MANONMANIAM SUNDARANAR UNIVERSITY – TIRUNELVELI

PG **PROGRAMMES**

OPEN AND DISTANCE LEARNING(ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

M.Sc. CHEMISTRY

Semester	Course	Title of the Course	Course Code	Course Type
I	Core I	Organic Reaction Mechanism - I	SCHM11	Theory
	Core II	Structure and Bonding in Inorganic Compounds	SCHM12	Theory
	Core III	Organic Chemistry - Practical - I	SCHP11	Practical
	Core IV	Physical Chemistry - Practical	SCHP12	Practical
	Elective-I	Nano Materials and Nano Technology	SCHE11	Theory
	Elective-II	Molecular Spectroscopy	SCHE12	Theory

ORGANIC REACTION MECHANISM - I

Course Outline	**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 stereo chemical evidence. Effect of structure on reactivity: Hammett and Taft equations. Linear free energy relationship, 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, partial rate factor 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**: SE2 and SEi, SE1-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 Substitution**: 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' and 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.

STRUCTURE AND BONDING IN INORGANIC COMPOUNDS

Course Outline	**UNIT I - CHEMICAL BONDING** **Valence Bond theory**: Lewis structure – Concepts and VB theory of H_2 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) – σ , π ,δ and quadruple bond. – M.O. diagrams of hetero nuclear diatomic molecules (CO, NO, HF) and triatomic molecules (BeH_2, H_2O, CO_2) – 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 tructure 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; Linear defects and its effects due to dislocations and colour centers.
Recommended Text	1. A R West, Solid state Chemistry and its applications, 2ndEdition (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, 4^{th} 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: NewYork, 1983.

ORGANIC CHEMISTRY PRACTICAL-I

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, UniversitiesPress, 2004

PHYSICAL CHEMISTRY PRACTICAL

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_3COOH Vs NaOH. 7. Conductometric titration of NH_4Cl Vs NaOH. 8. Conductometric titration of CH_3COONa 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.

NANO MATERIALS AND NANO TECHNOLOGY

Course Outline	**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. 6^{th} ed., PEARSON Press, 2007.

MOLECULAR SPECTROS COPY

Course Outline	**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-Q 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, Xray photoelectron spectroscopy (XPS). Lasers: Laser action, population inversion, properties of laser radiation, examples of simple laser systems.
	UNIT-IV: NMR and Mass Spectrometry: 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, AX2, AB types. Vicinal, germinal and long-range coupling-spin decoupling. Nuclear Overhauser effect (NOE), Factors influencing coupling constants and Relative intensities. ^{13}C NMR and structural correlations – DEPT. Brief introduction to 2D NMR – COSY, NOESY and HETCOR. Introduction to ^{31}P, ^{19}F NMR. Mass Spectrometry: **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.