

**DEPARTMENT OF CHEMISTRY**  
**OSMANIA UNIVERSITY**  
 (Effective from academic year 2016-2017 for Campus and Constituent colleges  
*[UNDER CBCS Scheme]*)

**Semester I**

	<b>Hrs. /week internal assessment</b>		<b>Semester exam</b>	<b>Total</b>	<b>Credits</b>
CH101T (*)	4	20 marks	80 marks	100 marks	4
CH102T (*)	4	20 marks	80 marks	100 marks	4
CH103T (*)	4	20 marks	80 marks	100 marks	4
CH104T (*)	4	20 marks	80 marks	100 marks	4
CH151P (IC LAB*)	6			75 marks	3
CH152P (OC LAB*) (4h + 2T)				50 marks	2
CH153P (PC LAB*)	6			75 marks	3
<b>Total</b>				<b>600 marks</b>	<b>24</b>

(\*Core= compulsory papers common to all students admitted to M.Sc Chemistry, OU)

**Semester II**

	<b>Hrs. /week internal assessment</b>		<b>Semester exam</b>	<b>Total</b>	<b>Credits</b>
CH201T (*)	4	20 marks	80 marks	100 marks	4
CH202T (*)	4	20 marks	80 marks	100 marks	4
CH203T (*)	4	20 marks	80 marks	100 marks	4
CH204T (*)	4	20 marks	80 marks	100 marks	4
CH251P (IC LAB*)	6			75 marks	3
CH252P (OC LAB*)	6			75 marks	3
CH253P (PC LAB*) (4h + 2T)				50 marks	2
<b>Total</b>				<b>600 marks</b>	<b>24</b>

(\*= compulsory papers common to all students admitted to M.Sc Chemistry, OU)

**M.Sc CHEMISTRY SYLLABUS**  
(Effective from academic year 2016-2017 for Campus and Constituent colleges.)

**SEMESTER –I**

Semester-I and Semester-II syllabus is common for all specializations i.e., Inorganic-Analytical, Organic, Physical, Physical- Organic and Chemistry (Pharmacoinformatics).

**Paper 1 CH 101 (INORGANIC CHEMISTRY)**

IC 01: Symmetry of molecules

IC 02: Bonding in Metal Complexes - I

IC 03: Coordination equilibria

IC 04: Ligational aspects of diatomic molecules

Teaching hours-4/week

Marks-80

**IC-01: Symmetry of Molecules:**

**15 hrs**

Concept of Symmetry in Chemistry – Symmetry Operations – Symmetry Elements: Rotational Axis of Symmetry and Types of Rotational Axes, Plane of Symmetry and types of Planes, Improper Rotational Axis of Symmetry , Inversion Center and Identity Element – More about Symmetry Elements – Molecular Point Groups: Definition and Notation of Point Groups, Classification Molecules in to  $C_1$ ,  $C_s$ ,  $C_i$ ,  $C_n$ ,  $C_{nv}$ ,  $C_{nh}$ ,  $C_{\infty v}$ ,  $D_n$ ,  $D_{nh}$ ,  $D_{nd}$ ,  $D_{\infty h}$ ,  $S_n$  ( $n$ =even),  $T_d$ ,  $O_h$ ,  $I_h$ ,  $K_h$  Groups. Descent in Symmetry with Substitution – Exercises in Molecular Point Groups – Symmetry and Dipole moment – Symmetry criteria for Optical activity.

**IC – 02: Bonding in metal complexes – I:**

**15 hrs**

Crystal Field Theory: Salient features of CFT. d-orbital splitting patterns in regular Octahedral, tetragonally distorted octahedral, Jahn-Teller theorem , trigonal bipyramidal, trigonal planar, Pentagonal bipyramidal, and linear geometries. Concept of weak field and strong fields. - Calculation of crystal field stabilization energies (CFSE's) in six and four coordinate complexes.

Types of magnetic behaviour – magnetic susceptibility – calculation of magnetic moment from magnetic susceptibility spin only formula , - Quenching of orbital angular momentum – Determination of magnetic moment from Guoy's method.. Applications of magnetic moment data for the determination of oxidation states, bond type and stereochemistry. Spin crossover: High spin, low spin cross over phenomenon in  $[\text{Fe}(\text{Ophen})_2(\text{NCS})_2]$  and  $[\text{Fe}(\text{R}_2\text{NCS}_2)_3]$ . Spinels.

**IC-03: Coordination Equilibria:**

**15 hrs**

Solvation of metal ions- Metal complex formation in solution-Binary metal complexes. Stability constants (types and relationships between them). – Factors influencing the stability constants: (i) Metal ion effects (charge/size, IP, crystal field effect, John-Teller effect, Pearson theory of hard and soft acids and bases (HSAB), electronegativity and hardness and softness, symbiosis. (ii) Ligand effects (Basicity , Substituent effect , Steric , Chelate(size and number of chelate rings), Macrocyclic and Cryptate effects- crown ethers , crypton, size match selectivity or concept of hole size, limitations, Macrocycles with pendent groups– Methods used for the determination of Stability constants (Basic Principles only): pH metric, Spectrophotometric and Polarographic methods.

Ternary Metal Complexes – definition – Formation of ternary metal complexes – Step-wise and simultaneous equilibria with simple examples.

#### IC – 04: Ligational Aspects of Diatomic molecules

15 hrs

**Metal Carbonyls:-** Carbon monoxide as a ligand – Molecular orbitals of CO - Donor and Acceptor molecular orbitals of CO; Bonding modes of CO- Terminal and Bridging; Evidence for multiple bonding from Bond lengths and Stretching frequencies; 18 Valence electron rule and its application.

**Metal Nitrosyls:** - NO as a ligand – Molecular orbitals of NO – Donor and Acceptor components; Bonding modes of NO – Terminal (Linear, Bent) and Bridging; Structural aspects of  $[\text{IrCl}(\text{PPh}_3)_2(\text{CO})(\text{NO})]^+$  and  $[\text{RuCl}(\text{PPh}_3)_2(\text{NO})_2]^+$ .

Stereo chemical control of valence in  $[\text{Co}(\text{diars})_2(\text{NO})]^{2+}$  and  $[\text{Co}(\text{diars})_2(\text{NO})(\text{SCN})]^+$ .

**Metal Dinitrogen complexes:** -  $\text{N}_2$  as a ligand – Molecular orbitals of  $\text{N}_2$ ; Bonding modes – Terminal and Bridging; Stretching frequencies; Structures of Ru (II) and Os(II) dinitrogen complexes; Chemical fixation of dinitrogen.

#### Suggested References:

1. Symmetry and Group theory in Chemistry, Mark Ladd, Marwood Publishers, London (2000).
2. Molecular Symmetry and Group Theory, Robert L.Carter, John Wiley & Son (1998).
3. Symmetry and Spectroscopy of Molecules. K.Veera Reddy, New Age International (P) Limited (1999).
4. Advanced Inorganic Chemistry. F.A.Cotton, G.Wilkinson, C.A.Murillo and M.Bochmann, 6<sup>th</sup> Edition, Wiley Interscience, N.Y (1999)
5. Inorganic Chemistry, J.E. Huheey, K.A.Keiter and R.L.Keiter 4 th Edition Harper Cottens College Publications (1993).
6. Homogeneous Catalysis by Metal complexes Vol I, M M Taqui Khan and A E Martell, Academic Press NY (1974).
7. Inorganic Chemistry, Keith F.Purcell and John C.Kotz, Holt-Saunders International Editions, London (1977).

#### Paper-II: CH 102 T (Organic Chemistry)

OC-01: Stereochemistry

OC-02: Reaction mechanism-1

OC-03: Conformational analysis (Acyclic systems)

OC-04: Heterocyclic compounds & Natural products

#### OC-01: Stereochemistry

15 hrs

**Molecular representations:** Wedge, Fischer, Newman and Saw-horse formulae, their description and interconversions.

**Molecular Symmetry & Chirality:** Symmetry operations and symmetry elements ( $C_n$  &  $S_n$ ). Criteria for Chirality. Desymmetrization.

**Axial, planar and helical chirality:** Axially chiral allenes, spiranes, alkylidene cycloalkanes, chiral biaryls, atropisomerism, planar chiral ansa compounds and trans- cyclooctene, helically chiral compounds and their configurational nomenclature

**Relative and absolute configuration:** Determination of configuration by chemical correlation methods.

**Racemisation and resolution techniques:** Racemisation, resolutions by direct crystallization, diastereoisomer salt formation chiral chromatography and asymmetric transformation.

**Determination of configuration in E, Z-isomers:** Spectral and Chemical methods of configuration determination of E,Z isomers. Determination of configuration in aldoximes and ketoximes.

#### **OC-02: Reaction mechanism-I**

**15 hrs**

**Electrophilic addition to carbon carbon double bond:** Stereoselective addition to carbon carbon double bond; *anti* addition- Bromination and epoxidation followed by ring opening. *Syn* addition of OsO<sub>4</sub> and KMnO<sub>4</sub>.

**Elimination reactions** Elimination reactions E2, E1, E1CB mechanisms. Orientation and stereoselectivity in E2 eliminations. Pyrolytic *syn* elimination and  $\alpha$ -elimination, elimination Vs substitution.

**Determination of reaction mechanism:** Determination of reaction mechanism: Energy profiles of addition and elimination reactions, transition states, product isolation and structure of intermediates, use of isotopes, chemical trapping and crossover experiments. Use of IR and NMR in the investigation of reaction mechanism.

#### **OC-03: Conformational analysis (acyclic systems)**

**15 hrs**

**Conformational isomerism:** Introduction to the concept of dynamic stereochemistry. Conformational diastereoisomers and conformational enantiomers. Study of conformations in ethane and 1,2-disubstituted ethane derivatives like butane, dihalobutanes, halohydrin, ethylene glycol, butane-2, 3-diol amino alcohols and 1,1,2,2-tetrahalobutanes. Klyne-Prelog terminology for conformers and torsion angles

**Conformations of unsaturated acyclic compounds:** Propylene, 1-Butene, Acetaldehyde Propionaldehyde and Butanone.

**Factors affecting the conformational stability and conformational equilibrium:**

Attractive and repulsive interactions. Use of Physical and Spectral methods in conformational analysis.

**Conformational affects on the stability and reactivity of acyclic diastereoisomers:** Steric and stereoelectronic factors-examples. Conformation and reactivity. The Winstein-Holness equation and the Curtin – Hammett principle

#### **OC-4: Heterocyclic compounds & Natural products**

**15 hrs**

**Heterocyclic compounds:** Introduction, Nomenclature Synthesis and reactivity of indole, quinoline, isoquinoline, carbazole and acridine

**Natural products :** Importance of natural products as drugs.

**Terpenoids :** General methods in the structure determination of terpenes. Isoprene rule. Structure determination and synthesis of  $\beta$ -carotene,  $\alpha$ -terpeniol and camphor.

**Alkaloids:** General methods of structure determination of alkaloids. Structure determination and synthesis of papaverine

#### **References:**

1. Stereochemistry of carbon compounds by Ernest L. Eliel and Samuel H. Wilen
2. Stereochemistry of organic compounds- Principles and Applications by D. Nasipuri
3. Heterocyclic Chemistry, T.L. Gilchrist, Longman UK Ltd, London (1985).
4. Benzofurans A. Mustafa, Wiley-Interscience, New York (1974).

5. Heterocyclic Chemistry, 3<sup>rd</sup> Edn J.A. Joule, K. Mills and G..F. Smith, Stanley Thornes Ltd, UK, (1998)
6. The Chemistry of Indole, R.J. Sunderberg, Academic Press, New York (1970).
7. An introduction to the chemistry of heterocyclic compounds, 2<sup>nd</sup> Edn. R.M. Acheson, Interscience Publishers, New York, 1967.
8. Advanced Organic Chemistry by Jerry March
9. Mechanism and Structure in Organic Chemistry S. Mukerjee

### **Paper CH 103 ( PHYSICAL CHEMISTRY)**

- PC-01: Thermodynamics-I  
 PC-02: Electrochemistry-I  
 PC-03: Quantum Chemistry-I  
 PC-04: Chemical Kinetics-I

#### **PC-01: Thermodynamics-I**

15 hrs

Concept of Entropy, Entropy as a function of V and T, Entropy as a function of P and T. Entropy change in isolated systems- Clausius inequality. Entropy change as criterion for spontaneity and equilibrium.

Third law of thermodynamics. Evaluation of absolute entropies from heat capacity data for solids, liquids and gases. Standard entropies and entropy changes of chemical reactions.

Thermodynamic relations. Gibbs equations. Maxwell relations.

Gibbs equations for non-equilibrium systems. Material equilibrium. Phase equilibrium. Clausius-Clapeyron equation. Conditions for equilibrium in a closed system.

Chemical potential of ideal gases. Ideal-gas reaction equilibrium-derivation of equilibrium constant. Temperature dependence of equilibrium constant-the van't Hoff equation.

Solutions: Specifying the Solution composition. Partial molar properties-significance. Relation between solution volume and partial molar volume. Measurement of partial molar volumes- slope and intercept methods. The chemical potential. Variation of chemical potential with T and P. Gibbs-Duhem equation-derivation and significance.

#### **PC-02: Electrochemistry- I**

15 hrs

**Electrochemical Cells:** Derivation of Nernst equation – problems. Chemical and concentration cells (with and without transference). Liquid junction potential (LJP) – derivation of the expression for LJP – its determination and elimination. Types of electrodes. Applications of EMF measurements: Solubility product, potentiometric titrations; determination of pH using glass electrode, equilibrium constant measurements.

Decomposition potential and its significance. Electrode polarization – its causes and elimination. Concentration over-potential.

Concept of activity and activity coefficients in electrolytic solutions. The mean ionic activity coefficient. Debye-Huckel theory of electrolytic solutions. Debye-Huckel limiting law (derivation not required). Calculation of mean ionic activity coefficient. Limitations of Debye-Huckel theory. Extended Debye-Huckel law.

Theory of electrolytic conductance. Derivation of Debye-Huckel-Onsager equation – its validity and limitations.

Concept of ion association – Bjerrum theory of ion association (elementary treatment)-ion association constant – Debye-Huckel-Bjerrum equation.

**PC-03: Quantum Chemistry- I**

15 hrs

A brief review of Black body radiation-Planck's concept of quantization-Planck's equation, average energy of an oscillator (derivation not required), Wave particle duality and uncertain principle-significance of these for microscopic entities. Emergence of quantum mechanics. Wave mechanics and Schrödinger wave equation.

Operators- Operator algebra. Commutation of operators, linear operators. Complex functions. Hermitian operators. Operators  $\nabla$  and  $\nabla^2$ . Eigenfunctions and eigenvalues. Degeneracy. Linear combination of eigenfunctions of an operator. Well behaved functions. Normalized and orthogonal functions.

Postulates of quantum mechanics: Physical interpretation of wave function. Observables and Operators. Measurability of operators. Average values of observables. The time dependent Schrodinger equation. Separation of variables and the time-independent Schrodinger equation. Theorems of quantum mechanics. Real nature of the eigen values of a Hermitian operator-significance. Orthogonal nature of the eigen values of a Hermitian operator-significance of orthogonality. Expansion of a function in terms of eigenvalues. Eigen functions of commuting operators-significance. Simultaneous measurement of properties and the uncertainty principle. Particle in a box- one dimensional and three dimensional. Plots of  $\psi$  and  $\psi^2$ -discussion. Degeneracy of energy levels. Calculations using wave functions of the particle in a box-orthogonality, measurability of energy, position and momentum, average values and probabilities. Application to the spectra of conjugated molecules.

**PC-04: Chemical Kinetics- I**

Theories of reaction rates: Collision theory, steric factor. Transition state theory. Thermodynamic formulation of transition state theory. Potential energy surface diagram, Reaction coordinate, Activated complex. Activation parameters and their significance. The Eyring equation. Unimolecular reactions and Lindamann's theory.

Complex reactions- Opposing reactions, parallel reactions and consecutive reactions (all first order type). Chain reactions-general characteristics, steady state treatment. Example-  $H_2$ - $Br_2$  reaction. Derivation of rate law.

Effect of structure on reactivity- Linear free energy relationships. Hammett and Taft equations-substituent ( $\sigma$  and  $\sigma^*$ ) and reaction constant ( $\rho$  and  $\rho^*$ ) with examples. Deviations from Hammett correlations, reasons- Change of mechanism, resonance interaction. Taft four parameter equation. Correlations for nucleophilic reactions. The Swain – Scott equation and the Edward equation. Reactions in solutions: Primary and secondary salt effects.

The reactivity-selectivity principle – Isokinetic temperature -Iselectivity rule, Intrinsic barrier and Hammond's postulate.

**References:**

1. Atkin's Physical Chemistry, Peter Atkins and Julio de Paula, Oxford University press
2. Physical Chemistry, Ira N. Levine, McGraw Hill
3. Physical Chemistry-A Molecular approach, D.A. McQuarrie and J.D. Simon, Viva Books Pvt. Ltd
4. Molecular Thermodynamics, D.A. McQuarrie and J.D. Simon, University Science Books
5. Quantum Chemistry, Ira N. Levine, Prentice Hall
6. Introduction to Quantum Chemistry, A.K. Chandra, Tata McGraw Hill
7. Chemical Kinetics, K.J. Laidler, McGraw Hill

8. Kinetics and Mechanism of Chemical Transformations, J. Rajaraman and J. Kuriacose, McMillan
9. Introduction to Electrochemistry, S. Glasstone
10. Modern Electrochemistry, J. O. M. Bockris & A. K. N. Reddy, Plenum
11. Principles of physical chemistry, Samuel H. Maron and Carl F. Prutton, Oxford & IBH
12. The Physical Basis of Organic Chemistry by Howard Maskill, Oxford University Press (New York)
13. Chemical Kinetics and Reaction Mechanisms, J. H. Espenson, McGraw Hill
14. Physical Organic Chemistry, N. S. Isaacs, ELBS
15. Elementary Quantum Chemistry, F. L. Pilar, McGraw Hill.
16. Quantum Chemistry – D.A. McQuarri Viva Publications

**Paper-IV: CH 104 (ANALYTICAL TECHNIQUES and SPECTROSCOPY- I)**

ASP 01: Techniques of Chromatography

ASP 02: NMR spectroscopy-I ( $^1\text{H}$  NMR)

ASP 03: Rotational and Vibrational spectroscopy

ASP 04: Electronic spectroscopy

**ASP-01: Techniques of Chromatography**

**15 hrs**

- i. Introduction, Classification of chromatographic techniques, differential migration rates, partition ratio, retention time, relation between partition ratio and retention time, capacity factor, selectivity factor. Efficiency of separation- resolution, diffusion, plate theory and rate theory.
- ii. **GC:** Principle, instrumentation, detectors- TCD, FID, ECD. Derivatisation techniques, PTGC.
- iii. **HPLC:** Principle, instrumentation, detectors- UV detectors, Photodiode array detector, fluorescence detector.
- iv. Applications: Methods of quantitation for GC and HPLC: GC analysis of hydrocarbons in a mixture, GC assay of methyl testosterone in tablets, atropine in eye drops. HPLC assay of paracetamol and aspirin in tablets.

**ASP 02: NMR spectroscopy-I ( $^1\text{H}$  NMR )**

**15 hrs**

**$^1\text{H}$  NMR spectroscopy:** Magnetic properties of nuclei, Principles of NMR Instrumentation, CW and pulsed FT instrumentation, equivalent and non equivalent protons, enantiotopic and diastereotopic protons, Chemical shifts, factors affecting the chemical shifts, electronegativity and anisotropy, shielding and deshielding effects, Signal integration, Spin-spin coupling: vicinal, germinal and long range, Coupling constants and factors affecting coupling constants.

Applications of  $^1\text{H}$  NMR spectroscopy: Reaction mechanisms (cyclic bromonium ion, electrophilic and nucleophilic substitutions, carbocations and carbanions), E, Z isomers, conformation of cyclohexane and decalins, keto-enol tautomerism, hydrogen bonding, proton exchange processes (alcohols, amines and carboxylic acids), C-N rotation. Magnetic resonance imaging (MRI).  $^1\text{H}$  NMR of organic molecules and metal complexes: ethyl acetate, 2-butanone, mesitylene, paracetamol, aspirin, ethylbenzoate, benzyl acetate, 2-chloro propionic acid,  $[\text{HNi}(\text{OPEt}_3)_4]^+$ ,  $[\text{HRh}(\text{CN})_5]$  (Rh  $I=1/2$ ),  $[\text{Pt}(\text{acac})_2]$ .

**ASP 03: Rotational, Vibrational and Raman spectroscopy****15 hrs**

**a). Microwave Spectroscopy:** Classification of molecules based on moment of inertia. Diatomic molecule as rigid rotator and its rotational energy levels. Selection rules (derivation not required). Calculation of bond lengths from rotational spectra of diatomic molecules. Isotope effect on rotational spectra. Calculation of atomic mass from rotational spectra. Brief description of microwave spectrometer.

**b). Vibrational Spectroscopy.** Vibrational energy levels of diatomic molecules, selection rules (derivation not required). Calculation force constant from vibrational frequency. Anharmonic nature of vibrations. Fundamental bands, overtones and hot bands, Fermi Resonance. Vibration-rotation spectra diatomic molecules. Vibrations of poly atomic molecules. Normal modes of vibration, concept of group frequencies. Characteristics of vibrational frequencies of functional groups; Stereochemical effects on the absorption pattern in carbonyl group, cis-trans isomerism and hydrogen bonding. Isotopic effect on group frequency. IR spectra of metal coordinated  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  ions.

**c) Raman Spectroscopy-** Classical and Quantum theories of Raman effect. Rotational Raman and Vibrational Raman spectra, Stokes and anti- Stokes lines. Complementary nature of IR and Raman spectra.

**ASP 04:Electronic spectroscopy****15 hrs**

**Electronic spectroscopy:** Electronic spectra: Elementary energy levels of molecules-selection rules for electronic spectra; types of electronic transitions in molecules. Chromophores: Congugated dienes, trienes and polyenes, unsaturated carbonyl compounds, Benzene, mono substituted derivative (Ph-R), di substituted derivative ( $\text{R-C}_6\text{H}_4\text{-R}'$ ) and substituted benzene derivatives ( $\text{R-C}_6\text{H}_4\text{-COR}'$ ), Woodward-Fieser rules. Polynuclear aromatic compounds (Biphenyl, stilbene, naphthalene, anthracene, phenanthrene and pyrene). Heterocyclic systems. Absorption spectra of charge transfer complexes. Solvent and structural influences on absorption maxima, stereochemical factors. Cis-trans isomers, and cross conjugation. Beer's law application to mixture analysis and dissociation constant of a weak acid.

**References:**

1. Fundamentals of Molecular Spectroscopy, Banwell and McCash.
2. Introduction to Molecular Spectroscopy, G.M. Barrow.
3. Absorption Spectroscopy of Organic Compounds, J.R. Dyer.
4. Biochemistry: Hames and Hooper.
5. Introduction to Spectroscopy, Pavia Lampman Kriz.
6. Pharmaceutical analysis, Watson
7. NMR in Chemistry- A multinuclear introduction, William Kemp.
8. Organic Spectroscopy, William Kemp.
9. Spectroscopy of organic compounds, P.S. Kalsi.
10. Structural methods n Inorganic chemistry, E.A.V Ebsworth.
11. Organic Spectroscopy, LDS Yadav
12. Organic Spectroscopy, Y.R. Sharma
13. Molecular Spectroscopy – Arhuldas
14. Vibrational spectroscopy – D.N. Satyanarayana



**Practicals:****Paper CH 151: Inorganic chemistry practicals: 6 hrs/week****I. Calibrations:**

- (i) Calibration of weights.
- (ii) Calibration of pipettes.
- (iii) Calibration of standard flasks.
- (iv) Calibration of burette.

**II. EDTA back-titrations:**

- (i) Estimation of  $\text{Ni}^{2+}$ .
- (ii) Estimation of  $\text{Al}^{3+}$ .

**III. EDTA substitution titrations:**

Estimation of  $\text{Ca}^{2+}$ .

**IV. Redox Titrations**

- (i) Estimation of Ferrocyanide and Ferricyanide in a mixture

**V. Preparation of complexes:**

- (i). Hexaammine nickel (II) chloride.
- (ii). Tris (acetylacetonato) manganese.
- (iii). Tris (ethylenediamine) nickel (II) thiosulphate.
- (iv). Mercury tetrathiocyanato cobaltate (II).
- (v). Chloro pentaammine cobalt (III) chloride
- (vi). Tetrammine copper (II) sulphate and estimation of  $\text{NH}_3$  and calculation of % purity.
- (vii) One component gravimetric estimations
  - (i) Estimation of  $\text{Zn}^{2+}$
  - (ii) Estimation of  $\text{Ba}^{2+}$  (as  $\text{BaSO}_4$ )

**Paper CH 152 Organic Chemistry Lab course 6 hours/ week**

**Synthesis of the following compounds:** p-Bromoacetanilide, p- Bromoaniline, 2,4,6-tribromoaniline, 1,3,5-tribromobenzene, aspirin, tetrahydrocarbazole, 7-hydroxy-4-methyl coumarin, m-dinitrobenzene, m-nitroaniline, hippuric acid, azlactone, anthracene-maleic anhydride adduct, Phthalimide, 2,4-dihydroxyacetophenone

**References.**

1. Text book of practical organic chemistry, Vogel
2. Text book of practical organic chemistry, Mann and Saunders.

**Paper 153 Physical Chemistry Lab course: 6 hrs / week****Physical properties:**

Data analysis I: Significant figures, Precision and accuracy

**Distribution:**

- Distribution of acetic acid between n-butanol and water
- Distribution of iodine between hexanes and water

**Chemical kinetics:**

- Acid-catalyzed hydrolysis of methyl acetate
- Peroxydisulphate- I reaction (overall order)
- Oxidation of iodide ion by hydrogen peroxide- iodine clock reaction

**Conductometry:**

- Titration of strong acid vs strong base
- Titration of weak acid vs strong base
- Determination of cell constant
- Determination of dissociation constant of a weak acid

**Potentiometry:**

- Titration of strong acid vs strong base
- Titration of weak acid vs strong base
- Determination of dissociation constant of a weak acid
- Determination of single electrode potential

**Polarimetry:**

- Determination of specific rotation of sucrose
- Acid-catalyzed hydrolysis of sucrose (inversion of sucrose)

**Adsorption and others:**

- Adsorption of acetic acid on animal charcoal or silica gel
- Determination of critical solution temperature of phenol-water system
- Effect of added electrolyte on the CST of phenol-water system

Determination of **molecular weight of a polymer by viscometry.**

**References:**

1. Senior Practical Physical Chemistry: B.D. Khosla, V.C. Garg and A. Khosla
2. Experimental Physical Chemistry: V. Athawale and P. Mathur.
3. Practical Physical Chemistry: B. Vishwanathan and P.S. Raghavan.
4. Practical in Physical Chemistry: P.S. Sindhu
5. Advanced Practical Physical chemistry: J.B. Yadav
6. Vogel Text book of Quantitative Analysis, 6<sup>th</sup> edition, Pearson education Ltd. 2002.

**SEMESTER –II**

(Semester-I and Semester-II syllabus is common for all specializations i.e., Inorganic-Analytical, Organic, Physical, Chemistry (Pharmacoinformatics) and Physical- Organic.)

**Paper CH 201 INORGANIC CHEMISTRY**

IC 05: Reaction mechanisms of transition metal complexes

IC 06: Bonding in metal complexes-II

IC 07: Metal clusters

IC 08: Biocoordination chemistry

Teaching hours/week-4

Marks-80

**IC-05: Reaction mechanisms of transition metal complexes:****15 hrs**Ligand substitution reactions:

Energy profile of a reaction – Transition state or Activated Complex. Types of substitution reactions (SE, SN, SN<sup>1</sup>, SN<sup>2</sup>). Langford and Grey classification – A mechanism, D-Mechanism, I<sub>a</sub>, I<sub>d</sub>, and Intimate mechanism.

Ligand substitution reactions in octahedral complexes:

Aquation or Acid hydrolysis reactions, Factors effecting Acid Hydrolysis , Base Hydrolysis, Conjugate Base Mechanism, Evidences in favour of SN<sup>1</sup>CB Mechanism.

Substitution reactions with out Breaking Metal-Ligand bond. Anation reaction

Ligand Substitution reactions in Square-Planar complexes: Mechanism of Substitution in Square-Planar complexes- Trans-effect, Trans-influence, Grienberg's Polarization theory and Π - bonding theory – Applications of Trans-effect in synthesis of Pt (II) complexes.

Electron Transfer Reactions (or Oxidation-Reduction Reactions) in Coordination compounds:

Mechanism of One-electron Transfer Reactions: Atom (or group) Transfer or Inner Sphere Mechanism, Direct electron Transfer or Outer Sphere Mechanism. Factors affecting direct electron transfer reactions, Cross reactions and Marcus-Hush theory.

**IC-06: Bonding in Metal Complexes – II:****15 hrs**

Free ion terms and Energy levels: Configurations, Terms, States and Microstates – Formula for the calculation of Microstates p<sup>n</sup> and d<sup>n</sup> configurations – L-S (Russel-Saunders) coupling scheme – j-j coupling scheme – Determination of terms for various p<sup>n</sup> and d<sup>n</sup> configurations of metal ions. Hole formalism – Energy ordering of terms ( Hund's rules) Inter – electron repulsion Parameters ( Racah parameters) – Spin-Orbital coupling parameters. Effect of weak cubic crystal fields on S,P,D and F terms- Orgel Diagrams.

**IC-07: Metal Clusters:****15 hrs**

Carbonyl clusters: Factors favouring Metal-Metal bonding – Classification of Clusters – Low Nuclearity Clusters : M<sub>3</sub> and M<sub>4</sub> clusters , structural patterns in M<sub>3</sub>(CO)<sub>12</sub> (M=Fe,Ru,Os) and M<sub>4</sub>(CO)<sub>12</sub> (M=Co,Rh,Ir) Clusters. Metal carbonyl scrambling – High Nuclearity clusters M<sub>5</sub>, M<sub>6</sub>, M<sub>7</sub>, M<sub>8</sub> and M<sub>10</sub> Clusters-, Polyhedral skeletal electron pair theory and Total Electron Count theory – Capping rule – Structural patterns in [Os<sub>6</sub>(CO)<sub>18</sub>]<sup>2-</sup>, [Rh<sub>6</sub>(CO)<sub>16</sub>], {Os<sub>7</sub>(CO)<sub>21</sub>}, {Rh<sub>7</sub>(CO)<sub>16</sub>}<sup>3-</sup>, [Os<sub>8</sub>(CO)<sub>22</sub>]<sup>2-</sup>, [Os<sub>10</sub>C(CO)<sub>24</sub>]<sup>2-</sup> and [Ni<sub>5</sub>(CO)<sub>12</sub>]<sup>2-</sup>.

Metal Halide clusters: Major structural types in Dinuclear Metal-Metal systems – Edge sharing Bioctahedra, Face sharing Bioctahedra, Tetragonal prismatic and Trigonal antiprismatic structures -. Structure and bonding in  $[\text{Re}_2\text{Cl}_8]^{2-}$  and Octahedral halides of  $[\text{Mo}_6(\text{Cl})_8]^{4+}$  and  $[\text{Nb}_6(\text{Cl})_{12}]^{2+}$ . Trinuclear halides of Re(III). Hoffman's Isolobal analogy and its Structural implications. Boranes, carboranes, STYX Rule. Stereo chemical non-rigidity in  $[\text{Rh}_4(\text{CO})_{12}]$  and  $[\text{Fe}_2(\text{Cp})_2(\text{CO})_4]$ .

### IC-08: Bio coordination chemistry:

15 hrs

Metal ions in Biological systems: Brief survey of metal ions in biological systems. Effect of metal ion concentration and its physiological effects. Basic principles in the biological selection of elements.

Oxygen transport and storage: Hemoglobin (Hb) and Myoglobin (Mb) primary, secondary, tertiary and quarternary structures and non-covalent bonds present in them. Oxygenation equilibria for Mb and Hb. Factor effecting oxygenation equilibria. Cooperativity and its mechanism. Spin state of iron. Spatial and electronic aspects of dioxygen binding. Allosteric models (T and R states). Role of globin. Transport of NO and CO<sub>2</sub>. Hemocynin (Hc) and Hemerythrin (Hr): Introduction-structure of active sites with oxygen and without oxygen. Comparison of Hemerythrin and Hemocyanin with hemoglobin.

Photosynthesis: Structural aspects of Chlorophyll. Photo system I and Photo system II.

Vitamin B<sub>6</sub> model systems: Forms of vitamin B<sub>6</sub> with structures. Reaction mechanisms of (1) Transamination (2) Decarboxylation and (3) Dealdolation in presence of metal ions.

### References:

1. Inorganic Reaction Mechanisms. M.L.Tobe and John Burgess, Addison Wesley Longman (1999).
2. Metal ions in Reaction Mechanisms. K.Veera Reddy. Goltotia Publications (P) Ltd
3. Mechanisms of Reactions in Transition Metal Sites. Richard A Henderson, Oxford Science Publications, London (1993).
4. Inorganic Reaction Mechanisms, F.Basolo and R.G.Pearson, New York (1967).
5. Advanced Inorganic Chemistry. F.A.Cotton, G.Wilkinson, C.A.Murillo and M.Bochmann, 6 Th Edition, Wiley Interscience, N.Y (1999)
6. Inorganic Chemistry, J.E.Huheey , K.A.Keiter and R.L.Keiter 4 th Edition Harper Cottens College Publications (1993).
7. Inorganic Biochemistry Edited by G.L.Eichorn, Volume 1 Elsevier ( 1982).
8. The Chemistry of Metal Cluster Complexes. D.F.Shriver, H.D.Kaerz and R.D.Adams (Eds), VCH, NY (1990).
9. Inorganic Chemistry, Keith F.Purcell and John C.Kotz, Holt-Saunders International Editions, London (1977).
10. Bioinorganic Chemistry, I.Bertini, H.B.Gray, S.J.Lippard and S.J.Valentine, Viva Low-Priced Student Edition, New Delhi (1998).
11. Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, W.Kain and B.Schwederski, John Wiley and Sons, NY (1999).

**Paper-II: CH 202 T (Organic Chemistry)**

OC-05: Reaction mechanism-II

OC-06: Pericyclic reactions-I

OC-07: Photochemistry

OC-08: Reactive intermediates and molecular rearrangements

**OC-05: Reaction mechanism-II****15 hrs**

**Nucleophilic Aromatic substitution:** Aromatic Nucleophilic substitution:  $S_N1(Ar)$ ,  $S_N2(Ar)$ , and benzyne mechanisms; evidence for the structure of benzyne. Von Richter rearrangement. Definition and types of ambident nucleophiles.

**Neighbouring group participation :** Criteria for determining the participation of neighbouring group. Enhanced reaction rates, retention of configuration, isotopic labeling and cyclic intermediates. Neighbouring group participation involving Halogens, Oxygen, Sulphur, Nitrogen, Aryl, Cycloalkyl groups,  $\sigma$  and  $\pi$ - bonds. Introduction to nonclassical carbocations.

**Electrophilic substitution at saturated carbon and single electron transfer reactions.**

Mechanism of aliphatic electrophilic substitution.  $S_E1$ ,  $S_E2$ , and  $S_{Ei}$ . SET mechanism.

**OC-06 Pericyclic reactions****15 hrs.**

Introduction, Classification of pericyclic reactions,

**Electrocyclic reactions:** con rotation and dis rotation. Electrocyclic closure and opening in  $4n$  and  $4n+2$  systems.

**Cycloaddition reactions:** suprafacial and antarafacial additions in  $4n$  and  $4n+2$  cycloadditions.

**Sigmatropic reactions:** [i, j] shifts- suprafacial and antarafacial shifts, Cope and Claisen rearrangement reactions.

**Approaches for the interpretation of mechanism of pericyclic reactions:** Aromatic Transition States (ATS)/Perturbation Molecular Orbitals (PMO) approach-Concept of Huckel –Möbius aromatic and antiaromatic transition states. Framing Woodward-Hofmann selection rules for all the pericyclic reactions by ATS approach. Solving problems based on ATS approach.

**Molecular orbitals:** ethylene, 1, 3-butadiene, 1, 3, 5-hexatriene, allyl cation, allyl radical, pentadienyl cation, pentadienyl radical.

**Frontier Molecular Orbital (HOMO-LUMO) approach-concept:** Framing Woodward-Hofmann selection rules for all the pericyclic reactions by Frontier Molecular Orbital (FMO) approach. Solving problems based on FMO approach.

**Conservation of orbital symmetry:** (Correlation Diagrams) approach- for electrocyclic and cycloadditions & cycloreversions.

**OC-07 Photochemistry****15hrs**

**Photochemistry:** Photochemistry of  $\pi$ - $\pi^*$  transitions: Excited states of alkenes, cis-trans isomerisation, and photo stationary state. Photochemistry of 1,3-butadiene Electrocyclisation and sigmatropic rearrangements, di- $\pi$  methane rearrangement. Intermolecular reactions, photocycloadditions, photodimerisation of simple and conjugated olefins. Addition of olefins to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds. Excited states of aromatic compounds, Photoisomerisation of benzene.

**Photochemistry of (n- $\pi^*$ ) transitions:** Excited states of carbonyl compounds, homolytic cleavage of  $\alpha$ - bond, Norrish type I reactions in acyclic and cyclic ketones and strained cycloalkane diones.

Intermolecular abstraction of hydrogen: photoreduction-influence of temperature, solvent, nature of hydrogen donor and structure of the substrate.

Intramolecular abstraction of hydrogen: Norrish type II reactions in ketones, esters and 1,2 diketones, Addition to carbon-carbon multiple bonds, Paterno-Buchi reaction, Photochemistry of nitrites-Barton reaction.

### **OC-08: Reactive intermediates and Molecular rearrangements 15 hrs**

**Reactive Intermediates:** Generation, detection, structure, stability and reactions of carbocations, carbanions, carbenes, nitrenes and free radicals.

**Molecular rearrangements:** Definition and classification. Molecular rearrangements involving 1) electron deficient carbon: Wagner- Meerwein, Pinacol-Pinacolone, Allylic and Wolf rearrangement. 2) electron deficient Nitrogen: Hofmann, Lossen, Curtius, Schmidt and Beckmann rearrangements 3) electron deficient Oxygen: Baeyer-Villiger oxidation. 4) Base catalysed rearrangements: Benzilic acid, Favorski, Transannular, Sommelet-Hauser and Smiles rearrangement

#### **References :**

1. Stereochemistry of Carbon compounds by Ernest L Eliel / Samuel H. Wilen
2. Stereochemistry of organic compounds – Principles and Applications by D Nasipuri
3. The third dimension in organic chemistry, by Alan Bassindale
4. Stereochemistry: Conformation and Mechanism by P S Kalsi
5. Stereochemistry by V M Potapov
6. Advanced Organic Chemistry by Jerry March
7. Mechanism and Structure in Organic Chemistry S. Mukerjee
8. Organic chemistry Vol.I and II by I.L.Finar
9. Comprehensive organic chemistry Vol.5 D.H.R.Barton and W.D..Ollis

### **Paper CH 203 PHYSICAL CHEMISTRY**

PC-05: Thermodynamics-II & Statistical Thermodynamics

PC-06: Photochemistry-I

PC-07: Quantum Chemistry-II

PC-08: Solid state chemistry

#### **PC-05:Thermodynamics-II & Statistical Thermodynamics**

**15 hrs**

Ideal solutions. Thermodynamic properties of ideal solutions. Mixing quantities. Vapour pressure -Raoult's law. Thermodynamic properties of ideally dilute solutions. Vapour pressure- Henry's law.

Nonideal systems. Concept of fugacity, fugacity coefficient. Determination of fugacity. Non ideal solutions. Activities and activity coefficients. Standard-state conventions for non ideal solutions. Determination of activity coefficients from vapour pressure measurements. Activity coefficients of nonvolatile solutes using Gibbs-Duhem equation.

Multicomponent phase equilibrium: Vapour pressure lowering, freezing point depression and boiling point elevation

**Statistical Thermodynamics:**

Partition Functions: Concepts of distribution and probability, Boltzmann distribution law. Interpretation of partition functions- translational, rotational, vibrational and electronic partition functions. Relationship between partition functions and thermodynamic functions (only S & G).

**PC-06: Photochemistry –I****15 hrs**

Electronic transitions in molecules. The Franck Condon principle. Electronically excited molecules- singlet and triplet states. Radiative life times of excited states-theoretical treatment. Measured life times. Quantum yield and its determination. Experimental set up of a photochemical reaction. Actinometry-ferrioxalate and uranyl oxalate actinometers – problems. Derivation of fluorescence and phosphorescence quantum yields. E-type delayed fluorescence- evaluation of triplet energy splitting( $\Delta E_{ST}$ ). Photophysical processes- photophysical kinetics of unimolecular reactions. Calculation of rate constants of various photophysical processes-problems, State diagrams

Photochemical primary processes. Types of photochemical reactions- electron transfer, photodissociation, addition, abstraction, oxidation and isomerization reactions with examples. Effect of light intensity on the rates of photochemical reactions. Photosensitization. Quenching-Stern-Volmer equation. Introduction to fast reactions- Principle of flash photolysis.

**PC-07: Quantum chemistry-II****15 hrs**

Cartesian, Polar and spherical polar coordinates and their interrelations.

*Schrodinger equation for the hydrogen atom-* separation into three equations. Hydrogen like wave functions. Radial and angular functions. Quantum numbers  $n$ ,  $l$  and  $m$  and their importance. The radial distribution functions. Hydrogen like orbitals and their representation. Polar plots, contour plots and boundary diagrams.

*Many electron systems.* Approximate methods. The variation method-variation theorem and its proof. Trial variation function and variation integral. Examples of variational calculations. Particle in a box. Construction of trial function by the method of linear combinations. Variation parameters. Secular equations and secular determinant.

*Bonding in molecules.* Molecular orbital theory-basic ideas. Construction of MOs by LCAO,  $H_2^+$  ion. The variational integral for  $H_2^+$  ion. Detailed calculation of Wave functions and energies for the bonding and antibonding MOs. Physical picture of bonding and antibonding wave functions. Energy diagram. The MO wave function and the energy of  $H_2$  molecule MO by LCAO method and Valence bond method (detailed calculations not required)-comparison of MO and VB models.

**PC-08: Solid state chemistry****15 Hrs**

**Electronic properties of metals, insulators and semi-conductors:** Electronic structure of solids, Band theory, band structure of metals, insulators and semi-conductors. Electrons, holes and Excitons. The temperature dependence of conductivity of extrinsic semi-conductors. Photo conductivity and photovoltaic effect – p-n junctions.

Superconductivity: Occurrence of superconductivity. Destruction of superconductivity by magnetic fields – Meissner effect. Types of superconductors. Theories of super conductivity – BCS theory.

High temperature superconductors: Structure of defect perovskites. High  $T_c$  superconductivity in cuprates. Phase diagram of Y-Ba-Cu-O system. Crystal structure of  $YBa_2Cu_3O_{7-x}$ . Preparation of 1-2-3 materials. Origin of high  $T_c$  superconductivity.

### **Nanoparticles and their applications:**

Introduction to nanoparticles. Reduced dimensionality in solids – zero dimensional systems, fullerenes, quantum dots. One dimensional systems, carbon nano tubes, preparation of nano particles –top down and bottom up methods. Preparation of nanomaterials- – sol gel methods, and chemical vapour deposition method; thermolysis. Characterization of nanoparticles – experimental methods – powder X-ray diffraction, transmission electron microscopy (TEM), and atomic force microscopy (AFM) ( detailed theory and instrumentation are not required). Optical properties of nanoparticles, Applications of nanoparticles.

### **References:**

1. Atkin's Physical Chemistry, Peter Atkins and Julio de Paula, Oxford University press
2. Physical Chemistry, Ira N. Levine, McGraw Hill
3. Physical Chemistry-A Molecular approach, D.A. McQuarrie and J.D. Simon, Viva Books Pvt Ltd
4. Molecular Thermodynamics, D.A. McQuarrie and J.D. Simon, University Science Books
5. Quantum Chemistry, Ira N. Levine, Prentice Hall
6. Introduction to Quantum Chemistry, A.K. Chandra, Tata McGraw Hill
7. Introduction to Solids, Leonid V. Azaroff, Tata McGraw Hill
8. Solid state Chemistry, D.K. Chakrabarty, New Age International
9. Solid state Chemistry and its applications, A.R. West, Plenum.
10. Fundamentals of Photochemistry, K.K.Rohtagi-Mukherji, Wiley-Eastern
11. Molecular Photochemistry, N.J. Turro, Benjamin
12. Photochemistry, R.P.Kundall and A. Gilbert, Thomson Nelson
13. Essentials of Molecular Photochemistry by A. Gilbert and J. Baggott, Blackwell Scientific Publications.
14. Organic Photochemistry by J.M.Coxon and B.Halton, Cambridge University press.
15. Introductory Photochemistry by A.Cox and T.J.Kemp. McGraw-Hill, London.
16. Principles of the Solid State, H. V. Keer, New Age International
17. Elements of Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press
18. Elements of Statistical Thermodynamics, L. K. Nash, Addison – Wesley
19. Introduction to Statistical Thermodynamics, T. L. Hill, Addison Wiley
20. Statistical Thermodynamics, M. C. Gupta, New Age International
21. Quantum Chemistry, D.A. McQuarrie, Prentice Hall
22. Elementary Quantum Chemistry, F. L. Pilar, McGraw Hill.
23. Nanostructured Materials and Nanotechnology, edited by Hari Singh Nalwa, Academic Press
24. Self-Assembled Nanostructures, Jin Zhang, Zhong-lin Wang, Jun Liu, Shaowei Chen & Gan-Yu-Liu, Kluwer Academic/Plenum
25. Introduction to Nanotechnology, Charles P. Poole Jr, F. J. Owens, Wiley India Pvt. Ltd.
26. The physics and chemistry of solids by Stephen Elliott, Wiley Publishers.
27. Introductory Photochemistry by A.Cox and T.J.Kemp. McGraw-Hill, London.



**Paper-IV: CH 204 (ANALYTICAL TECHNIQUES and SPECTROSCOPY - II)**

ASP-05: Electro and thermal analytical Techniques.

ASP-06: NMR- II

ASP-07: Mass Spectroscopy

ASP-08: Photoelectron &amp; ESR spectroscopy

**ASP-05: Electro and thermal Analytical Techniques****15 hrs****I: Types and Classification of Electro analytical Methods:**

a) D.C Polarography: Instrumentation - Dropping mercury electrode- -polarogram. Types of Currents: Residual, Migration, Limiting. Two and Three electrode assemblies. Ilkovic equation (derivation not necessary) and its consequences. Applications of polarography in qualitative and quantitative analysis. Analysis of mixtures. Application to inorganic and organic compounds. Determination of stability constants of complexes.

b) Brief account of following techniques and their advantages over conventional d.c.polarography.

(i) A.C.polarography (ii) Square-wave polarography (iii) Pulse polarography (iv) Differential pulse polarography

c) Amperometric titrations: Principle, Instrumentation. Types and applications of amperometric titrations. Determination of  $\text{SO}_4^{2-}$ , metal ions viz.,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and other substances.

d) Cyclic Voltammetry: Principle, instrumentation, Applications. Cyclic voltammetric study of insecticide parathion.

**II: Thermal Analysis:** Thermal techniques-Introduction, types of thermo analytical methods. Thermogravimetry principle and applications of thermogravimetry, differential thermal analysis- principle and applications of DTA. Differential scanning calorimetry. DSC: Principle, and application of DSC.

**ASP 06: NMR spectroscopy-II ( $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR)****15 hrs**

**$^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  and solid state NMR spectroscopy:** First order and non first order spectra e.g., AX,  $\text{AX}_2$ ,  $\text{AX}_3$ ,  $\text{A}_2\text{X}_3$ , AMX and AB, ABC. Simplification of complex spectra: increased field strength, deuterium exchange, Lanthanide shift reagents and double resonance techniques. Discrimination of enantiomers by use of chiral NMR solvents (CSAs), chiral lanthanide shift reagents and Mosher's acid. Nuclear Overhauser enhancement (NOE). Fluxional molecules bullvalene,  $[\eta^5\text{-C}_5\text{H}_5\text{M}]$ ,  $[\eta^5\text{-(C}_5\text{H}_5)_2\text{Ti}\eta^1\text{-(C}_5\text{H}_5)_2]$  and  $[\eta^4\text{C}_8\text{H}_8\text{Ru(CO)}_3]$ .

$^{19}\text{F}$  NMR spectroscopy:  $^{19}\text{F}$  chemical shifts, coupling constants. Applications of  $^{19}\text{F}$  NMR involving coupling with  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{31}\text{P}$ : 1,2 dichloro-1,1 difluoro ethane,  $\text{BrF}_5$ ,  $\text{SF}_4$ ,  $\text{PF}_5$ ,  $\text{ClF}_3$ ,  $\text{IF}_5$ ,  $\text{CF}_3\text{CH}_2\text{OH}$

$^{31}\text{P}$  NMR spectroscopy:  $^{31}\text{P}$  chemical shifts, coupling constants. Applications of  $^{31}\text{P}$  NMR involving coupling with  $^{31}\text{P}$ ,  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$ : ATP,  $\text{Ph}_3\text{PSe}$ ,  $\text{P}_4\text{S}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{HPF}_2$ ,  $\text{PF}_6^-$ ,  $\text{PH}_3$ ,  $[\text{Rh}(\text{PPh}_3)\text{Cl}_3]$  ( $\text{Rh } I=1/2$ )

Introduction to solid state NMR: Magic angle spinning (MAS). Applications of solid state NMR.

**ASP 07: Mass spectrometry****15 hrs**

Origin of mass spectrum, principles of EI mass spectrometer. Types of fragments: odd electron and even electron containing neutral and charged species (even electron rule), Nitrogen rule, isotopic peaks, determination of molecular formula, metastable ion peaks. High resolution mass spectrometry. Salient features of fragmentation pattern of organic compounds including  $\beta$ -cleavage, McLafferty rearrangement, retro Diels – Alder fragmentation and ortho effect. Principle of EI, CI, Fast Atom Bombardment (FAB), Secondary Ion Mass Spectrometry (SIMS), Electrospray (ESI) ionization and Matrix Assisted Laser Desorption Ionization (MALDI) methods. Introduction to principle and applications of Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid chromatography-Mass Spectrometry (LC-MS) techniques.

### **ASP-08: Photoelectron & ESR spectroscopy**

**15 hrs**

#### **Photoelectron Spectroscopy**

Principle and Instrumentation, Types of Photoelectron Spectroscopy – UPS & XPS. Binding Energies, Koopman's Theorem, Chemical Shifts. Photoelectron Spectra of Simple Molecules: N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, - Vibrational Structure of PES Bands, Potential energy curves, Interpretation of Vibrational spectral data for ionized (M<sup>+</sup>) species, Prediction of Nature of Molecular Orbitals. ESCA in qualitative analysis, Principles of Auger electron spectroscopy.

#### **Electron Spin Resonance**

Introduction, principle, instrumentation, selection rules, interpretation of Lande's factor 'g'. Hyperfine and super hyperfine Coupling. Anisotropy in 'g' values and hyperfine coupling constants. Zero field splitting, Kramer's degeneracy and quadrupolar interactions. Study of free radicals and transition metal complexes. Evidence for covalency in complexes, ex. Cu(II) Bissalicylaldehyde, Bis-acetylacetonovanadyl(II) and hexachloroiridium(IV) complexes.

#### **References:**

1. Spectroscopic identification of organic compounds by R.M. Silverstein and F.X. Webster.
2. Organic spectroscopy by William Kemp
3. Mass Spectrometry for Chemists and biochemists by M. Rose and R.A. W. Johnstone
4. Spectroscopic methods in organic chemistry by D.H. Williams and I. Fleming
5. Practical Pharmaceutical Chemistry by A. H. Beckett and J.B. Stenlake
6. Biological Mass Spectrometry by A.L. Burlingame
7. Principles and Practice of Biological Mass Spectrometry by Chhabil Das
8. Spectroscopic identification of organic compounds by R.M. Silverstein. G.C. Bassler and T.E. Morrill
9. NMR-A multinuclear introduction by William Kemp
10. Stereochemistry of Carbon compounds by Ernest L Eliel / Samuel H. Wilen
11. Principles of Polarography, Heyrovsky.
12. Principles of Polarography, Kapoor.
13. Modern Electroanalytical methods, edited by C. Charlot, Elsevier Company.
14. Principles of Instrumental analysis, Skoog, Holler and Nieman, Harcourt Asia PTE Ltd.
15. Analytical Chemistry-An Introduction, Skoog, West, Holler and Crouch, Saunders College Publishing.
16. Principles of Instrumental Analysis, Skoog and Leary, Saunders College Publishing.
17. International series of Monographs, Vol. 53: Photoelectron Spectroscopy, Edited by D. Becker and D. Betteridge 1972.
18. Structural methods in inorganic chemistry, E.A.V. Ebsworth

**Practicals:****Paper CH 251 : Inorganic chemistry practicals****I. Analysis of Two component mixtures:**

- (i). Separation of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in a mixture and estimation of  $\text{Ni}^{2+}$  (gravimetric) and  $\text{Cu}^{2+}$  (volumetric).
- (ii). Separation of  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  in a mixture and estimation of  $\text{Fe}^{2+}$  volumetrically and  $\text{Al}^{3+}$  gravimetrically.
- (iii). Separation of  $\text{Ag}^+$  and  $\text{Ca}^{2+}$  in a mixture and estimation of  $\text{Ag}^+$  volumetrically and  $\text{Ca}^{2+}$  volumetrically

**II. Analysis of three component mixtures:**

- (i). Separation of ( $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ ) from  $\text{Mg}^{2+}$  in the given mixture and estimation of  $\text{Mg}^{2+}$  (Gravi).

**III Applied titrimetric analysis**

- (i) Determination of Iron and calcium in Cement
- (ii) Determination of Calcium in calcium tablets
- (iii) Determination of alkali content in antacid

**IV. Ion exchange methods of analysis:**

- (i). Determination of capacity of an ion exchange resin.
- (ii). Separation of Zinc and Magnesium on an anion exchange resin and estimation of  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ .

**Suggested Books:** (For both semesters).

1. (i). Text book of Quantitative Inorganic Analysis by A.I.Vogel, 3<sup>rd</sup> edition, ELBS 1969.
- (ii). Vogel's text book of Quantitative Inorganic analysis. Jeffery et al, 4<sup>th</sup> edition, ELBS 1988.
- (iii). Vogel's text book of Quantitative Inorganic Analysis. 6<sup>th</sup> edition, Pearson education ltd 2002.
2. Practical Inorganic chemistry By G.Marr and R.W.Rockett 1972.
3. Experimental Inorganic/Physical Chemistry – An Investigative integrated approach to Practical Project work. By Mounir A.Malati, 1999.
4. Advanced experimental Inorganic chemistry by. Ayodhya Singh.
5. Practical Inorganic Chemistry by G. Pass & H. Sutchiffe, 2<sup>nd</sup> edn John Wiley & sons

**Paper CH 252 Organic Chemistry Lab 6 hours/ week****Identification of organic compounds systematic qualitative analysis:**

Physical data BP / MP, Ignition test, solubility classification, Extra elements-N,S & Halogens, (Lassaigne sodium fusion test, Beilstein test)

Functional groups tests, Preparation of crystalline derivative and determination of their m.p.s and reference to literature to identify the compounds

A minimum of **8** following compounds to be studied as unknown covering atleast one from each of the solubility classes

Glucose, benzoic acid, 2-chloro benzoic Acid, Anisic acid, p-Nitrobenzoic acid; p-Cresol, p-Chlorophenol,  $\beta$ -Naphthol; Aniline, o/m/p-Chloroanilines; N-Methyl aniline/N-Ethylaniline, N,N-Dimethylaniline, Benzamide, Benzaldehyde, Anisaldehyde, Acetophenone, benzophenone, Ethylbenzoate, methylbenzoate, Nitrobenzene, chlorobenzene, bromobenzene, naphthalene, biphenyl anthracene.

**Identification of unknown organic compounds from their IR, UV,  $^1\text{H}$  nmr and MS:**

Analysis of recorded spectra of 6 compounds belonging to i) aromatic carboxylic acid ii) alcohols and phenols iii) aldehydes and ketones iv) amides v) esters vi) alkenes and alkynes

### References

1. Text book of practical organic chemistry, Vogel
2. Text book of practical organic chemistry, Mann and Saunders.
3. Spectral identification of organic compounds Bassler, Silverstein 5<sup>th</sup> Edition

### Paper CH 253: Physical Chemistry Lab: 6 hrs /week

Data analysis II: Mean and standard deviation; absolute and relative errors; linear regression; covariance and correlation coefficient.

#### *Distribution:*

- 1) Distribution of I<sub>2</sub> between hexanes / cyclo hexanes / CCl<sub>4</sub> and aq.KI solution- calculation of equilibrium constant.
- 2) Study of complex formation between ammonia and metal ion

#### **Chemical Kinetics**

- 1) Stoichiometry of peroxydisulphide- iodide reaction
- 2) Peroxydisulphide- iodide reaction: order w.r.t [I<sup>-</sup>] by isolation method
- 3) Peroxydisulphide- iodide reaction: order w.r.t [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] by initial rate method

#### **Conductometry:**

- 1) Titration of a mixture of strong and weak acids vs strong base
- 2) Determination of the hydrolysis constant of aniline hydrochloride
- 3) Determination of solubility product

#### **Potentiometry:**

- 1) Titration of Fe<sup>+2</sup> vs Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (redox titration)
- 2) Titration of Cl<sup>-</sup> vs Ag<sup>+</sup> (precipitation titration)
- 3) Determination of solubility product

#### **Polarimetry:**

- 1) Determination of specific rotation of glucose and fructose
- 2) Enzyme catalysed inversion of sucrose

#### **Colorimetry:**

- 1) Verification of Beer's law and calculation of molar absorption coefficient using CuSO<sub>4</sub> and KMnO<sub>4</sub> solutions

#### **pH metry:**

- 1) Calibration of a pH meter and measurement of pH of different solutions
- 2) Preparation of phosphate buffers
- 3) Titration of strong acid vs strong base

### References:

1. Senior Practical Physical Chemistry: B.D. Khosla, V.C. Garg and A. Khosla
2. Experimental Physical Chemistry: V. Athawale and P. Mathur.
3. Practical Physical Chemistry: B. Vishwanathan and P.S. Raghavan.
4. Practical in Physical Chemistry: P.S. Sindhu
5. Advanced Practical Physical chemistr: J.B.Yadav
6. Vogel Text book of Quantitative Analysis, 6<sup>th</sup> edition, Pearson education Ltd. 2002