Central University of Himachal Pradesh

Dept. of Chemistry & Chemical Sciences

School of Physical & Material Sciences

Syllabus for Spring Semester 2020 for M.Sc. Chemistry 4th Semester

Detail Syllabi:

CCS 504- ORGANIC CHEMISTRY SPECIALIZATION III [Credit-4]

UNIT I: **Organometallic Chemistry of Transitional Elements**

Preparative structural and characteristic aspects. Bonding of hydrocarbon ligands, metallocenes, oxidative insertion, reductive elimination, ligand migration from metal to carbon; organometallics as electrophiles. Davies rules, catalytic nucleophilic addition and substitution, coupling reactions, Heck, Suzuki and Stille reactions, hydrogenation hydroformylation, carbonylation of methanol, oxidations, alkene polymerisation, Ziegler-Natta reaction, olefin metathesis, Tebbe's reagent, Pauson-Khand reaction, Volhardt cotrimerisation. Fluctional organometallic compounds. Chemistry and use of organo-derivatives of non-transitional metals- tin, thalium, mercury, lead.

UNIT II: **Synthetic Methodology II**

Organophosphorus compounds-Chemistry of organophosphorus compounds, phosphorus ylids and chiral phosphines.

Organosulphur compounds-Chemistry of organo sulphur compounds, sulphur stabilized anions and cations, sulphonium salts, sulphonium and sulphoxonium ylids, chiral sulphoxide.

Organosilicon compounds - Synthetic uses of silyl ethers, silylenol ethers, TMSCl, TMSI, TMSCN, alkene synthesis, alkynyl, vinyl, aryl, allyl and acylsilanes; Brook rearrangement, silicon Baeyer Villiger rearrangement

UNIT III: **Advanced Pericyclic Reactions**

General perturbation molecular orbital theory in cycloadditions : Reactivity, regioselectivity and periselectivity. Cheletropic reactions, 1,3-dipolar cycloadditions, cycloaddition involving more than 6 electrons, charged species, three-component and four component cycloadditions. Ene reactions, group-transfer reactions and eliminations. Electrocyclic reactions of charged systems (cations and anions) Sigmatropic rearrangements : [1,j] shifts-[1,5] and [1,7] carbon shifts in neutral systems and [1,4] shifts in charged species : [i,j] shifts- [3,3] shifts, fluctional molecules; [5,5] shifts, [2,3] shifts in ylids.

CCS 507- ORGANIC CHEMISTRY SPECIALIZATION VI (Credit-2)

Photo Organic Chemistry and Free Radical Reactions

UNIT I: **Photo Organic Chemistry:** Basic principles, Jablonsky diagram, exciplex, photochemistry of alkenes-intramolecular reactions of olefinic bond- geometrical isomerism, cyclization reactions, rearrangements of 1,4 and 1,5 dienes. Photochemistry of carbonyl compounds intramolecular reactions of saturated-, cyclic- and acyclic-, α,β-unsaturated- and γ,β-unsaturated carbonyl compounds, cyclohexadienones. Intramolecular cycloaddition reaction dimerization and oxetane formation. Norrish type I and type II reactions, di-pi-methane rearrangements. Photochemistry of aromatic compounds : isomerisation, addition and substitution reactions. Miscellaneous photochemical reactions. Photo-Fries reactions of anilides, Photo-Fries rearrangement, Barton reaction.

UNIT II: **Free Radical Reactions**: a) Methods of generation and detection of free radicals (trapping, ESR, NMR- CIDNP). b) Reactivity pattern of radicals, substitution and addition reactions, neighbouring group assistance. Reactivity of typical aromatic and aliphatic substractes at a bridge head, the effect of solvent on reactivity, oxidation of aldehydes to carboxylic acids, autooxidation, coupling of alkynes. Radical rearrangement. c) Radical cations and radical anions, single electron transfer reactions, SRN1 reactions.

CCS 531- PHYSICAL CHEMISTRY SPECIALIZATION VI (Credit-2)

Applications of NMR/ESR/Mossbauer Spectra

UNIT I: *NMR phenomenon*, spin ½ nuclei, (^{1}H, ^{13}C, ^{31}P and ^{19}F), ^{1}H NMR, Zeeman splitting, effect of magnetic field strength on sensitivity and resolution, chemical shift d, inductive and anisotropic effects on d, chemical structure correlations of d, chemical and magnetic equivalence of spins, spin-spin coupling, structural correlation to coupling constant J, first order patterns. Multinuclear NMR of B, Al, Si, F and P nuclei; structure and dynamics of representative inorganic molecules, deriving activation and thermodynamic parameters;

UNIT II: Introduction to 2D NMR: NOESY, COSY, HETCOR, HOMCOR, INADEQUATE, INDOR, INEPT for simple compounds and problems.

UNIT III: *ESR*: hyperfine splitting in various systems, factors affecting the magnitude of g-value, Anisotropy in the hyperfine coupling constants, zero-field splitting and Kramers' degeneracy, nuclear quadrupole interactions, Application.

UNIT IV: *Mössbauer*: Gamma ray emission and absorption by nuclei, Mössbauer effect, Isomer shift, quadrupole splitting, Application to the elucidation of structure and bonding of Fe^{III} and Fe^{II}, Sn^{IV} and Sn^{II} compounds, detection of oxidation states and inequivalent MB atoms.

CCS 564 Asymmetric Organic Catalysis Synthesis Credit: 2

UNIT I : Asymmetric catalysis

Asymmetry, Conditions for Asymmetry, Selectivity in organic synthesis, Specificity vs Selectivity, Methods for Obtaining Enantiopure Compounds,Introduction to asymmetric hydrogenation, important parameters in asymmetric hydrogenation. Chiral Pool, Asymmetric synthesis (Via Substitution Reactions)

Chiral Pool Synthesis , New Chiral Centres through Substitution Reactions , Synthesis of Unnatural Amino Acids, Synthesis of Natural Amino Acids, Chiral Auxiliary, Asymmetric Enolate Alkylation, Terminology of Chiral Auxiliary Approach to Asymmetric Synthesis. The significance of chirality and stereoisomeric discrimination.

UNIT II : Organocatalysis

General classification of the activation mode of several representative classes of molecules in organocatalysis., rganocatalysis categories, Asymmetric Counteranion Directed Catalysis, The Proline-Catalyzed Asymmetric Aldol Reaction: Scope, Mechanism and Consequences Organocatalytic Synthesis of Bioactive Natural Products, Assymetric oxidation Sharpless epoxidation, Jacobsen epoxidation, Organocatalysed Michael addition, Synthesis of anticancer thiazolone derivatives by organocatalytic aza-Mannich reaction, Cinchona Alkaloids.

UNIT III: Green Chemistry and catalysis

Atom efficient catalytic processes, classical aromatic chemistry, non-classical aromatic chemistry, two routes to hydroquinone, the development of organic synthesis, catalysis by solid acids and bases, catalytic oxidation, catalytic reduction, paracetamol intermediate via ammoximation, Enantioselective Catalysis , Hoechst-Celanese process for ibuprofen, Risky Reagents.

References:

1. Anastas P, Warner J. C. (Eds.), *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
2. Reetz M.T., List B., Jaroch S, *Organocatalysis* H. Weinmann 2007
3. Berkessel A, Gröger H (eds.) *Asymmetric Organocatalysis*. VCH, Weinheim) (2004)
4. Guo-qiang lin Yue-ming li Albert s. C. Chan *Principles and Applications of Asymmetric synthesis* Copyright (2001 by John Wiley & Sons, Inc.

CCS 527- PHYSICAL CHEMISTRY SPECIALIZATION II (Credit-4)

UNIT I: **Group Theory-Introduction**

Symmetry Elements and Point Group: Symmetry in nature, symmetry elements and symmetry operations. Symmetry properties of atomic orbitals. Elements of group theory. Elements of group theory: groups, subgroups, classes and characters, classes of symmetry operations, symmetry point groups; representation of groups by matrices. Representation of symmetry operator transformation of basis vector, Symmetry transformation of operators; The Great Orthogonality Theorem (without proof) and its consequences; construction and applications of character tables.

UNIT II: **Photochemistry**

Jablonski diagram, Fluorescence and phosphorescence, Delayed fluorescence, quantum yield, Mechanism and decay kinetics of photophysical processes. Fluorescence quenching (dynamic and static), Stern - Volmer equation. Energy transfer (Forster's dipole coupling), Proton transfer phenomenon, complex formation phenomenon (excimer, exciplex). Interaction of electromagnetic radiation with matter, Transition probabilities, Transition moment integral and its applications. Electric and megnetic dipole moments. Selection rules. Violation of Franck Condon principle, oscillator strength. Nature of transitions (e.g., n–π*, π–π*, d–d, charge transfer) solvent effect on absorption and emission spectra, Stoke's shift. Properties of electronically excited molecules: Life–time, redox potential, dipole moment, pK values. Potential energy diagram for donor acceptor system, Polarized luminescence.Crossing of potential energy surface (Franck-Condon factor). Adiabatic and non adiabatic cross over. Kasha's rule.

UNIT III: **Electrochemistry**

Ion Solvent interactions: Concept, experimental determination, application to equilibria, kinetics, universal scales of potential acidity and basicity in different solvents. Absolute heats of hydration (Halliwel & Nyburg Method). Solvation number and its determination. Ion-solvent-non-electrolyte interactions: Salting-in and salting-out phenomena. Structure of electrified interfaces, electrical double layers and 'zeta potential'.

Ion-Association: Bjerrum and Fuoss equation for ion-pair formation. Conductance minima, Ion-triplet, Ion-quadruplets; Walden's empirical rule and Fuoss treatment of conductance minima. Fuoss Shedlovsky's method of determination of association constant.

Ion-transport in solution: Limiting Debye Huckel-Onsager Expression. (Electrophoretic effect, Relaxation effect and time of relaxation). Transport number as a function of concentration. Wien Effect, Debye-Falkenhagen effect.

Rate equation for electrode processes; Kinetic derivation of the Nernst equation. Overvoltage. Butler- Volmer equation, Tafel equation, exchange current density. electrolytic conductance – Kohlrausch's law and its applications. Phenomenon of corrosion- electrochemical view

CCS 530- PHYSICAL CHEMISTRY SPECIALIZATION V (Credit-2)

Principles & Basic Instrumentation of NMR/ESR/NQR/Mossbauer Spectra

UNIT I: *Nuclear Magnetic Resonance (NMR) Spectroscopy*: Basic instrumentation, nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift, and its measurements, factors influencing chemical sift, deshielding, spin-spin interactions, factors influencing coupling constant `J`. Classification of molecules: (ABX, AMX, ABC, A2B2, etc. types), spin decoupling. FT NMR (qualitative idea) and its advantages, Applications of NMR in medical diagnosis.

UNIT II: *Electron Spin Resonance (ESR) Spectroscopy*: Basic principles, zero field splitting, and Kramer`s degeneracy, factors affecting the `g` value. Isotropic and anisotropic hyperfine coupling constants, spin densities and McConnell relationship.

UNIT IIII: *Nuclear Quadruple Resonance (NQR) Spectroscopy*: Quadrupole nuclei, quadrupole moments, electric field gradient, coupling constant, splitting and simple applications.

UNIT IV: *Mössbauer (MB) Spectroscopy*: Basic principle, instrumentation, spectral parameters and spectrum display, center shift, qudrupole and magnetic interactions.

Course Code: INORGANIC CHEMISTRY SPECIALIZATION -II
Course Code: CCS 515
Credit Hours =04

UNIT-I

Nuclear Magnetic Resonance Spectroscopy:- Introduction to Nuclear Magnetic Resonance, Chemical shift, Mechanism of electron shielding and factors contributing to the magnitude of chemical shift, Nuclear overhausser effect, Double resonance, Chemical exchange, Lanthanide shift reagents and NMR spectra of paramagnetic ions. Contact shifts. Factors contributing to the magnitude of chemical shift. Experimental technique(CW and FT).

Stereochemical non-rigidity and fluxionality: Introduction, use of NMR in its detection

UNIT-II

Nuclear Quadrupole Resonance Spectroscopy: Basic concepts of NQR (Nuclear electric quadrupole moment, Electric field gradient, Energy levels and NQR frequencies), Effect of magnetic field on spectra, Factors affecting the resonance signal (Line shape, position of resonance signal) Relationship between electric field gradient and molecular structure.

UNIT-III

Mössbauer Spectroscopy: Introduction**,** Principle, Conditions for Mössbauer Spectroscopy, parameters from Mössbauer Spectra, Isomer shift, Electric Quadrupole Interactions, Magnetic Interactions MB experiment, Application of MB spectroscopy in structural determination

Photo electron Spectroscopy: Basic Principle of Photo electron Spectroscopy.

UNIT-VI

Electron Spin Resonance Spectroscopy:-. Introduction, Similarities between ESR and NMR, Behaviour of a free electron in an external Magnetic Field, Basic Principle of an Electron Spin Resonance Spectrometer, Presentation of the spectrum, Hyperfine coupling in Isotropic Systems (methyl, benzene and Naphthalene radicals). Factors affecting the magnitude of g-values. Zero field splitting and Kramer's Degeneracy, Line width in solid state ESR, Double resonance technique in e.s.r. (ENDOR) Applications of ESR

UNIT-IV

Infrared Spectroscopy: Theory of IR absorption, Types of vibrations, Observed number of modes of vibrations, Intensity of absorption bands, Theoretical group frequencies, Factors affecting group frequencies and band shapes (Physical state, Vibrational Coupling, Electrical effects, Resonance, Inductive effects, Ring strain). Basic Principle of Raman Spectroscopy, Differences between IR and Raman spectra.

Course Name: INORGANIC CHEMISTRY SPECIALIZATION V
Course Code: **CCS 518**
Credit Hours:2

Unit –I Chemistry of Complex Equilibria:
Stability of Coordination Compounds Determination of stability constants by:
(i) Spectrophotometric methods (Job's method, Mole ratio and slope ratio method).
(ii) Bjerrum's method
(iii) Leden's method
(iv) Polarographic method
Factors affecting the stability constants (with special reference to metal and ligand ions).

Unit II Electro analytical methods: Polarography (NPP/DPP): Ilkovic equation, half wave potential and its significance; amperometric, coulometry, cyclic voltametry, ion-selective electrode.

Unit III Flame photometric techniques: AAS, AES, and atomic fluorescence methods, ICP techniques, Fluorimetric analysis. UV-VIS-spectrophotometric methods: Photometric titration, derivative spectrophotometry, simultaneous determination of two components in a mixture.

Unit IV Thermogravimatric analysis: Introduction, Factors affecting thermogravimetric curves, instrumentation, applications to inorganic compounds (analysis of binary mixtures i.e. Ca and Mg, TG curves of calcium oxalate,

Course code: CCS 520
Course name: INORGANIC CHEMISTRY SPECIALIZATION VII
Credit-2

UNIT I :Inorganic Photochemistry : Basic principles, Basic photochemical processes, Kashia's rule, Thexi state, Photochemical behaviour of transition metal complexes, charge transfer spectra, photochemical reactions of coordination compounds, oxidation-reduction reactions, Photo substitution reactions, Adamson's rules and photosubstitution reactions of cobalt(III) complexes and ruthenium (II) complexes

UNIT II: Inorganic Reactions and Mechanism: Substitution reactions in octahedral complexes, acid hydrolysis reactions, base hydrolysis and anation reactions, substitution reaction, reactions occurring without rupture of metal-ligand bond. Substitution reactions of square planar complexes. Theories of trans-effect and application, labile and inert complexes. Mechanism of redox reactions.

Course Code: CCS 558

Course Name: Advance Characterisation Techniques

Credit: 04

1. Scanning Electron Microscopy: Brief History, Interaction Volume, Electron-Specimen interaction, Elastic and Inelastic Scattering. Secondary Electrons: Generation, Properties and Use in sample analysis. Backscattered Electrons: Generation, Properties and Use in Sample Analysis.,. SEM Instrumentation and Imaging Modes. SEM Detectors. Field Emission SEM. Few Applications of SEM.
2. HR-TEM: Introduction and discussion of electron optics. TEM instrument, Electron scattering and diffraction. Practical uses of electron diffraction. Imaging in TEM with discussion of different imaging modes and image contrast. Brief discussion of High-resolution TEM and Scanning TEM with few discussions relevant to material and biological sciences.
3. Brief Introduction and History, Atomic Force Microscopy Instrumentation: Role and Function of Various Parts including Cantilevers and probes. Various modes of operations of AFM; Constant Force and Constant Height Mode of Operation, Contact, Non-Contact and Intermittent Contact Mode of operation with their limitations and applications. Detailed Discussion of Force Distance curves and its interpretation in image analysis. Applications of AFM in Physical and Material Sciences, Nanotechnology and Biological Sciences and Few Industrial Applications.
4. Brief Introduction to X-rays, generation and properties, X-ray diffraction by crystals. Crystal structure and Bragg's Law. X-ray diffraction methods like powder and single crystal method. Study of various factors related to crystal and electron density maps.

CCS 506- ORGANIC CHEMISTRY SPECIALIZATION V (Credit-2)

UNIT I: Oxidation reactions

Oxidation of hydrocarbons, oxidation of alcohols by various reagents and methods, oxidation of carbon-carbon double bonds to diols and epoxides, Woodward and Prevost Reaction, reactions of epoxides, photosensetised oxidation of alkenes, oxidation of ketones. Oxidation with ruthenium tetroxide, iodobenzene diacetate, and thallium (III) nitrate.

UNIT II: Reduction reactions

Catalytic hydrogenation-the catalyst, selectivity of reduction, reduction of functional groups, stereochemistry and mechanism, homogeneous hydrogenation. Reduction by dissolving metals-reduction with metal and acid, reduction of carbonyl compounds, Birch Reduction. Reduction by

hydride transfer reagents-aluminium alkoxides, LAH and NaBH4, lithiumhydridoalkoxyaluminates, diisobutylaluminiumhydride, sodiumcyanoborodydride, trialkylborohydrides. Other methods-desulphurisation of thio-acetals, di-imides, low-valent titanium species, trialkyltinhydrides.

UNIT III: Chemistry of Medicinally Important Molecules-I

Bacterial and animal cells, antibacterial agents – mechanism with reference to β-lactam antibiotics; General method of synthesis of β-lactam ring: synthesis of penicillin, 6-APA, cephalosporin, 7-ACA; Morin – Jackson rearrangement

UNIT IV: Chemistry of Medicinally Important Molecules-II

Synthesis and mechanism of action of (i) fluoroquinolones – norfloxacin, ciprofloxacin, levofloxacin (ii) anti AIDS drugs – AZT, lamivadine (iii) antihypertensive agent – captopril (iv) calcium channel blocker – amlodipine (v) gastric secretion inhibitor – omeprazole.