



MANONMANIAM SUNDARANAR UNIVERISTY,  
TIRUNELVELI-12

## SYLLABUS

### PG - COURSES – AFFILIATED COLLEGES

Course Structure for M. Sc. Chemistry

(Choice Based Credit System)

(with effect from the academic year 2023-2024 onwards )



Semester-I				
Part	Subject Status	Subject Title	Subject Code	Credit
3	Core	ORGANIC REACTION MECHANISM-I		4
3	Core	STRUCTURE AND BONDING IN INORGANIC COMPOUNDS		4
3	Practical	ORGANIC CHEMISTRY PRACTICAL I		3
3	Practical	PHYSICAL CHEMISTRY PRACTICAL I		3
3	Elective I	(GENERIC / DISCIPLINE SPECIFIC) (ONE FROM GROUP A) PHARMACEUTICAL CHEMISTRY/ NANOMATERIALS AND NANOTECHNOLOGY		3
3	Elective II	(GENERIC / DISCIPLINE SPECIFIC) (ONE FROM GROUP B) ELECTROCHEMISTRY/ MOLECULAR SPECTROSCOPY		3



**Total Marks: 100 Internal Exam: 25 marks + External Exam: 75 marks**

**A. Scheme for internal Assessment:**

Maximum marks for written test: **15 marks**

**3 internal tests**, each of **1 hour** duration shall be conducted every semester.

To the average of the **best two** written examinations must be added the marks scored in. The **assignment** for 5 marks and Seminar for 5 marks

The break up for internal assessment shall be:

Written test- 15 marks; Assignment -5 marks; Seminar-5 Marks Total - 25 marks

**B. Scheme of External Examination**

**3 hrs.** examination at the end of the semester

A – Part : 1 mark question two - from each unit

B – Part : 5 marks question one - from each unit

C – Part : 8 marks question one - from each unit

➤ **Conversion of Marks into Grade Points and Letter Grades**

S.No.	Percentage of Marks	Letter Grade	Grade Point	Performance
1	90 - 100	O+	10	Outstanding
2	80 - 89	O	9	Excellent
3	70 - 79	A+	8	Very Good
4	60 - 69	A	7	Good
5	55 - 59	B+	6	Above Average
6	50 - 54	B	5	Pass
7	0 - 49	RA	-	ReAppear
8	Absent	AA	-	Absent

➤ **Cumulative Grade Point Average (CGPA)**

$$\text{CGPA} = \frac{\Sigma (\text{GP} \times \text{C})}{\Sigma \text{C}}$$

- **GP** = Grade point, **C** = Credit
- CGPA is calculated only for Part-III courses
- CGPA for a semester is awarded on cumulative basis

➤ **Classification**

- a) First Class with Distinction : CGPA  $\geq 7.5^*$
- b) First Class : CGPA  $\geq 6.0$
- c) Second Class : CGPA  $\geq 5.0$  and  $< 6.0$
- d) Third Class : CGPA  $< 5.0$



# ORGANIC REACTION MECHANISM - I

## Objectives of the course

- To understand the feasibility and the mechanism of various organic reactions.
- To comprehend the techniques in the determination of reaction mechanisms.
- To understand the concept of stereochemistry involved in organic compounds.
- To correlate and appreciate the differences involved in the various types of organic reaction mechanisms.
- To design feasible synthetic routes for the preparation of organic compounds.

## UNIT - I

**Methods of Determination of Reaction Mechanism:** Reaction intermediates, The transition state, Reaction coordinate diagrams, Thermodynamic and kinetic requirements of reactions: Hammond postulate. **Methods of determining mechanism:** Kinetic methods of determination: Rate law – Primary and secondary isotope effect. Non- Kinetic methods of determination: Testing and Trapping of intermediates, Isotopic labeling, Cross-over experiment, Product analysis and stereochemical evidence.

Effect of structure on reactivity: Hammett and Taft equations. Linear free energy relationship, partial rate factor, substituent and reaction constants.

## UNIT - II

### Aromatic and Aliphatic Electrophilic Substitution:

**Aromaticity:** Aromaticity in benzenoid, non-benzenoid, heterocyclic compounds and annulenes.

**Aromatic electrophilic substitution:** Orientation and reactivity of di- and polysubstituted phenol, nitrobenzene and halobenzene. Reactions involving nitrogen electrophiles: nitration, nitrosation and diazonium coupling; Sulphur electrophiles: sulphonation; Halogen electrophiles: chlorination and bromination; Carbon electrophiles: Friedel-Crafts alkylation, acylation and arylation reactions.

**Aliphatic electrophilic substitution Mechanisms:**  $S_N2$  and  $S_N1$ ,  $S_Ni$ - Mechanism and evidences.

## UNIT - III Aromatic and Aliphatic Nucleophilic Substitution:

**Aromatic nucleophilic substitution:** Mechanisms -  $S_NAr$ ,  $S_N1$  and Benzyne mechanisms - Evidences - Reactivity, Effect of structure, leaving group and attacking nucleophile. Reactions: Oxygen and Sulphur-nucleophiles, Bucherer and Rosenmund reactions, Von Richter, Sommelet- Hauser and Smiles rearrangements.

**Aliphatic nucleophilic substitutions:**  $S_N1$ , ion pair,  $S_N2$  mechanisms and evidences. Aliphatic nucleophilic substitutions at an allylic carbon, aliphatic trigonal carbon and vinyl carbon.  $S_N1$ ,  $S_N2$ ,  $S_Ni$  mechanism and evidences, Swain- Scott, Grunwald-Winstein relationship - Ambident nucleophiles.

## UNIT - IV

**Stereochemistry-I:** Introduction to molecular symmetry and chirality – axis, plane, center, alternating axis of symmetry. Optical isomerism due to asymmetric and dissymmetric molecules with C, N, S based chiral centers. Optical purity, prochirality,



enantiotopic and diastereotopic atoms, groups, faces, axial and planar chirality, chirality due to helical shape, methods of determining the configuration.

Racemic modifications: Racemization by thermal, anion, cation, reversible formation, epimerization, mutarotation. D, L system, Cram's and Prelog's rules: R, S-notations, proR, proS, side phase and re phase Cahn-Ingold-Prelog rules, absolute and relative configurations. Configurations of allenes, spiranes, biphenyls, cyclooctene, helicene, binaphthyls, ansa and cyclophanic compounds, exo-cyclic alkylidene-cycloalkanes. Topicity and prostereoisomerism, chiral shift reagents and chiral solvating reagents. Criteria for optical purity: Resolution of racemic modifications, asymmetric transformations, asymmetric synthesis, destruction. Stereoselective and stereospecific synthesis.

## UNIT - V

**Stereochemistry-II:** Conformation and reactivity of acyclic systems, intramolecular rearrangements, neighbouring group participation, chemical consequence of conformational equilibrium - Curtin-Hammett Principle. Stability of five and six-membered rings: mono-, di- and polysubstituted cyclohexanes, conformation and reactivity in cyclohexane systems. Fused and bridged rings: bicyclic, poly cyclic systems, decalins and Brett's rule.

Optical rotation and optical rotatory dispersion, conformational asymmetry, ORD curves, octant rule, configuration and conformation, Cotton effect, axial haloketone rule and determination of configuration.

### Recommended Text

1. J. March and M. Smith, Advanced Organic Chemistry, 5th edition, John-Wiley and Sons. 2001.
2. E. S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston Inc., 1959.
3. P. S. Kalsi, Stereochemistry of carbon compounds, 8th edition, New Age International Publishers, 2015.
4. P. Y. Bruice, Organic Chemistry, 7th edn, Prentice Hall, 2013.
5. J. Clayden, N. Greeves, S. Warren, Organic Compounds, 2nd edition, Oxford University Press, 2014.

### Reference Books

1. F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry Part A and B, 5th edition, Kluwer Academic / Plenum Publishers, 2007.
2. G. Morris, Stereochemistry, RSC Tutorial Chemistry Text 1, 2001.
3. N.S. Isaacs, Physical Organic Chemistry, ELBS, Longman, UK, 1987.
4. L. Eliel, Stereochemistry of Carbon Compounds, Tata-McGraw Hill, 2000. I. L. Finar, Organic chemistry, Vol-1 & 2, 6th edition, Pearson Education Asia, 2004.

### Website and e-learning source

1. <https://sites.google.com/site/chemistryebookscollection02/home/organic-chemistry/organic>
2. <https://www.organic-chemistry.org/>



# STRUCTURE AND BONDING IN INORGANIC COMPOUNDS

## Objectives of the course

- To determine the structural properties of main group compounds and clusters.
- To gain fundamental knowledge on the structural aspects of ionic crystals.
- To familiarize various diffraction and microscopic techniques.
- To study the effect of point defects and line defects in ionic crystals.
- To evaluate the structural aspects of solids.

## UNIT - I

### CHEMICAL BONDING

**Valence Bond theory:** Lewis structure – Concepts and VB theory of H<sub>2</sub> molecule - Stereochemistry of hybrid orbitals – Calculation of s and p characters of equivalence and nonequivalence of hybrid orbitals - VSEPR theory.

**M.O. theory** – Linear combination of Atomic orbitals ( s – s, s – p, d – p, p – p and d – d overlapping) –  $\sigma$ ,  $\pi$ ,  $\delta$  and quadruple bond. – M.O. diagrams of hetero nuclear diatomic molecules (CO, NO, HF) and triatomic molecules (BeH<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>) – Walsh diagrams – Structure and hybridization - Bents rule and apicophilicity.

**Ionic Bond:** Lattice energy - Born- Lande equation, Born Haber cycle and Kapustinskii equation.

## UNIT - II

**Structure of main group compounds and clusters:** Structure of silicates - applications of Pauling's rule of electrovalence - isomorphous replacements in silicates – ortho, meta and pyro silicates – one dimensional, two dimensional and three-dimensional silicates. Structure of silicones, Structural and bonding features of B-N, S-N and P-N compounds; Poly acids – types, examples and structures; Borane cluster: Structural features of closo, nido, arachano and klado; carboranes, hetero and metalloboranes; Wade's rule to predict the Structure of borane cluster; main group clusters – zintl ions.

## UNIT – III

**Solid state chemistry – I:** Ionic crystals: Packing of ions in simple, hexagonal and cubic close packing, voids in crystal lattice, Radius ratio, Crystal systems and Bravais lattices, Symmetry operations in crystals, glide planes and screw axis; point group and space group; X-ray diffraction technique: Bragg's law, Powder diffraction method – Principle and Instrumentation.

## UNIT - IV

**Solid state chemistry – II:** Structural features of the crystal systems: Rock salt, zinc blende & wurtzite, fluorite and anti-fluorite, rutile and anatase, cadmium iodide and nickel arsenide; Spinels -normal and inverse types and perovskite structures. Crystal Growth methods: From melt and solution (hydrothermal, sol-gel methods) – principles and examples.



**UNIT – V****Band theory and defects in solids**

Band theory – features and its application of conductors, insulators and semiconductors, Intrinsic and extrinsic semiconductors; Defects in crystals – point defects (Schottky, Frenkel, metal excess and metal deficient) and their effect on the electrical and optical property, laser and phosphors; Linear defects and its effects due to dislocations.

**Recommended Text**

1. A R West, Solid state Chemistry and its applications, 2nd Edition (Students Edition), John Wiley & Sons Ltd., 2014.
2. A K Bhagi and G R Chatwal, A textbook of inorganic polymers, Himalaya Publishing House, 2001.
3. L Smart, E Moore, Solid State Chemistry – An Introduction, 4th Edition, CRC Press, 2012.
4. K. F. Purcell and J. C. Kotz, Inorganic Chemistry; W.B. Saunders company: Philadelphia, 1977.
5. J. E. Huheey, E. A. Keiter and R. L. Keiter, Inorganic Chemistry; 4th ed.; Harper and Row: New York, 1983.

**Reference Books**

1. D.E. Douglas, D.H. McDaniel and J. J. Alexander, Concepts and Models in Inorganic Chemistry, 3rd Ed, 1994.
2. R J D Tilley, Understanding Solids - The Science of Materials, 2nd edition, Wiley Publication, 2013.
3. C N R Rao and J Gopalakrishnan, New Directions in Solid State Chemistry, 2nd Edition, Cambridge University Press, 199.
4. T. Moeller, Inorganic Chemistry, A Modern Introduction; John Wiley: New York, 1982.
5. D.F. Shriver, P. W. Atkins and C.H. Langford; Inorganic Chemistry; 3rd ed.; Oxford University Press: London, 2001.

**Website and e-learning source**

1. [https://ocw.mit.edu/courses/3-091-introduction-to-solid-state-chemistry-fall-2018/video\\_galleries/lecture-videos/](https://ocw.mit.edu/courses/3-091-introduction-to-solid-state-chemistry-fall-2018/video_galleries/lecture-videos/)



# ORGANIC CHEMISTRY PRACTICAL

## Objectives of the course

- To understand the concept of separation, qualitative analysis and preparation of organic compounds.
- To develop analytical skill in the handling of chemical reagents for separation of binary and ternary organic mixtures.
- To analyze the separated organic components systematically and derivative them suitably.

## Course Outline

A. Qualitative analysis of Organic mixture (atleast six two component mixtures):

- Separation of organic mixtures
- Elemental analysis
- Functional group(s) identification
- Preparation of derivatives
- Physical properties determination (melting point and boiling point) for both components and their derivatives.

Analysis may be performed in micro (or) macro scale depending upon the conditions of the laboratory.

## B. For Class work:

Three component mixtures (Separation)

## Recommended Text

1. A.I. Vogel, Elementary Practical Organic Chemistry: Small Scale Preparations, Qualitative Organic Analysis, Quantitative Organic Analysis, Pearson Education, 2011.
2. K.Bansal Raj, Laboratory Manual of Organic Chemistry, New Age International, 2009.
3. V.Venkateswaran, R. Veeraswamy and A. R. Kulandaivelu, Basic Principles of Practical Chemistry, Sultan Chand & Sons, 2004.
4. V.K. Ahluwalia, and R. Aggarwal, Comprehensive Practical Organic Chemistry, Universities Press, 2004

## Reference Books

1. R.G. Engel, D.L. Pavia, G.M. Lampman and G.S. Kriz, A Microscale approach to Organic Laboratory, 5th edition, Paperback – International Edition, 2012.
2. P.B. Cranwell, L.M. Harwood, and C. J. Moody, Experimental Organic Chemistry, 3rd edn, Wiley-Blackwell, 2017.
3. J.Leonard, B. Lygo and G. Procter, Advanced Practical Organic Chemistry, 3rd edn, CRC Press, 2013.

## Website and e-learning source

1. [https://ocw.mit.edu/courses/3-091-introduction-to-solid-statechemistry-fall-2018/video\\_galleries/lecture-videos/](https://ocw.mit.edu/courses/3-091-introduction-to-solid-statechemistry-fall-2018/video_galleries/lecture-videos/)



# PHYSICAL CHEMISTRY PRACTICAL

## Objectives of the course

- To understand the principle of conductivity experiments through conductometric titrations.
- To evaluate the order of the reaction, temperature coefficient and activation energy of the reaction by following pseudo first order kinetics.
- To construct the phase diagram of two component system forming congruent melting solid and find its eutectic temperatures and compositions.

## Course Outline

### UNIT-I: Conductivity Experiments

1. Determination of equivalent conductance of a strong electrolyte & the verification of DHO equation.
2. Verification of Ostwald's Dilution Law & Determination of pKa of a weak acid.
3. Verification of Kohlrausch's Law for weak electrolytes.
4. Determination of the equivalent conductance of a weak acid at different concentrations and verifying Ostwald dilution law.
5. Calculation of the dissociation constant of the acid. Determination of the equivalent conductance of a strong electrolyte at different concentrations and examining the validity of the Onsager's theory as limiting law at high dilutions.
6. Conductometric titration of a mixture of HCl and CH<sub>3</sub>COOH Vs NaOH.
7. Conductometric titration of NH<sub>4</sub>Cl Vs NaOH.
8. Conductometric titration of CH<sub>3</sub>COONa Vs HCl.

### UNIT-II: Kinetics

1. Study the kinetics of acid hydrolysis of an ester; determine the temperature coefficient and also the activation energy of the reaction.
2. Study the kinetics of the reaction between acetone and iodine in acidic medium by half-life method and determine the order with respect to iodine and acetone.

### UNIT-III: Phase diagram

Construction of phase diagram for a simple binary system

1. Naphthalene-phenanthrene
2. Benzophenone- diphenyl amine.

### Recommended Text

1. B.Viswanathan and P.S.Raghavan, Practical Physical Chemistry, Viva Books, New Delhi, 2009.
2. Sundaram, Krishnan, Raghavan, Practical Chemistry (Part II), S. Viswanathan Co. Pvt., 1996.
3. V.D. Athawale and Parul Mathur, Experimental Physical Chemistry, New Age International (P) Ltd., New Delhi, 2008.
4. E.G. Lewers, Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics, 2nd Ed., Springer, New York, 2011.

### Reference Books

1. J.B.Yadav, Advanced Practical Physical Chemistry, Goel Publishing House, 2001.
2. G.W.Garland, J.W. Nibler, D.P. Shoemaker, Experiments in Physical Chemistry, 8th edition, McGraw Hill, 2009.
3. J.N.Gurthu and R. Kapoor, Advanced Experimental Chemistry, S. Chand and Co., 1987.
4. Shailendra K Sinha, Physical Chemistry: A laboratory Manual, Narosa Publishing House Pvt, Ltd., New Delhi, 2014.
5. F.Jensen, Introduction to Computational Chemistry, 3rd Ed., Wiley- Blackwell.

### Website and e-learning source

1. [https://web.iitd.ac.in/~nkurur/2015-16/Isem/cmp511/lab\\_handout\\_new.pdf](https://web.iitd.ac.in/~nkurur/2015-16/Isem/cmp511/lab_handout_new.pdf)





## PHARMACEUTICAL CHEMISTRY

### Objectives of the course

- To understand the advanced concepts of pharmaceutical chemistry.
- To recall the principle and biological functions of various drugs.
- To train the students to know the importance as well the consequences of various drugs.
- To have knowledge on the various analysis and techniques.
- To familiarize on the drug dosage and its structural activities.

### UNIT - I

**Physical properties in Pharmaceuticals:** Physical properties of drug molecule: physical properties. Refractive index- Definition, explanation, formula, importance, determination, specific & molar refraction. Optical activity\rotation- monochromatic & polychromatic light, optical activity, angle of rotation, specific rotation examples, measurement of optical activity. Dielectric constant & Induced Polarization- Dielectric constant explanation & determination. Rheology of pharmaceutical systems: Introduction, Definition, Applications, concept of viscosity, Newton's law of flow, Kinematic, Relative, Specific, Reduced & Intrinsic viscosity. Newtonian system, non-Newtonian system- Plastic flow, Pseudoplastic flow, Dilatent flow. Viscosity measurements- selection of viscometer for Newtonian and non-Newtonian system.

### UNIT - II

**Isotopic Dilution analysis:** principle and applications, Neutron activation analysis: Principle, advantages and limitations, Scintillation counters: Body scanning. Introduction to radiopharmaceuticals. Properties of various types of radiopharmaceuticals, Radiopharmaceuticals as diagnostics, as therapeutics, for research and sterilization. Physico Chemical Properties and drug action. Physico chemical properties of drugs (a) Partition coefficient, (b) solubility (c) surface activity, (d) degree of ionization.

### UNIT - III

**Drug dosage and product development:** Introduction to drug dosage Forms & Drug Delivery system – Definition of Common terms. Drug Regulation and control, pharmacopoeias formularies, sources of drug, drug nomenclature, routes of administration of drugs products, need for a dosage form, classification of dosage forms.

### UNIT – IV

#### Development of new drugs:

Introduction, procedure followed in drug design, the research for lead compounds, molecular modification of lead compounds. Structure-Activity Relationship (SAR): Factors effecting bioactivity, resonance, inductive effect, isoterism, bioisosterism, spatial considerations, biological properties of simple functional groups, theories of drug activity, occupancy theory, rate theory, induced-fit theory. Quantitative structure activity relationship(QSAR): Development of QSAR, drug receptor



interactions, the additivity of group contributions, physico-chemical parameters, lipophilicity parameters, electronic parameter, ionization constants, steric parameters, chelation parameters, redox potential, indicator-variables.

## UNIT - V

**Computers in Pharmaceutical Chemistry:** Need of computers for chemistry. Computers for Analytical Chemists- Molecular Docking – Selection of binding protein – RCSB – Druglikeness of the ligand – ADMET properties – Detection using online servers – AutoDock Vina – Methods and Result analysis – Visualization of the Ligand-Protein interaction.

### Recommended Text

1. Physical Chemistry- Bahl and Tuli.
2. Text Book of Physical Pharmaceutics, IInd edition, Vallabh Prakashan-. C.V.S. Subramanyam.
3. Medicinal Chemistry (Organic Pharmaceutical Chemistry), G.R Chatwal, Himalaya Publishing house.
4. Instrumental method of Analysis: Hubert H, Willard, 7th edition.
5. Textbook of Pharmaceutical Chemistry by, Jayshree Ghosh, S. Chand & company Ltd. Pharmaceutical Chemistry by Dr. S. Lakshmi, Sultan chand & Sons.

### Reference Books

1. Computers in chemistry, K.V. Raman, Tata Mc.Graw-Hill, 1993.
2. Computers for Chemists, S.K Pundir, Anshu bansal, A pragate prakashan., 2 nd edition, New age international (P) limited, New Delhi.
3. Physical Pharmacy and Pharmaceutical Sciences by Martins, Patrick J. Sinko, Lippincott. William and Wilkins.
4. Cooper and Gunn's Tutorial Pharmacy ,6th edition by S.J. Carter, CBS Publisher Ltd.
5. Ansels pharmaceutical Dosage forms and Drug Delivery System by Allen Popvich and Ansel, Indian edition-B.I. Publication Pvt. Ltd.

### Website and e-learning source

1. <https://www.ncbi.nlm.nih.gov/books/NBK482447/>
2. <https://training.seer.cancer.gov/treatment/chemotherapy/types.html>



# NANO MATERIALS AND NANO TECHNOLOGY

## Objectives of the course

- To understand the concept of nano materials and nano technology.
- To understand the various types of nano materials and their properties.
- To understand the applications of synthetically important nano materials.
- To correlate the characteristics of various nano materials synthesized by new technologies.
- To design synthetic routes for synthetically used new nano materials.

## UNIT – I

**Introduction of nanomaterials and nanotechnologies:** Introduction-role of size, classification-0D, 1D, 2D, 3D. Consolidation of Nano powders. Features of nanostructures, Background of nanostructures. Techniques of synthesis of nanomaterials - Bottom –Up, Top–Down, Tools of the nanoscience. Applications of nanomaterials and technologies.

## UNIT - II

**Synthetic Methods:** Bonding and structure of the nanomaterials, Predicting the Type of Bonding in a Substance crystal structure. Metallic nanoparticles, Surfaces of Materials, Nanoparticle Size and Properties. Synthesis- Physical and chemical methods - inert gas condensation, arc discharge, laser ablation, sol-gel, solvothermal and hydrothermal-CVD-types, metallo organic, plasma enhanced, and low-pressure CVD. Microwave assisted and electrochemical synthesis.

## UNIT – III

**Mechanical Properties of Nanomaterials:** Mechanical properties of materials, theories relevant to mechanical properties. Techniques to study mechanical properties of nanomaterials, adhesion and friction, thermal properties of nanomaterials Nanoparticles: gold and silver, metal oxides: silica, iron oxide and alumina - synthesis and properties.

## UNIT - IV

**Electrical Properties of Nanomaterials:** Electrical properties, Conductivity and Resistivity, Classification of Materials based on Conductivity, magnetic properties, electronic properties of materials. Classification of magnetic phenomena. Semiconductor materials – classification-Ge, Si, GaAs, SiC, GaN, GaP, CdS,PbS. Identification of materials as p and n –type semiconductor-Hall effect - quantum and anomalous, Hall voltage - interpretation of charge carrier density. Applications of semiconductors: p-n junction as transistors and rectifiers, photovoltaic and photogalvanic cell.

## UNIT - V

**Nano Composites:** Nano thin films, nanocomposites. Application of nanoparticles in different fields. Core-shell nanoparticles - types, synthesis, and properties. Nanocomposites - metal-, ceramic- and polymer-matrix composites-applications.



Characterization – SEM, TEM and AFM - principle, instrumentation and applications.

### Recommended Text

1. S. Mohan and V. Arjunan, Principles of Materials Science, MJP Publishers, 2016.
2. Arumugam, Materials Science, Anuradha Publications, 2007.
3. Giacavazzo et. al., Fundamentals of Crystallography, International Union of Crystallography. Oxford Science Publications, 2010
4. Woolfson, An Introduction to Crystallography, Cambridge University Press, 2012.
5. James F. Shackelford and Madanapalli K. Muralidhara, Introduction to Materials Science for Engineers. 6th ed., PEARSON Press, 2007.

### Reference Books

1. S. Mohan and V. Arjunan, Principles of Materials Science, MJP Publishers, 2016.
2. Arumugam, Materials Science, Anuradha Publications, 2007.
3. Giacavazzo et. al., Fundamentals of Crystallography, International Union of Crystallography. Oxford Science Publications, 2010
4. Woolfson, An Introduction to Crystallography, Cambridge University Press, 2012.
5. James F. Shackelford and Madanapalli K. Muralidhara, Introduction to Materials Science for Engineers. 6th ed., PEARSON Press, 2007.

## ELECTROCHEMISTRY

### Objectives of the course

- To understand the behavior of electrolytes in terms of conductance, ionic atmosphere, interactions.
- To familiarize the structure of the electrical double layer of different models.
- To compare electrodes between current density and over potential.
- To discuss the mechanism of electrochemical reactions.
- To highlight the different types of over voltages and its applications in electroanalytical techniques.

### UNIT - I

**Ionics:** Arrhenius theory -limitations, van't Hoff factor and its relation to colligative properties. Deviation from ideal behavior. Ionic activity, mean ionic activity and mean ionic activity coefficient-concept of ionic strength, Debye Huckel theory of strong electrolytes, activity coefficient of strong electrolytes Determination of activity coefficient ion solvent and ion-ion interactions. Born equation. Debye-Huckel Bjerrum model. Derivation of Debye-Huckel limiting law at appreciable concentration of electrolytes modifications and applications. Electrolytic conduction-Debye-Huckel



Onsager treatment of strong electrolyte-qualitative and quantitative verification and limitations. Evidence for ionic atmosphere. Ion association and triple ion formations.

## UNIT - II

**Electrode-electrolyte interface:** Interfacial phenomena -Evidences for electrical double layer, polarizable and non-polarizable interfaces, Electrocapillary phenomena - Lippmann equation electro capillary curves. Electro-kinetic phenomena electro-osmosis, electrophoresis, streaming and sedimentation potentials, colloidal and poly electrolytes. Structure of double layer: Helmholtz -Perrin, Guoy- Chapman and Stern models of electrical double layer. Zeta potential and potential at zero charge. Applications and limitations.

## UNIT - III

**Electrodics of Elementary Electrode Reactions:** Behavior of electrodes: Standard electrodes and electrodes at equilibrium. Anodic and Cathodic currents, condition for the discharge of ions. Nernst equation, polarizable and non-polarizable electrodes. Model of three electrode system, over potential. Rate of electro chemical reactions: Rates of simple elementary reactions. Butler-Volmer equation-significance of exchange current density, net current density and symmetry factor. Low and high field approximations. symmetry factor and transfer coefficient Tafel equations and Tafel plots.

## UNIT - IV

**Electrodics of Multistep Multi Electron System:** Rates of multi-step electrode reactions, Butler - Volmer equation for a multi-step reaction. Rate determining step, electrode polarization and depolarization. Transfer coefficients, its significance and determination, Stoichiometric number. Electro-chemical reaction mechanisms-rate expressions, order, and surface coverage. Reduction of  $I_3^-$ ,  $Fe^{2+}$ , and dissolution of Fe to  $Fe^{2+}$ . Overvoltage - Chemical and electro chemical, Phase, activation and concentration over potentials. Evolution of oxygen and hydrogen at different pH. Pourbiax and Evan's diagrams.

## UNIT - V

**Concentration Polarization, Batteries and Fuel cells:** Modes of Transport of electro active species - Diffusion, migration and hydrodynamic modes. Role of supporting electrolytes. Polarography-principle and applications. Principle of square wave polarography. Cyclic voltammetry- anodic and cathodic stripping voltammetry and differential pulse voltammetry. Sodium and lithium-ion batteries and redox flow batteries.

Energy production systems: Fuel Cells: classification, alkaline fuel cells, phosphoric acid fuel cells, high temperature fuel cells.

## Recommended Text

1. D.R. Crow, Principles and applications of electrochemistry, 4th edition, Chapman & Hall/CRC, 2014.
2. J. Rajaram and J.C. Kuriakose, Kinetics and Mechanism of chemical



transformations Macmillan India Ltd., New Delhi, 2011.

3. S. Glasstone, Electro chemistry, Affiliated East-West Press, Pvt., Ltd., New Delhi, 2008.
4. Viswanathan, S. Sundaram, R. Venkataraman, K. Rengarajan and P.S. Raghavan, Electrochemistry-Principles and applications, S. Viswanathan Printers, Chennai, 2007.
5. Joseph Wang, Analytical Electrochemistry, 2nd edition, Wiley, 2004.

### Reference Books

1. J.O.M. Bockris and A.K.N. Reddy, Modern Electro chemistry, vol.1 and 2B, Springer, Plenum Press, New York, 2008.
2. J.O.M. Bockris, A.K.N. Reddy and M.G. Aldeco Morden Electro chemistry, vol. 2A, Springer, Plenum Press, New York, 2008.
3. Philip H. Rieger, Electrochemistry, 2nd edition, Springer, New York, 2010.
4. L.I. Antropov, Theoretical electrochemistry, Mir Publishers, 1977.
5. K.L. Kapoor, A Text book of Physical chemistry, volume-3, Macmillan, 2001.

### Website and e-learning source

1. <https://www.pdfdrive.com/modern-electrochemistry-e34333229>

## MOLECULAR SPECTROSCOPY

### Objectives of the course

- To understand the influence of rotation and vibrations on the spectra of the polyatomic molecules.
- To study the principle of Raman spectroscopy, ESR spectroscopy, EPR spectroscopy and fragmentation patterns in Mass spectroscopy.
- To highlight the significance of Franck-Condon principle to interpret the selection rule, intensity and types of electronic transitions.
- To interpret the first and second order NMR spectra in terms of splitting and coupling patterns using correlation techniques such as COSY, HETCOR, NOESY.
- To carry out the structural elucidation of molecules using different spectral techniques.

### UNIT - I

**Rotational and Raman Spectroscopy:** Rotational spectra of diatomic and polyatomic molecules. Intensities of rotational spectral lines, effect of isotopic substitution. Non-rigid rotators. Classical theory of the Raman effect, polarizability as a tensor, polarizability ellipsoids, quantum theory of the Raman effect, Pure rotational Raman spectra of linear and asymmetric top molecules, Stokes and anti-Stokes lines. Vibrational Raman spectra, Raman activity of vibrations, rule of mutual exclusion,



rotational fine structure-O and S branches, Polarization of Raman scattered photons.

## UNIT - II

**Vibrational Spectroscopy:** Vibrations of molecules, harmonic and anharmonic oscillators- vibrational energy expression, energy level diagram, vibrational wave functions and their symmetry, selection rules, expression for the energies of spectral lines, computation of intensities, hot bands, effect of isotopic substitution. Diatomic vibrating rotor, vibrational-rotational spectra of diatomic molecules, P, R branches, breakdown of the Born-Oppenheimer approximation. Vibrations of polyatomic molecules – symmetry properties, overtone and combination frequencies. Influence of rotation on vibrational spectra of polyatomic molecule, P, Q, R branches, parallel and perpendicular vibrations of linear and symmetric top molecules.

## UNIT - III

**Electronic spectroscopy:** Electronic Spectroscopy: Electronic spectroscopy of diatomic molecules, Frank-Condon principle, dissociation and predissociation spectra.  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  transitions and their selection rules. Photoelectron Spectroscopy: Basic principles, photoelectron spectra of simple molecules, X-ray photoelectron spectroscopy (XPS). Lasers: Laser action, population inversion, properties of laser radiation, examples of simple laser systems.

## UNIT – IV

**NMR and ESR spectroscopy:** Chemical shift, Factors influencing chemical shifts: electronegativity and electrostatic effects; Mechanism of shielding and deshielding. Spin systems: First order and second order coupling of AB systems, Simplification of complex spectra. Spin-spin interactions: Homonuclear coupling interactions - AX, AX<sub>2</sub>, AB types. Vicinal, germinal and long-range coupling-spin decoupling. Nuclear Overhauser effect (NOE), Factors influencing coupling constants and Relative intensities. <sup>13</sup>C NMR and structural correlations, Satellites. Brief introduction to 2D NMR – COSY, NOESY. Introduction to <sup>31</sup>P, <sup>19</sup>F NMR.

**Mass Spectrometry:** Ionization techniques- Electron ionization (EI), chemical ionization (CI), desorption ionization (FAB/MALDI), electrospray ionization (ESI), isotope abundance, molecular ion, fragmentation processes of organic molecules, deduction of structure through mass spectral fragmentation, high resolution. Effect of isotopes on the appearance of mass spectrum.

Structural elucidation of organic compounds by combined spectral techniques.

## UNIT – V

### ESR and Mossbauer Spectroscopy

ESR spectroscopy Characteristic features of ESR spectra, line shapes and line widths; ESR spectrometer. The g value and the hyperfine coupling parameter (A), origin of hyperfine interaction. Interpretation of ESR spectra and structure elucidation of organic radicals using ESR spectroscopy; Spin orbit coupling and significance of g-tensors, zero/non-zero field splitting, Kramer's degeneracy, application to transition metal complexes (having one to five unpaired electrons) including biological molecules and inorganic free radicals. ESR spectra of magnetically dilute samples.



Principle of Mossbauer spectroscopy: Doppler shift, recoil energy. Isomer shift, quadrupole splitting, magnetic interactions. Applications: Mossbauer spectra of high and low-spin Fe and Sn compounds.

### Recommended Text

1. C.N. Banwell and E. M. McCash, Fundamentals of Molecular Spectroscopy, 4th Ed., Tata McGraw Hill, New Delhi, 2000.
2. R.M. Silverstein and F. X. Webster, Spectroscopic Identification of Organic Compounds, 6th Ed., John Wiley & Sons, New York, 2003.
3. W. Kemp, Applications of Spectroscopy, English Language Book Society, 1987.
4. D.H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, 4th Ed., Tata McGraw-Hill Publishing Company, New Delhi, 1988.
5. R.S. Drago, Physical Methods in Chemistry; Saunders: Philadelphia, 1992.

### Reference Books

1. P.W. Atkins and J. de Paula, Physical Chemistry, 7th Ed., Oxford University Press, Oxford, 2002.
2. I.N. Levine, Molecular Spectroscopy, John Wiley & Sons, New York, 1974.
3. A.Rahman, Nuclear Magnetic Resonance-Basic Principles, Springer-Verlag, New York, 1986.
4. K. Nakamoto, Infrared and Raman Spectra of Inorganic and coordination Compounds, Part B: 5th ed., John Wiley & Sons Inc., New York, 1997.
5. J.A. Weil, J. R. Bolton and J. E. Wertz, Electron Paramagnetic Resonance; Wiley Interscience, 1994.

### Website and e-learning source

1. [https://onlinecourses.nptel.ac.in/noc20\\_cy08/preview](https://onlinecourses.nptel.ac.in/noc20_cy08/preview)
2. <https://www.digimat.in/nptel/courses/video/104106122/L14.html>

