral, Coulomb's integral, bond order, charge density calculations for ethylene, allyl system, butadiene system, cyclo butadiene cyclo propenyl system.

**5. The Approximate Methods (6 Hrs.):**

Need for approximation methods, Perturbation and Variation methods and their application to Helium atom.

**Books Suggested:**

1. Physical Chemistry, A Molecular Approach by MacQuarrie and Simon.
2. Quantum Chemistry, Ira N. Levine, Prentice Hall.
3. Quantum Chemistry, H. Eyring, Kimball and Walter.
4. Quantum Chemistry, Atkin.
5. Fundamentals of Quantum Chemistry, Anantharaman. R.

**Course-XI**  
**REACTION MECHANISMS AND METAL CLUSTERS**

**45 Hrs.****Time: 3 Hrs.****Max. Marks: 50****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 Marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 Marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 Marks.

**Reaction Mechanism of Transition Metal Complexes (25)**

Inert and labile complexes, mechanisms of substitution (dissociative, associative interchange mechanism, the conjugate mechanism, substitution in *trans* complexes, substitution in *cis* complexes, isomerism of chelate rings), *trans* effect, explanation for *trans* effect, Ligand replacement reactions of square planar and octahedral complexes: their factors and mechanism of substitution, orbital occupation mechanisms. Anation reaction, Metal carbonyl reactions species with 17 electrons. Electron transfer processes with mechanism, key ideas concerning electron transfer reactions between transition Metals. Cross reactions and thermodynamics. Marcus theory, its kinetics and applications. Doubly bridged inner sphere transfer and other electron transfer reactions. Two electron transfer, non-complementary reactions. Stereochemical nonrigidity of coordinate and organometallic compounds, trigonal bipyramid, system with six or more coordination number. Isomerization and racemization of trischelates, metal carbonyl scrambling.

**Metal-ligand Equilibria in Solution (5 Hrs.)**

Stepwise and overall formation constant and their interaction, trends in step wise constant, factors affecting the stability of metal complex with reference to the nature of metal ion and ligand chelate effect and its thermodynamic origin. Determination of binary formation constants by pH-meter, Job's method and spectrophotometry.

**Inorganic Rings, Chains and Metal Cluster (15 Hrs.)**

Borazines, Phosphazenes and other heterocyclic inorganic ring, systems, homocyclic inorganic systems, cages of P and S, oxides & sulphides, Higher boranes and carboranes, methods of classifying boranes, Molecular orbit view of chlorohydroborane ions and carboranes metallocarboranes, isopoly and heteropoly acids and salts; metal-metal bonds and bi-, tri-, tetra-, penta-, and hexanuclear clusters, electron counting schemes for HNCC's. Approaches to systematic cluster synthesis; mention of seven, eight and nine atom clusters. Isolobal analogy and examples of application of analogy.

**Books Recommended:**

1. K.P. Purcell and J. V. Kotz: Inorganic Chemistry W.B. Saunders Co. London, (1977).
2. G. L. Miessler, D. A. Tarr, Inorganic Chemistry, 3<sup>rd</sup> edition, Pearson Education.
3. F.A. Cotton & Wilkinson: Inorganic Chemistry V & VI Ed. Willy Eastern – (1999).
4. J.E. Huheey: Inorganic Chemistry III & IV Ed. Pearson Education Asia – (2002).

**Course–XII****SPECTROSCOPY – B: Techniques for Structure Elucidation of Inorganic Compounds****60 hrs.****Max. Marks: 75****Time: 3 hrs.****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 75 marks, each question will be of  $1\frac{1}{2}$  marks, total weightage being 15 marks.

**Section-B:** Twelve short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In paper having 75 marks, each question will be of  $4\frac{1}{2}$  marks, total weightage being 36 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In paper having 75 marks, each question will be of 12 marks, total weightage being 24 marks.

**Unit – I****Symmetry and Point Groups: (Book 2) (6 Hrs.)**

Definition of symmetry, symmetry elements, determination of point groups, introduction to use of character table in determining irreducible representation and symmetry of the atomic orbitals.

**Unit – II****Vibration and Rotation Spectroscopy: Infrared, Raman and Microwave (Book 2) (20 Hrs.)**

- Harmonic and Anharmonic oscillators, vibrational energies of diatomic molecules. Potential energy function for a chemical bond. Absorption of radiations by molecular vibration. Selection rules, force constant.

- Rotational energies of linear molecules. Rotational energy level populations, merits and demerits of microwave spectroscopy, rotational spectra of rigid, linear molecules, non-rigid rotators. Determination of moment of inertia and bond length from rotational spectra, relative intensities of spectral lines. Rotational spectra of non-linear molecules (brief mention), vibrations in polyatomic molecules. Effects giving rise to absorption bands. Group vibrations and limitations of group vibration concepts.

- Polarisation of light. Theories of Raman Effect, Merits and demerits of Raman spectroscopy. Pure rotational Raman spectra of linear molecules. Vibrational Raman spectra selection rules. Rule of mutual exclusion. Rotational Fine IR spectra, vibronic coupling.

- Sample handling. Factors affecting absorption frequencies. Interpretation and finger printing regions. Use of symmetry considerations to determine the number of active I.R. and Raman lines (character tables to be provided in the Examination). Applications of Raman and IR selection rules to the determination of Inorganic structure with special emphasis on:

- (i) Metal carbonyls.
- (ii)  $\text{NSF}_3$
- (iii) Geometrical isomerism – differentiation between Cis and trans.  $[\text{Co}(\text{bipy})_2\text{Cl}_2]\text{Cl}$ .
- (iv) Structures of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ , chlorocomplexes of mercury, cadmium and zinc and some octahedral complexes  $\text{ML}_6$  (eg.  $\text{SiF}_6^{2-}$ ,  $\text{PF}_5^-$ ,  $\text{SF}_6$ ).
- (v) Changes in the spectra of donor molecules upon coordination with special emphasis on N, N – dimethyl – acetamide and DMSO with  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  ions.  
I.R spectroscopy and modes of coordination of  $\text{SO}_4^{2-}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ .

### Unit – III

#### Photo Electron Spectroscopy (Book 1, 2 and 3) (6 Hrs.)

Introduction, excitation & ejection of electrons, electronic energy levels in atoms and molecules, Core level photoelectron spectroscopy, symmetry & molecular orbitals, valence electron photo electron spectroscopy, valence excitation spectroscopy. Dissociation, Predissociation, change of shape on excitation.

### Unit – IV

#### Electron Spin Resonance Spectroscopy (Book 1, 2, 3 and 5) (13 Hrs.)

Features of ESR spectra, measurement technique hyperfine coupling in isotropic system ( $\text{C}_5\text{H}_5$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_{14}\text{H}_{10}$ , biphenyl) Anisotropic splitting, Electron – electron interaction, Transition metal complexes g-value and factors affecting g-value, zero field splitting, Kramer's degeneracy, Rate of electron exchange, Application to p – benzenesemiquinone DPPH, pyrazine.  
Double resonance technique ENDOR, ELDOR.

### Unit – V

#### Nuclear Quadrupole Resonance Spectroscopy (Book 2) (6 Hrs.)

Introduction, effects of magnetic field on the spectra. Relationship between the electric field gradient and molecular structure. Interpretation of eQ, data, the effect of crystal lattice on the magnitude of eQ, double resonance technique, Application ( $\text{PCl}_4$ ,  $\text{PCl}_6$ ),  $\text{TeCl}_4$ ,  $\text{Na}^+\text{GaCl}_4^-$ , group 14 tetra halides,  $\text{R}_3\text{MgX}_2$

A) Polyhalide ion,  $\text{BrCN}$ ,  $\text{HIO}_3$  (1,2)

B) p-dichloro benzene, p-chloroaniline, haloalkanes and haloarenes.

### Unit – VI

#### Mossbauer Spectroscopy (Book 1,2,4,6) (9 Hrs.)

Introduction, principles, conditions of MB spectra, parameters from MB spectra. Isomer shift electric quadrupole interaction, magnetic interaction, use of additive partial quadrupole splittings to predict quadrupole coupling. Application of  $\{^{57}\text{Fe}$ ,  $^{119}\text{Sn}$ ,  $^{151}\text{Eu}$  compounds, to biological systems to surface study,  $\text{I}_2\text{Cl}_6$ ,  $\text{IBr}_2\text{Cl}_4$ ,  $\text{XeF}_4$ ,  $\text{XeCl}_4$ .

**Books Recommended:**

1. E.A.V Ebsworth; W.H Renkin; Cradock, Structure Methods in Inorganic Chemistry.
2. R.S Drago, Physical Methods for Chemists (Ist and IInd Edition).
3. C.N Banwell, Fundamentals of Molecular Spectroscopy.
4. S. Walker and H. Straugh an Spectroscopy, Vol.I.
5. J.E. Wertz & J.R. Bolton, Electron Spin Resonance (p.49-65).
6. N.N. Greenwood & T.C Tibb, Mossbauer Spectroscopy.
7. K. Nakamoto, Infrared Spectra of Inorganic and co-ordination Compounds.

**Course – XIII**  
**MATHEMATICS FOR CHEMISTS**  
**(For Medical Students)**

30 hrs.

Time: 2 Hrs.

Max. Marks: 25

**Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions will be compulsory. Each question will be of  $1/2$  Mark (Total 5 Marks).

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. Each question carries  $1\frac{1}{2}$  Mark (Total 12 Marks).

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. Each question carries 4 Marks (Total 8 Marks).

**1. Trigonometry (7 Hrs.)**

Definition of sin, cos, tan, cot, sec, cosec functions with the help of unit circle, values of  $\sin x$ ,  $\cos x$ ,  $\tan x$  for  $x = 0, \pi/6, \pi/3, \pi/2$ . Meaning of a trigonometrical identity. The following identities (no need of derivation and proof. However, application has to be emphasized).

$$\cos^2 x + \sin^2 x = 1$$

$$\sin(x - 2\pi) = \sin x; \sin^2 x = 1 - \cos^2 x$$

$$\cos(x - 2\pi) = \cos x$$

$$\cos(-x) = \cos x; \sin(-x) = -\sin x$$

$$\sin(\pi - x) = \sin x; \cos(\pi - x) = -\cos x$$

$$\sin(\pi + x) = -\sin x; \cos(\pi + x) = -\cos x$$

$$\sin 2x = 2 \sin x \cos x$$

$$\cos 2x = 2 \cos x \cos x - 1$$

$$\cos 2x = 2 \cos^2 x - 1$$

$$\tan(x) = \frac{\sin x}{\cos x}$$

$$\tan(x) = \frac{\sin(x/2)}{\cos(x/2)} = \cot(x)$$

$$\tan(\pi - x) = -\tan x$$

$$\tan 2x = \frac{2 \tan x}{1 - \tan^2 x}$$

**2. Determinants and Matrices: (5 Hrs.)**

Definition and expansion properties of determinants, product of two determinants of  $3^{\text{rd}}$  order.

Introduction to various terms Matrix, row, column, diagonal unit. Sub, square, equal matrices, null, symmetric, order of, character of, transpose of, adjoint of, inverse of matrices. Addition multiplication, diagonalization, similarity transformation of matrices, characteristic equation statement of Cayley Hamilton theorem. Rank of matrix, condition of consistency of a system of linear equations. Eigen vectors and Eigen values using matrices.

**3. Differential Calculus 1 (8 Hrs.)**

Differentiation of standard functions, theorems relating to the derivative of the sum, difference, product and quotient of functions, derivative of trigonometric functions, inverse trigonometric functions, logarithmic functions and exponential functions, differentiation of implicit functions, logarithmic differentiation.

**4. Integral Calculus (10 Hrs.)**

Integration as an inverse of differentiation summation, area under a curve, indefinite integrals of standard forms, method of substitution, method of partial fractions, integration by parts, definite integrals, reduction formulae, definite integrals of limit of a sum and geometrical interpretation.

**Books Recommended:**

1. Santi Narayan – Differential Calculus.
2. Santi Narayan - Integral Calculus.
3. B.S. Grewal – Higher Engineering Mathematics.
4. Joseph B. Dence – Mathematical Techniques in Chemistry.
5. Margenau and Murphy, the Mathematics of Physics and Chemistry.
6. B.L. Moncha and H.R. Choudhary – A Text Book of Engineering Mathematics.

**Course – XIII**  
**BIOLOGY FOR CHEMISTS**  
**(For Non-Medical Students)**

**30 hrs.**

**Time: 2 Hrs.**

**Max. Marks: 25**

**Note 1: The students are allowed to use Non-Programmable Calculator.**

**2: The question paper will consist of three sections as under:**

**Section A:** It will consist of ten questions compulsory. Each question carry  $\frac{1}{2}$  mark (total 5 Marks).

**Section B:** Candidates will be required to attempt any eight out of the given twelve questions. Each question carry  $1\frac{1}{2}$  marks (total 12 marks).

**Section C:** Candidates will be required to attempt any two out of the given four questions. Each question carry 4 marks (total 8 marks).

**The Organisation of Life (10 hrs.):**

1. Biologically important molecules: Carbohydrates, lipids, proteins and nucleic acids.
2. The life of cells – The cell theory, general characteristics of cells, difference between prokaryotic and eukaryotic cells, difference between plant and animal cells, cell organelles.
3. Tissues, organs and organ systems: Animal tissues; epithelial tissues, connective tissues, muscle tissue, nervous tissue and neoplasias; plant tissue: meristematic tissue, permanent tissues.

**Genetics (10 hrs.):**

4. The basic principle of heredity: Mendel's law, monohybrid cross, dihybrid cross.
5. DNA – Double helix structure and replication.
6. Genes expression: Transcription and translation, genetic code.

**The Diversity of Life (10 hrs.)**

7. The classification of Living things – Criteria of classification, Whittaker's systems of classification, their characteristics with an example of each.
8. Viruses, structure of Viruses.

**Book Recommended:**

1. Cord Biology - South Western Educational Publications, Texas, 2000.

**COURSE XIV**  
**ORGANIC CHEMISTRY (PRACTICAL)**

**Hrs: 60****Max. Marks: 75****Multistep Organic Synthesis**

1. Synthesis of 2-chloro-4-bromoaniline from aniline (Bromination and chlorination) Book 1, page 292.
2. Synthesis of methyl orange from aniline.  
(Aromatic electrophilic substitution and diazocoupling). Book 2, page 250.
3. Synthesis of benzpinacol and its pinacol rearrangement.
4. Synthesis of o-chlorobenzoic acid from phthalimide. Synthesis of acridone from o-chlorobenzoic acid. (Hofmann bromamide and Sandmeyer's reaction).
5. Synthesis of 2,4-dinitrophenyl hydrazine from chloro benzene. (Electrophilic and nucleophilic substitution reactions on aromatic ring).
6. Synthesis of triphenylcarbinol from bromobenzene. (Grignard reaction) Book 2, page 220.

**B: Quantitative Analysis of Organic Compounds:**

1. Estimation of phenol/aniline using bromate-bromide solution.  
(The application to find the purity of the sample and to determine the amount in given solution).
2. Determine the number of hydroxyl and amino groups in the given sample by the acetylation method.
3. Determine the mol. wt. of the given ketone by using 2,4-DNP method.
4. Estimation of reducing sugar by Fehling solution method.
5. To determine the saponification value of the given fat or oil sample.
6. To determine the iodine number of the given fat or oil sample.

**Books Recommended:**

1. An Introduction to Modern Experimental Organic Chemistry, R. M. Roberts, J. C. Gilbert, L.B.Rodewald and A. S. Wingrove Holt, Ranehart and Winston Inc. New York.
2. Introduction to Organic Laboratory Techniques – A Contemporary Approach. D. L. Pavia, G. M. Lampmana and G. S. Kriz, W. B. Saunders Company, 1976.
3. Laboratory Experiments in Organic Chemistry, R. Adams, J. R. Johnson and C. F. Wilcox. The Macmillan Limited, London.
4. Text Book of Practical Organic Chemistry, A. I. Vogel.

**COURSE-XV**  
**Physical Chemistry (Practical)**

**Hrs: 60****Max. Marks: 75**

1. To determine the strength of given acid by  $pH$  metrically.
2. To determine dissociation constant of given acid  $pH$  metrically
3. Titration of weak acid conductometrically
4. Titration of strong acid conductometrically
5. To determine dissociation constant of given acid conductometrically
6. Determine the dissociation constant of acetic acid in DMSO, DMF, dioxane by titrating it with KOH.
7. Determine the activity coefficient of an electrolyte at different molalities by e.m.f. measurements.
8. Compare the cleansing powers of samples of two detergents from surface tension measurements.
9. Determine the specific refraction, molar refraction and atomic parachor with the help of Abbe's refractometer.
10. To study the distribution of benzoic acid between benzene and water.
11. Determine the equilibrium constant of reaction  $KI + I_2 \rightarrow KI_3$  by distribution law and hence find the value of  $G_o$  of the above reaction
12. Compare the relative strength of  $CH_3COOH$  and  $ClCH_2COOH$  from conductance measurements.
13. Determine the solubility (g/litre) of sparingly soluble lead sulphate from conductance measurements.
14. Titrate a given mixture of HCl and  $CH_3COOH$  against NaOH solution conductometrically..
15. Compare the relative strength of:
  - i) HCl and ii)  $H_2SO_4$  by following the kinetics of inversion of cane sugar polarimetrically.

**Course –XVI**  
**BIO-INORGANIC CHEMISTRY**

**45 Hrs.****Time: 3 Hrs.****Max. Marks: 50****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about 1/3<sup>rd</sup> of a page. All questions are compulsory. In paper having 50 marks, each question will be of 1 mark, total weightage being 10 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 50 marks, each question will be of three marks, total weightage being 24 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 50 marks, each question will be of 8 marks, total weightage being 16 marks.

**Metal Ions in Biological Systems-** Essential and trace elements, periodic survey of essential and trace elements, biological importance and relative abundance, Na<sup>+</sup>/ K<sup>+</sup> ion pump.

**Transport and Storage of Dioxygen-** Oxygen carriers-Hb and Mb: Structure and mechanism of their function, cooperativity, inhibition and poisoning by ligands and metal ions, hemocyanins and hemerythrin, model complexes of iron, cobalt and copper.

**Bioenergetics and ATP Cycle-** Process concept to phosphate hydrolysis, Nucleotide transfer-DNA polymerase, phosphate transfer pyruvate kinase, phosphoglucomutase, creatine kinase, ATPase. Photosynthesis and respiration – chlorophyll : structure, function and its synthetic model.

**Bioredox Agents and Mechanism-** Enzymes and their functioning, Vitamin B<sub>12</sub> coenzyme, its function and application in organic syntheses, intake of alcohol and its remedy.

**Biochemistry of Iron-** Availability of iron, competition for iron, iron toxicity and nutrition.

**Electron Transfer in Biology-** Cytochromes-structure and function, CN<sup>-</sup> and CO poisoning, Ferredoxin and rubredoxin.

**Nitrogenase-** Biological N<sub>2</sub> fixation, molybdenum nitrogenase, spectroscopic and other evidence, other nitrogenases model systems.

**Metal Storage, Transport-** Ferritin, transferring and siderophores.

**Metalloenzymes-** Zinc enzymes-carboxypeptidase and carbonic anhydrase, Copper enzymes-superoxide dismutase.

**Calcium in Biology-** Calcium in living cell, transport and regulation, molecular aspects of intramolecular processes,

**Metals in Medicine-** Metal deficiency and disease, toxic effects of antibiotics and related compounds, chelate therapy.

**Books Recommended:**

1. Principles of Bioinorganic Chemistry, S. J. Lippard and Berg, University Science Books.
2. Inorganic Biochemistry, Vol I and II. Ed. G. L. Eichhorn, Elsevier.
3. J.E. Huheey : Inorganic Chemistry III & IV Ed. Pearson Education Asia – (2002).
4. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5<sup>th</sup> Edition.
5. Progress in Inorganic Chemistry, Vols 18 and 38 Ed. J. J. Lippard, Wiley

**COURSE-XVII**  
**ORGANIC SYNTHESIS**

**45 hrs.**

**Time: 3 Hrs.**

**Max. Marks 50**

**Instruction for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about 1/3<sup>rd</sup> of a page. All questions will be of 1 mark.

**Section-B:** 12 short question answers are to be set. Eight questions are to be attempted.

Maximum length of answer can be up to 2 pages. Each question will be of 3 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. Maximum length of answer can be up to of 5 pages. Each question carries 8 marks.

**1. Rearrangements (10 Hrs)**

General mechanistic considerations – nature of migration, migratory aptitude, memory effects. A detailed study of the following rearrangements: Pinacol-pinacolone, Wagner-Merwein, Demjanov, Benzil-Benzilic acid, Favorskii, Arndt-Eistert synthesis, Neber, Beckmann, Hofmann, Curtius, Schmidt, Baeyer-Villiger, Shapiro reaction.

**2. Polynuclear Compounds & Macro-Ring Compounds (5)**

Introduction, comparative study of aromatic character of Linear and non-Linear-ortho-fused polynuclear hydrocarbons, ortho-and peri-fused polynuclear hydrocarbons. General method of preparation and reactions of indene, fluorene anthracene and phenanthrene. Modern methods of synthesis of macro ring compounds-civiton, muscone and catenoids.

**3. Heterocyclic Synthesis (3 Hrs)**

Principles of heterocyclic synthesis involving cyclization reactions and cycloaddition reaction.

**4. Small Ring Heterocycles (3 Hrs)**

Three-membered and four-membered heterocyclic –synthesis and reactions of aziridines, oxiranes, thiiranes, azetidines, oxetanes and thietanes

**5. Six-Membered Heterocycles with one Heteroatom (5 Hrs)**

Synthesis and reactions of pyrylium salts and pyrones and their comparison with pyridinium & thiopyrylium salts and pyridones.

Synthesis and reactions of quinolizinium and benzopyrylium salts, coumarins and chromones.

**6. Seven-and Large-Membered Heterocycles (4 Hrs)**

Synthesis and reactions of azepines, oxepines, thiepinines, diazepines, thiazepines, azocines, diazocines, dioxocines and dithiocines.

**7. Reagents in Organic Synthesis (10 Hrs)** Use of the following reagents in organic synthesis and functional group transformations; Complex metal hydrides, Gilman's reagent, lithium dimethylcuprate, lithium diisopropylamide (LDA) dicyclohexylcarbodiimide. 1,3-Dithiane (reactivity umpolung), trimethylsilyl iodide, tri-n-butyltin hydride, Woodward and Prevost hydroxylation, osmium tetroxide, DDQ, selenium dioxide, phase transfer catalysts, crown ethers and Merrifield resin, Peterson's synthesis, Wilkinson's catalyst, Baker yeast.

**8. Supramolecular Chemistry (5 Hrs)**

Principles of molecular association and organization as exemplified in biological macromolecules like enzymes, nucleic acids, membranes and model systems like micelles and vesicles. Molecular receptors and design principles. Cryptands, cyclophanes, calixarenes, cyclodextrins, Supramolecular reactivity and catalysis.

Role of bond length, inter-bond angles, force constant, bond and molecular dipole moments, Molecular and bond polarizability, bond dissociation enthalpy, entropy, intermolecular forces, hydrophobic effects, electrostatic, induction, dispersion, resonance energy and hydrogen bond in elaboration of above process.

**Books Recommended:**

1. Heterocyclic Chemistry – Acheson.
2. Organic Chemistry – Jerry March
3. Advanced Organic Chemistry, F.R. Carey, R.J. Sunberg.
4. Highlights of Organic Chemistry, W.J.L. Nobel; An Advanced Text Book.

**COURSE-XVIII**  
**SURFACE AND POLYMER CHEMISTRY**

45 hrs.

Max. Marks: 50

Time: 3 hrs.

**Instruction for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions will be of 1 mark.

**Section-B:** 12 short question answers are to be set. Eight questions are to be attempted.

Maximum length of answer can be up to 2 pages. Each question will be of 3 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. Maximum length of answer can be up to of 5 pages. Each question carries 8 marks.

**1. Adsorption (Hrs 10)**

Surface tension, capillary action, pressure difference across curved surface (Laplace equations), vapor pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, estimation of surface area (BET equation), surface films on liquids (Electro-kinetic phenomena), catalytic activity at surfaces.

**2. Micelles (Hrs 8)**

Surface active agents, classification of surface active agents, micellization, hydrophobic interactions, critical micellar concentration (CMC), factors affecting CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization – phase separation and mass action models, solubilization, micro emulsion, reverse micelles.

**3. Macromolecules (Hrs 27)**

**(a) Polymer** – definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization, thermodynamics of polymerization.

Molecular mass, number and mass average molecular mass, molecular mass determination (osmometry, viscometry, diffusion and light scattering methods), sedimentation, chain configuration of macromolecules, calculations of average dimensions of various chain structures.

Importance of polymers, Basic concepts: monomers, repeat units, degree of polymerization. Linear, branched and network polymers. Classification of polymers. Polymerization: condensation, addition, radical chain-ionic and co-ordination and copolymerization. Polymerization conditions and polymer reactions. Polymerization in homogenous and heterogeneous systems. Number, weight and viscosity average weights.

**(b) Structure and Properties:**

Polymer structure and properties-crystalline melting point  $T_m$ -melting point of homogenous series, effect of chain flexibility and steric factors, entropy and heat of fusion. The glass transition temperature,  $T_g$ -Relationship between  $T_m$  and  $T_g$ , effects of molecular weight, diluents, chemical structure, chain topology, branching and chain linking. Property requirements and polymer utilization.

**Books Suggested:**

1. Physical Chemistry, P. W. Atkins.
2. Textbook of polymer science, F. W. Billmeyer Jr. Wiley.
3. Polymer science, V. R. Gowariker, N. V. Viswanathan and J. Sreedhar, Wiley-Eastern.

**Course-XIX**  
**Electrochemistry and Chemical Dynamics**

**45 Hrs.****Max. Marks: 50****Time: 3 hrs.****Instruction for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions will be of 1 mark.

**Section-B:** 12 short question answers are to be set. Eight questions are to be attempted. Maximum length of answer can be up to 2 pages. Each question will be of 3 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. Maximum length of answer can be up to of 5 pages. Each question carries 8 marks.

**Electrochemistry (15 Hrs.)**

Electrochemistry of solutions, Debye-Huckel-Onsager treatment and its extension, ion-solvent interactions, Debye-Huckel-Bjerrum mode, Thermodynamics of electrified interface equation, Derivation of electro-capillarity, Lipmann equation(surface excess), method of determination, structure of electrified interfaces, Guoy-Chpmann, Stern models, overpotential, exchange current density, derivation of Butler-Volmer equation, Tafel plot.

Semiconductor interface theory of double layer at semiconductor electrolyte solution interface, structure of double layer interfaces, effect of light at semiconductor solution interface.

Introduction to corrosion, homogeneous theory, forms of corrosion, corrosion monitoring and prevention

**Chemical Dynamics (18 Hrs.)**

Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius theory and activated complex theory, ionic reactions, kinetic salt effects,, treatment of uni molecular reactions, Lindemann-Hinshelwood theory.

Dynamic Chain (hydrogen bromine reaction, pyrolysis of acetaldehyde, decomposition of ethane), Photochemical reactions between hydrogen-bromine and hydrogen-chlorine, oscillatory reactions (Belousov-Zhabotinsky reactions), Homogeneous catalysis and kinetics of enzyme reactions, general features of fast reactions, study of fast reactions by flow method, , relaxation method, flash photolysis, nuclear resonance.

**Voltmometry and Polarography (12 Hrs.)**

Polarography, polarographic cells, polarogram, interpretation of polarographic waves, equation for the polarographic waves, effect of complex formation on polarographic wave, polarograms for irreversible reactions, dropping mercury electrode, current variations during life time of a drop, merits and demerits of dme, polarographic diffusion currents, Ilkovic equation, capillary characteristics, temperature, polarograms for mixture of reactants, anodic and cathodic waves, factors affecting polarographic currents, applications of polarography, treatment of data, organic and inorganic polarographic analysis, voltammetry at solid electrodes, cyclic voltammetry and interpretation of data, , pilot-ion and standard addition method for quantitative analysis

**Books Recommended:**

1. Chemical Kinetics, K. J. Laddler, McGraw-Hill
2. Modern Electrochemistry Vol.1,2,3, J. Bochriss and A.K.N. Reddy
3. Fundamentals of electrochemistry; P. Monk
4. Principles of Instrumental Analysis; Skoog, West; Saundres Publications

**COURSE-XX**  
**PHOTOCHEMISTRY AND PERICYCLIC REACTIONS**

**45 Hrs****Time: 3 Hrs.****Max. Marks 50****Instruction for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions will be of 1 mark.

**Section-B:** 12 short question answers are to be set. Eight questions are to be attempted.

Maximum length of answer can be up to 2 pages. Each question will be of 3 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. Maximum length of answer can be up to of 5 pages. Each question carries 8 marks.

**1. Pericyclic Reactions (15 Hrs)**

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene, allyl system, classification of pericyclic reactions FMO approach. Woodward-Hoffmann correlation diagrams method and Perturbation of molecular orbital (PMC) approach for the explanation of pericyclic reactions under thermal and photo-chemical conditions.

Electrocyclic reactions – conrotatory and disrotatory motions,  $4n$ ,  $4n+2$ , allyl systems secondary effects. Cycloadditions – antarafacial and suprafacial additions, notation of cycloadditions ( $4n$ ) and ( $4n+2$ ) systems with a greater emphasis on (2+2) and (4+2) cycloaddition-stereochemical effects and effects of substituents on the rates of cycloadditions, 1,3-dipolar cyclo-additions and cheletropic reactions.

Sigmatropic Rearrangements-suprafacial and antarafacial shifts [1,2]- sigmatropic shifts involving carbon moieties retention and inversion of configuration, (3,3) and (5,5) sigma-tropic rearrangements, detailed treatment of Claisen and Cope rearrangements, fluxional tautomerism, aza-cope rearrangements, introductions to Ene reactions, simple problems on pericyclic reactions. Electrocyclic rearrangement of cyclobutenes and 1,3 cyclohexadienes.

**2. Photochemistry****(i) Photochemical Reactions (4 Hrs.)**

Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry.

**(ii) Determination of Reaction Mechanism (4 Hrs.)**

Classification, rate constants and life times of reactive energy states –determination of rate constants of reactions. Effect of light intensity on the rate of photochemical reactions. Types of photochemical reactions – photodissociation, gas-phase photolysis.

**(iii) Photochemistry of Alkenes (6 Hrs.)**

Intramolecular reactions of the olefinic bond – geometrical isomerism, cyclisation reactions, rearrangement of 1,4- and 1, - dienes.

**(iv) Photochemistry of Carbonyl Compounds (8 Hrs.)**

Intramolecular reactions of carbonyl compounds – saturated, cyclic and acyclic,  $\alpha,\beta$ -unsaturated and  $\alpha,\gamma,\delta$ -unsaturated compounds, Cyclohexadienones. Intermolecular cycloaddition reactions – dimerisations and oxetane formation.

**(v) Photochemistry of Aromatic Compounds (4 Hrs.)**

Isomerisations, additions and substitutions.

**(vi) Miscellaneous Photochemical Reactions (4 Hrs)**

Photo-Fries reactions of anilides. Photo-Fries rearrangement. Barton reaction. Singlet molecular oxygen reactions. Photochemical formation of smog. Photodegradation of polymers. Photochemistry of vision.

**Books Recommended:**

1. Organic Photochemistry – Chapman and Depuy.
2. Organic Photochemistry – W.H. Horsepool.
3. Photochemistry of Excited States – J.D.Goyle.

**COURSE-XXI**  
**Inorganic Chemistry (Practical)**  
**(Preparations)**

**Time: 6 Hours****Course Hrs. 60****(Any 8 Complexes.)****Max. Marks: 50**

1. Preparation of  $\text{Co}(\text{acac})_3$ , its characterization using NMR, IR, UV-Vis and analysis of Cobalt. (ref. J. Chem. Edu., 1980, 57, 7, 525)
2. Preparation of  $\text{Co}(\text{acac-NO}_2)_3$ , its characterization using NMR, IR, UV-Vis and analysis of Cobalt. (ref. J. Chem. Edu., 1980, 57, 7, 525)
3. Preparation of  $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{N-salicyldeneglycinato})_2]_2 \cdot 3\text{H}_2\text{O}$ , its characterization using IR, UV-Vis, magnetic susceptibility and analysis of Iron. (ref. Inorganica Chimica Acta, 1977, 23, 35).
4. Preparation of  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  its characterization using IR, UV-Vis, magnetic susceptibility and analysis of Nickel and  $\text{NH}_3$ . (ref. Marr and Rockett, 1972).
5. Preparation of  $[\text{Ni}(\text{ethylenediamine})_3]\text{Cl}_2$  its characterization using IR, UV-Vis, magnetic susceptibility and analysis of Nickel. (ref. Marr and Rockett, 1972, page 270).
6. Preparation of  $[\text{Fe}(\text{NO})(\text{S}_2\text{CN}(\text{Et})_2)_2]$  its characterization using IR, UV-Vis, magnetic susceptibility and analysis of Fe(II). (ref. Marr and Rockett, 1972, page 262, J. Chem. Soc. 1962, 84, 3404).
7. Preparation of octahedral and tetrahedral complexes of dichlorodipyridylcobalt(II), differentiate them using IR, UV and magnetic properties. Estimate Co(II) from one of them. (ref. Marr and Rockett, 1972, page 375, Inorganic Chemistry, 1966, 5, 615).
8. Preparation of  $\text{VO}(\text{acac})_2$  and its piperidine complex, characterize using IR, UV and magnetic moment. Estimate for V(IV). (ref. Marr and Rockett, 1972, 243).
9. Preparation of diaquotetraacetataocopper(II), magnetic susceptibility IR and UV-Vis, analysis of Copper(II).
10. Preparation of cis- and trans- potassium dioxalato diaquochromate(III). Interpretation of IR, UV and magnetic properties. Estimation of Chromium. (ref. Marr and Rockett, 1972, page 386).
11. Preparation of  $\text{HgCo}(\text{NCS})_4$ , its IR and measure its magnetic moment. (ref. Marr and Rockett, 1972, page 365).

12. Preparation of sodium tetrathionate, interpretation of its IR and analysis using potassium iodate. (ref. Marr and Rockett, 1972, page 214).
13. Preparation of Potassium dithionate, interpretation of its IR and analysis using potassium iodate. (ref. Marr and Rockett, 1972, page 214).
14. Preparation of bis(acetylacetonato)copper(II), UV-Vis, and IR, magnetic studies, Demonstration of Jahn Teller effect by solution spectral studies. (ref. Bull. Chem. Soc. Japan, 1965, 29, 852).
15. Preparation of salicylamide complexes of Copper(II). IR, UV, magnetic data and analysis of Cu(II). (ref. Indian J. of Chem., 1977, 15A, No. 5, 459; *ibid*, 1971, 9, 1396).
16. To prepare a macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo tetradeca-4,11-dienedi(hydrogeniodide) and its complex with Ni(II). Study IR, NMR and UV-Vis of ligand and complex and magnetic properties of complex. To analyze for Ni and I. (J. Chem. Edu. 1977, 79, 581).
17. Preparation and resolution of tris (ethylenediamine) cobalt (III). UV-Vis, NMR, IR, optical rotation of the resolved complexes. ((ref. Marr and Rockett, 1972, page 386).

**Recommended Book:**

1. B.N. Figgis, Introduction to Ligand Field, Wiley Eastern.
2. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier.
3. A.Earnshaw, Introduction to Magnetochemistry, Academic Press.
4. J.E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, Harper Interscience.
5. R.S. Drago, Physical Method in Chemistry, W.B.Saunders Company.
6. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Interscience.
7. F.A. Cotton, Chemical Application of Group Theory, Wiley Eastern.

**COURSE-XXII****PHYSICAL CHEMISTRY (PRACTICAL)****60 hrs.****M. Marks: 75**

1. To determine the partial molar volume of  
(a) Glycine (b) Urea using dilatometer
2. To determine the partial molar volume of  
(a) methanol (b) n-propanol using dilatometer
3. To determine the surface tension (double capillary) of mixture of solid and water by differential method and hence find out parachor of the mixture.
4. To determine the specific and molar refractivity of n-propanol, butanol, hexane and carbon tetrachloride and calculate refraction equivalents of C, H and Cl.
5. To determine the molar refractivity of water, DMF, Dioxane and mixtures of water, DMF, water-Dioxane and verify the refractivity rule. Predict about the interactions between components of mixture by plotting graph between refractive index and mole fraction.
6. To determine the equivalent conductance of weak electrolyte acetic at infinite dilution using Kohlrausch law.
7. Determine equivalent conductance of strong electrolyte at several concentrations and hence verify Onsager's equation.
8. Determine equivalent conductance of weak electrolyte, say, acetic acid at different concentrations and hence test validity of Ostwald's dilution law. Also determine dissociation constant of the electrolyte.
9. To determine dissociation constant of a dibasic acid potentiometrically.
10. To study complex formation between Fe(III) and salicylic acid and find out the formula of the complex spectrophotometrically.
11. To determine the formula of the complex ion formed between Fe(III) and Thiocyanate ion by Job's method.
12. To study the kinetics of hydrolysis of crystal violet spectrophotometrically.
13. To determine the pH of a buffer solution (pH less than 8) using a quinhydrone electrode.
14. To determine the pH of various mixtures of sodium acetate and acetic acid in aqueous solution and hence determine the dissociation constant of the acid.
15. Titrate potentiometrically Zn (II) by  $K_4Fe(CN)_6$  and verify the composition of the complex  $K_2Zn_3[Fe(CN)_6]_2$
16. Determination of nitrite in water spectrophotometrically.
17. Determination of molecular weight of polymers by Turbiditymetry.
18. Determine the molar refraction of a solid substance by dissolving it in a solvent and its refractive index.

**Course-XXIII****ADVANCED INORGANIC CHEMISTRY****60 Hrs.****Time: 3 Hrs.****Max. Marks: 75****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 75 marks, each question will be of  $1^{1/2}$  marks, total weightage being 15 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 75 marks, each question will be of  $4^{1/2}$  marks, total weightage being 36 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 75 marks, each question will be of 12 marks, total weightage being 24 marks.

**1. Photo Inorganic Chemistry (25) :**

Basics of photochemistry- Absorption, excitation, photochemical laws, quantum yield, electronically excited states, life times- measurements of the times Flash photolysis, energy dissipation by radiative and non-radiative processes, absorption spectra, Franck-Condon principle, photochemical stages-primary and secondary processes, Kashia's rule, Thexi state, Photo substitution reactions, Adamson's rules, Photo substitution reactions of Cr(III)-Polypyridyls, Rh(III) Ammine Complexes, Ru-Polypyridyl complexes, Ligand photo reactions, photoredox reactions, comparison of Fe(II) and Ru(II) complexes, Photo reactions and Solar energy conversions, Photo synthesis in plants and Bacterio chlorophyll photosynthesis, photolysis of water using Inorganic precursors.

**2. Oxidative-Addition and Migration (Insertion Reactions) (15 Hrs.):**

Introduction: Acid base behaviour of metal atoms in complexes, Protonation and Lewis Base behaviour, acceptor properties of Lewis acidity of complexes, oxidative addition and reductive elimination, addition of specific molecules, Hydrogen addition, HX additions, Organic halides addition of some other molecules productive elimination, migration (Insertion) reaction promotion of alkyl migration, insertion of CO into M-H bonds, other aspects of CO insertion reactions, transfer of other molecules,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ , RCM, Insertion of alkenes and C-C unsaturated compounds, Cleavage of C-H bonds; alkane activation, Cyclometallation reactions. Reactions of free hydrocarbons.

**3. Transition Metal Compounds with Bonds to Hydrogen (5Hrs.)**

Characteristics of hydride complexes, synthetic methods, chemical behaviour of hydride compounds, mononuclear polyhydrides, homoleptic polyhydride anions; carbonyl hydrides and anion. Molecular hydrogen compounds; metal hydrogen interaction with C-H bonds; MH interactions; complexes of boron hydride and aluminohydrides, synthetic applications of metal hydrides.

**Transition Metal Complexes in Catalysis (15 Hrs.):**

Hydroformylation of unsaturated compounds, Reductive carbonylation of alcohols and other compounds; Carbonylation Reaction: Methanol and methyl acetate, Adipic ester. Synthesis and other carbonylation reactions, decarbonylation reactions. Catalytic addition of molecules to C-C multiple bonds homogeneous hydrogenation, hydrocyanation of unsaturated compounds, hydrosilation of unsaturated compounds, hydrocyanation of alkenes, Polymerization, Oligomerisation and metathesis reactions of alkenes and alkynes, Ziegler-Natta polymerisation of ethylene and propylene oligomerisation and related reactions, Cluster compounds in catalysis, supported homogeneous and phase transfer catalysis, Oxidation reaction: Oxidative carbonylations, Palladium catalysed oxidation of ethylene, Acrylonitrile synthesis, oxygen transfer from peroxy- and oxo- species, oxygen transfer from NO<sub>2</sub> groups.

**Books Recommended:**

1. Concepts of Inorganic Photochemistry, A. W. Adamson and P. D. Fleischauer, Wiley.
2. W.W. Porterfield, Inorganic Chemistry: A Unified Approach..
3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5<sup>th</sup> ed., John Wiley & Sons, New York.
4. C. Elschenbroich and A. Salzer, Organometallics: A Concise Introduction, 2<sup>nd</sup> Ed., VCH 1992.

**Course-XXIV: NATURAL PRODUCTS****60 hrs.****Time: 3 Hrs.****Max. Marks: 75****Note: The candidates are allowed to use Non-Programmable Calculator.****Instructions for the paper setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 75 marks, each question will be of  $1^{1/2}$  marks, total weightage being 15 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 75 marks, each question will be of  $4^{1/2}$  marks, total weightage being 36 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 75 marks, each question will be of 12 marks, total weightage being 24 marks.

**1. Studies on Biosynthetic Pathways of Natural Products (10 Hrs.)**

a) The acetate hypothesis, poly-ketoacids, their addol type cyclisations and meta orientations of hydroxyl groups in naturally occurring phenols. b) Isoprene rule, mechanism of formation of mevalonic acid from acetyl coenzyme, Biogenetic isoprene rule. Geranyl pyrophosphates and its conversion into alphapinene, thujene and borneol. Farnesyl pyrophosphate, geranyl, geranyl pyrophosphate and mechanistic considerations for their interconversions into cadinene and abietic acid.

**2. Terpenoids: (5 hrs)**

General classification, General Methods of structure determination, Chemistry of Camphor, Abietic acid, Santonin biosynthetic studies on tri and tetra terpenoids.

**3. Steroids: (5 Hrs).**

General biosynthetic studies on steroids, chemistry of Cholesterol, cortisone, progesterone, oestrone, transformations in steroid molecules.

**4. Alkaloids: (5 Hrs)**

Classification, chemistry of nicotine, quinine, papaverine, morphine and reserpine.

**5. Haemin and Chlorophyll: (5 Hrs.)**

Structure and synthesis of Porphyrins. Chemistry of Haemin and chlorophyll.

**6. Antibiotics: (5 Hrs.)**

Introduction, chemistry of penicillins, streptomycines, chloromphenicol, tetracyclins.

**7. Prostaglandins: (3 Hrs.)**

General study, nomenclature, structure of PGE and synthesis of PGE<sub>1</sub>, PGE<sub>2</sub>, PGF<sub>2x</sub>

**8. Carbohydrates: (8 Hrs.)**

Nomenclature and classification, types of naturally occurring sugars, deoxy sugars, sugars, methyl ethers and acid derivatives of sugars. General methods of structure and ring size determination, structure of maltose, lactose, sucrose, starch and cellulose.

**9. Peptides and Proteins: (6 Hrs)**

Sequence determination insulin and oxytocin, Proteins: structure conformation and properties. Enzymes, Kinetics, inhibition mechanism.

**10. Nucleic Acids: (8 Hrs.)**

Nucleosides, nucleotides, DNA, RNA structure and conformation, Replication, transcription.

**Course XXV- Chemistry of Materials.****60 hrs.****Max. Marks: 75****Time: 3 hrs.****Note: The students are allowed to use Non-Programmable Calculator.****Instructions for the Paper Setters:**

**Section-A:** Ten very short answer type questions are to be set. The maximum length of the answer can be about  $1/3^{\text{rd}}$  of a page. All questions are compulsory. In paper having 75 marks, each question will be of  $1^{1/2}$  marks, total weightage being 15 marks.

**Section-B:** 12 short answer type questions are to be set. Eight questions are to be attempted. Maximum length of the answer can be upto 2 pages. In papers having 75 marks, each question will be of  $4^{1/2}$  marks, total weightage being 36 marks.

**Section-C:** Four questions are to be set. Two questions are to be attempted. In this section there will be descriptive questions, derivations, synthesis, structure and bonding, reactions and conversions etc. Maximum length of answer can be upto 5 pages. In papers having 75 marks, each question will be of 12 marks, total weightage being 24 marks.

**Solid State Chemistry (15)**

Types of solids, band and bond theories, crystal lattice energy, point defects in metals and ionic compounds, energy and entropy of defects, their concentration, diffusion and electrical conduction via defects, non stoichiometry types, colour centres and electrical properties of alkali halides, electron theories for metal conduction in metals, in insulators, impurity semi conductors, reactions in organic solids, photochemical reactions, solid-solid reactions, decomposition and dehydration reaction.

**Macromolecules (15)**

Types of polymers, regular and irregular polymers, synthesis of polymers by chain and step reactions, physical properties of solid polymers (crystallinity, plasticity and elasticity), vulcanization of rubbers, molecular mass determination by osmometry, viscometry, light scattering and ultracentrifuge methods, number and mass average molecular masses, polymer solutions, factors affecting the solubility of polymers, conducting polymers, doping of polymers, mechanism of conduction, polarons and bipolarons,

**Glasses and Ceramics (15)**

Factors affecting glass formation, oxide glasses, electronegativity and bond type, viscosity, structural effects (Zachariasen's rule (1932)), criteria of Sun and Rawson, thermodynamics of glass formation, behavior of liquids on cooling, kinetics of crystallization and glass formation, structure of glasses: vitreous silica, silicate glasses, vitreous  $B_2O_3$  and borate glasses, viscosity, electrical conductivity of glasses and the mixed alkali effect, commercial silicate and borate glasses, metallic glasses, glass ceramics, refractories, important glass-ceramics compositions, properties of glass ceramics, applications.

**Smart Materials (15)**

Methods of preparation- conventional ceramic methods, hot pressing and hot static pressing techniques, precursor method, gel method, co-precipitation method, glass crystallization methods, vacuum techniques- chemical vapor deposition method. , organic superconductors, , magnetism in organic materials, magnetic nano materials, energy storage materials, nano materials for targeted drug delivery,, fullerenes as superconductors.High temperature ceramic superconductors, electrical and magnetic properties of superconductors, critical temperature  $T_c$ , thermodynamics of superconductors, London equation, BCS theory, applications.

**Books Recommended:**

1. Principles of polymer chemistry—P J Flory Cornell University Press
2. Physical chemistry of polymers—A J Tager, Mir Publishers
3. Physical chemistry of Macromolecules\_\_Tanford
4. Handbook of conducting polymers—T A Skotthem
5. Solid state physics—A J Dekker- MacMillan Publishers
6. Solid state chemistry and its applications—A R West ,Wiley Publishers
7. Solid state chemistry of drugs S R Byrn Academic Press
8. Chemistry of solid state—W.E.Garner Butterworth
9. Principles of physical chemistry—Puri-Sharma-Pathania, Vishal Publishers
10. Thermotropic Liquid crystals Ed. G W Gray John Wiley
11. Chemistry of polymers, Margarison and East
12. Polymer Chemistry, Malcolm, P, Stevens, Oxford University Press
13. Principles of Solid States, H. V. Keer, Wiley Eastern.

**Advanced Practicals**  
**Organic Synthesis (Practical)**

**Course Hrs.: 90****Credit Hrs. 06****Max.Marks: 50****Pass Marks: 20**

1. Synthesis and Reactivity of benzalacetophenone
  - a. Bromination (Electrophilic additions) & subsequent debromination (Elimination)
  - b. Epoxidation (Cycloaddition, nucleophilic) and ring opening with hydroxide ion.
  - c. Michael addition of aniline.
  - d. Conversion of benzalacetophenone to its oxime (nucleophilic addition at C=O)
  - e. Conversion of oxime to amide (Beckmann rearrangement ) and oxazole (Understand the reactivities at conjugated C=O and C=C) bond.
2. Synthesis of Cyclohexene from cyclohexanol and its conversion to 1, 2- *cis* and 1, 2- *trans* – cyclohexanediols.
  - a. Epoxidation with peracid (Cycloaddition) and *anti*- ring opening with sodium hydroxide to *cis*- cyclohexane -1, 2- diol.
  - b. Dihydroxylation with KMnO<sub>4</sub> (Mechanism of *syn*- and *anti*-cyclohexane-1,2-diol)
3. Preparation and characterization of the Aldol-dehydration products from various combinations of aromatic aldehydes and ketone.  
Effect of substituents on aromatic aldehydes on the product distribution.
  - a. Aldehyde: benzaldehyde, 4-methylbenzaldehyde. 4-methoxybenzaldehyde.
  - b. Ketone: acetone, cyclopentanones, cyclohexanone (Book 4)6.

**Books:**

1. An Introduction to Modern Experimental Organic Chemistry, R.M. Roberts, J.C. Gilbert, L.B. Rodewald and A.S Wingrove, Holt Rinehart and Winston Inc, New York. 1969.
2. Vogel's Text Book of Practical Organic Chemistry.
3. Laboratory Experiments on Organic Chemistry, R. Edemas, J.R. Johnson and C.F. Wilcox, The Macmillan Limited, London, 1970.
4. Modern Projects and Experiments in Organic Chemistry, J.R. Mohrig, C.N. Hammonad, P.F. Schatz and T.C. Morrill, W.H. Freeman and Company, New York 2003.

**Advanced Practicals**  
**Inorganic Synthesis (Practical)**

**Course Hrs.: 90**  
**Credit Hrs. 06**

**M. Marks: 50**  
**Pass Marks: 20**

1. Preparation of pipertidien complex of Bis(2,4-pentanedionato) vanadium(IV) oxide,  $\text{VO}(\text{acac})_2$ .
  - a) Preparation of  $\text{VO}(\text{acac})_2$  and its characterization by IR spectroscopic technique.
  - b) Preparation of  $[\text{VO}(\text{acac})_2 \text{HNC}_5\text{H}_{10}]$  and its characterization by IR spectroscopic technique.
  - c) Discuss the nature of the V-O bond in  $\text{VO}(\text{acac})_2$ .
  - d) Compare the  $\nu(\text{VO})$  in  $\text{VO}(\text{acac})_2$  and  $[\text{VO}(\text{acac})_2 \text{HNC}_5\text{H}_{10}]$  complexes.
  - e) Measure the magnetic susceptibility of  $[\text{VO}(\text{acac})_2 \text{HNC}_5\text{H}_{10}]$  and calculate the magnetic moment.
  
2. Preparation of cis- and trans- Potassiumdioxalato diaquachromate(III),  $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ .
  - a) Prepare cis- and trans- isomers.
  - b) Record and interpret the electronic absorption spectra of the two isomers and assign the observed transitions.
  - c) Analyse any of the isomers for oxalate by titration against standardized permanganate.
  
3. Synthesis and characterization of the Ni(II) complex of a Schiff-base ligand derived from Salicylaldehyde and ethylenediamine.
  - a) Synthesis the Schiff-base ligand.
  - b) Interpret the  $^1\text{H}$  NMR and IR spectra of the ligand.
  - c) Synthesis the Ni(II) complex of the ligand and compare its IR spectrum with that of the ligand.
  
4. Separation of the metal cations by
  - a) Column chromatography with gradient elution Co(II) and Ni(II). Analyse qualitatively the colored fractions collected for separated cations.
  - b) Paper chromatography [Fe(II), Co(II), Ni(II) and Cu(II)]. Determine the  $R_f$  values for the separate standard cations and use these to identify the cations present in the unknown mixture.

**Book: Practical Inorganic Chemistry by Marr and Rockett.**

**Advanced Practicals**  
**Physical Chemistry (Practical)**

**Course Hrs.: 90**  
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**CHEMICAL EQUILIBRIUM**

1. Study the effect of solvent on the conductance of AgNO<sub>3</sub>/Acetic acid and determine the degree of dissociation and equilibrium constant in different solvents and their mixtures (DMSO, DMF, dioxane, acetone, and water) and test the validity of DEBYE-HUCKEL-ONSAGER'S equation.
2. To determine acid and base dissociation constant of amino acid pH metrically.
3. To calculate thermodynamic parameters,  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  for the reaction,  
 $\text{Zn} + \text{Hg}_2\text{SO}_4 \rightarrow 2\text{Hg} + \text{Zn SO}_4$  by emf measurement.

**CHEMICAL KINETICS**

4. Study the salt effects and the solvent effect on the rate law of alkaline hydrolysis of crystal violet.
5. Determine the degree of hydrolysis and hydrolysis constant of CH<sub>3</sub>COONa/NaCl/aniline hydrochloride.
6. Determine the order of reaction by analyzing the kinetic dependence of individual reactant (e.g. saponification of ester).
7. Determine the energy of activation for the reaction studied above.

**ACTIVITY AND ACTIVITY COEFFICIENTS**

8. Determination of mean activity coefficient of given electrolyte by cryoscopy.
9. Determine activity coefficients by EMF method.

**PHASE EQUILIBRIUM**

10. Draw the phase diagram for any one of the following three component partially immiscible liquid systems.  
i) DMSO/water/benzene    ii) water/benzene/acetic acid

**POLAROGRAPHIC TECHNIQUES**

11. Estimation of ions in mixture of Pb<sup>2+</sup> and Cd<sup>2+</sup> by successive reduction. Evaluate diffusion coefficient of Cd<sup>2+</sup>
12. Polarographic determination of Cu and Zn in the given sample of brass.
13. Determine stability constants of Cd<sup>2+</sup> with EDTA.

**SPECTROPHOTOMETRIC METHODS**

14. To study the effect of extended conjugation on the wave length of maximum absorption of organic compounds.

**ADSORPTION**

15. To determine the adsorption isotherms of heavy metals like Cd, Zn, Cr, Pb, Ni by using nonconventional adsorbents.

**TURBIDIMETRY**

16. To determine concentration of sulphate ions with the help of turbidity meter.
17. Determine the CMC by turbidimetric method.

**LEAST SQUARE FITTING**

18. To draw calibration curve for the concentration determination of potassium ions by flame photometry and to study the least square fitting of the data.