Central University of Himachal Pradesh

Dept. of Chemistry & Chemical Sciences

School of Physical & Material Sciences

Syllabus for Spring Semester 2020 for M.Sc. Chemistry 2nd Semester

Detail Syllabi:

CCS 407-ORGANIC CHEMISTRY II [Credit -4]

UNIT I: **Pericyclic Reactions**

Molecular orbital symmetry, frontier orbitals of ethylene, 1,3-buta diene, 1,3,5-hexatriene and allyl systems. Classification of pericyclic reactions. Woodward – Hoffmann correlation diagrams. FMO and PMO approach, concept of aromaticity of pericyclic transition states. Selection rules and stereochemical aspects of electrocyclic reactions, cycloaddition and sigmatropic shifts. Electrocyclic reactions: conrotatory and disrotatory motions, 4n, 4n+2 and allyl systems. Cycloaddition reactions: antarafacial and suprafacial additions, 4n and 4n+2 systems; 2,2 addition of ketenes, 1,3 dipolar cycloadditions and cheleotropic reactions. Sigmatropic rearrangements: suprafacial and antarafacial shifts of H, sigmatropic shifts involving carbon moieties, 3,3- and 5,5-sigmatropic rearrangements. Sommelet-Hauser, Cope, Claisen, and aza-Cope rearrangements. Fluxional tautomerism. Ene reaction.

UNIT II: **Heterocyclic Chemistry**

Systematic nomenclature (Hantzch-Widman system) for monocycle and fused heterocycles. General approaches to heterocycle synthesis – cyclisation and cycloaddition routes. Umpolung, synthon approach; Stork annulation reactions and recent applications (synthesis of testosterone, estrone, progesterone, ranitidine, lansoprazole and/or recently discovered molecules etc.); Rearrangement and ring transformation involving 5- and 6-membered heterocycles with one heteroatom.

UNIT III: **Chemistry of Natural Products-Ia**

Structural types; Biogenesis; Structure Elucidation and chemistry of representative examples of the following classes of natural products. *Alkaloids*- Structural types General introduction to phenylethylamine, pyrrolidine, pyridine, indole, isoquinoline type alkaloids. Structure elucidation (by chemical and spectroscopical methods), synthesis, biogenesis, biosynthesis, biological activity of atropine, nicotine, coniine and papaverine.

UNIT IV: **Chemistry of Natural Products-Ib**

*Terpenoid*s – Isoprene rule; structure elucidation (by chemical and spectroscopical methods), synthesis, biogenesis, biosynthesis of representative examples of acyclic, monocyclic and bicyclic monoterpenes. Structural types – general introduction to sesqui-, di-, and tri-terpenes.

CCS 406- LIST OF PHYSICAL CHEMISTRY PRACTICALS (Credit-2)

Faculty can choose as per convenience

SET I:

1. Spectrophotometric experiment - determination of composition of a complex (Job's method)

2. Determination of cmc of surfactants: conductometry and spectrophotometry.

3. Determination of molecular weight of macromolecules by viscometry.

4. Determination of dipole moment.

5. Analytical experiments: Study of distribution of an organic acid in an organic solvent and water – determination of association constant (with the help of Nernst distribution law), determination of van't Hoff factor.

6. Determination of transport number.

7. Molecular structure determination – gas phase vibrational rotational spectra of HCl/DCl.

SET II:

(A) Conductometry: 1. Determination of strengths of strong and weak acids in a mixture conductometrically

2. Determination of strengths of halides in a mixture conductometrically by precipitation titrations

3. Determination of concentrations of halides and halogen acids in a mixture conductometrically by precipitation titrations (system: HCl + KCl mixture by titration with standard NaOH and standard $AgNO_3$ solutions

4. Verification of Ostwald's dilution law conductometrically

5. Determination of critical micelle concentration (CMC) of a surfactant by conductometric method

(B) Potentiometry / pH-metry: 6. Determination of strengths of strong and weak acids in a mixture potentiometrically / pH-metrically (system: acetic acid + HCl)

7. Determination E° value of redox couples (i). Quinhydrone electrode (ii). Ferricyanide-ferrocyanide couple (iii). AgCl/Ag electrode

8. Determination of strengths of halides in a mixture potentiometrically by precipitation titrations (0.02N KBr + 0.02N KI mixture with standard 0.1N $AgNO_3$)

9. Determination of concentration by potentiometric / pH- metric titrations: (i). Acid-base titration (standard oxalic acid vs. NaOH, acetic acid vs. NaOH) (ii). Determination of ferrocyanide ion using standard bromate solution (iii). Determination of iodide ion by differential redox titration using standard bromated solution (iv) Determination of composition of zinc-ferrocyanide complex by potntiometric titration

(C) Colourimetry: 10. Determination of pKa of an indicator by colourimetric method (systems: methyl red, methyl orange, alizarin red –S in aqueous solution)

11. Kinetic studies on iodination of aniline (d) Polarimetry:

12. Determination of specific rotation and molar rotation of dextro-tartaric acid

13. Polarimetric determination of rate constant of reactions: (i). Inversion of sucrose (ii). Mutarotation of glucose (determination catalytic coefficients: k_{H+} and k_{H2O})

SET III:

Group-a: Phase-rule; 1. Determination of critical solution temperature (system: phenol water)

2. To construct the phase diagram of a three component system: (i).Chloroform acetic acid-water (ii). Benzene-acetic acid-water (iii). Nitrobenzene-acetic acid-water

Group-b: Adsorption; 3. To study the surface tension – concentration relationship of solutions (Gibbs equation)

Group-c: Kinetics; 4. Determination of rate constant of reactions: (i). Iodination of acetone (zero order) (ii). Decomposition of H_2O_2 (first order) (iii). Oxidation of iodide ion by bromate ion (second order)

5. Determination of rate constant of oxidation of iodide by H_2O_2 and to study the kinetics of iodine-clock reaction

Group-d: Thermodynamics & Equlibrium; 6. Determination of exchange capacities of ion-exchange resins and studies on ion-exchange equilibria.

7. Determination of solubility and solubility product of salts (systems: PbI_2, Potassium hydrogen tartarate)

8. Determination of partition coefficients of a solute between two immiscible solvents (systems: benzoic acid between benzene and water)

9. Determination of composition of complexes formed in solution (systems: Cu^{2+} - NH_3, Ag^+ - NH_3).

10. Determination of equilibrium constant of hydrolysis of an ester.

11. Determination of isoelectric point by viscosity measurement

Course Code: CCS 102 (For Physics Honour's)

Course Name: CHEMISTRY II (Credits: Theory-04, Practicals-02)

Theory: 40+ Lectures

Objectives & Academic Requirements: The emphasis of course is to provide students with the basic foundation in physical, organic and inorganic chemistry needed to develop an understanding of materials at a molecular level. The students are to be examined entirely on the basis of problems (seen/unseen) and assignments. Students are expected to attend all lectures in order to be able to fully benefit from the course. A minimum of 75% attendance is a must failing which a student may not be permitted to appear in the examination.

Course Contents:

Unit I: Atomic Structure:

Review of: Bohr's theory and its limitations, dual behaviour of matter and radiation, de Broglie's relation, Heisenberg Uncertainty principle. Hydrogen atom spectra. Need of a new approach to Atomic structure. What is Quantum mechanics? Time independent Schrodinger equation and meaning of various terms in it. Significance of ψ and $\psi 2$, Schrödinger equation for hydrogen atom. Radial and angular parts of the hydogenic wavefunctions (atomic orbitals) and their variations for 1s, 2s, 2p, 3s, 3p and 3d orbitals (Only graphical representation). Radial and angular nodes and their significance. Radial

distribution functions and the concept of the most probable distance with special reference to 1s and 2s atomic orbitals. Significance of quantum numbers, orbital angular momentum and quantum numbers ml and ms. Shapes of s, p and d atomic orbitals, nodal planes. Discovery of spin, spin quantum number (s) and magnetic spin quantum number (ms). Rules for filling electrons in various orbitals, Electronic configurations of the atoms. Stability of half-filled and completely filled orbitals, concept of exchange energy. Relative energies of atomic orbitals, Anomalous electronic configurations. [10 hours]

Unit II: Chemical Bonding and Molecular Structure

Ionic Bonding: General characteristics of ionic bonding. Energy considerations in ionic bonding, lattice energy and solvation energy and their importance in the context of stability and solubility of ionic compounds. Statement of Born- Landé equation for calculation of lattice energy, Born-Haber cycle and its applications, polarizing power and polarizability. Fajan's rules, ionic character in covalent compounds, bond moment, dipole moment and percentage ionic character.

Covalent bonding: VB Approach: Shapes of some inorganic molecules and ions on the basis of VSEPR and hybridization with suitable examples of linear, trigonal planar, square planar,

tetrahedral, trigonal bipyramidal and octahedral arrangements. Concept of resonance and resonating structures in various inorganic and organic compounds. MO Approach: Rules for

the LCAO method, bonding and antibonding MOs and their characteristics for s-s, s-p and p-p combinations of atomic orbitals, nonbonding combination 10 of orbitals, MO treatment of

homonuclear diatomic molecules of 1st and 2nd periods (including idea of s-p mixing) and

heteronuclear diatomic molecules such as CO, NO and NO+. Comparison of VB and MO approaches. [10 hours]

Unit III: Fundamentals of Organic Chemistry

Physical Effects, Electronic Displacements: Inductive Effect, Electromeric Effect, Resonance and Hyperconjugation. Cleavage of Bonds: Homolysis and Heterolysis. Structure, shape and reactivity of organic molecules: Nucleophiles and electrophiles. Reactive Intermediates: Carbocations, Carbanions and free radicals. Strength of organic acids and bases: Comparative study with emphasis on factors affecting pK values. Aromaticity: Benzenoids and Hückel's rule. Stereochemistry: Conformations with respect to ethane, butane and cyclohexane. Interconversion of Wedge Formula, Newmann, Sawhorse and Fischer representations. Concept of chirality (upto two carbon atoms). Configuration: Geometrical and Optical isomerism; Enantiomerism, Diastereomerism and Meso compounds). Threo and erythro; D and L; cis – trans nomenclature; CIP Rules: R/ S (for upto 2 chiral carbon atoms) and E / Z Nomenclature (for upto two C=C systems).
[10 hours]

Unit IV: Aliphatic Hydrocarbons

Functional group approach for the following reactions (preparations & reactions) to be studied in context to their structure.

Alkanes: (Upto 5 Carbons). Preparation: Catalytic hydrogenation, Wurtz reaction, Kolbe's synthesis, from Grignard reagent. Reactions: Free radical Substitution: Halogenation.

Alkenes: (Upto 5 Carbons) Preparation: Elimination
reactions: Dehydration of alkenes and dehydrohalogenation of alkyl halides (Saytzeff's rule); cis alkenes (Partial catalytic hydrogenation) and trans alkenes (Birch reduction). Reactions: cis-addition (alk. $KMnO_4$) and trans-addition (bromine), Addition of HX (Markownikoff's and anti-Markownikoff's addition), Hydration, Ozonolysis, oxymecuration-demercuration, Hydroboration-oxidation.

Alkynes: (Upto 5 Carbons) Preparation: Acetylene from CaC2 and conversion into higher alkynes; by dehalogenation of tetra halides and dehydrohalogenation of vicinal- dihalides. Reactions: formation of metal acetylides, addition of bromine and alkaline KMnO4, ozonolysis and oxidation with hot alk. KMnO4. [10 hours]

Reference Books:

 Lee, J.D. Concise Inorganic Chemistry ELBS, 1991.

 Cotton, F.A., Wilkinson, G. & Gaus, P.L. Basic Inorganic Chemistry, 3rd ed., Wiley.

 Douglas, B.E., McDaniel, D.H. & Alexander, J.J. Concepts and Models in Inorganic Chemistry, John Wiley & Sons.

 Huheey, J.E., Keiter, E.A., Keiter, R.L. & Medhi, O.K. Inorganic Chemistry: Principles of Structure and Reactivity, Pearson Education India, 2006.

 Graham Solomon, T.W., Fryhle, C.B. & Dnyder, S.A. Organic Chemistry, John Wiley & Sons (2014).

 McMurry, J.E. Fundamentals of Organic Chemistry, 7th Ed. Cengage Learning India Edition, 2013.

 Sykes, P. A Guidebook to Mechanism in Organic Chemistry, Orient Longman, New Delhi (1988).

 Eliel, E.L. Stereochemistry of Carbon Compounds, Tata McGraw Hill education, 2000.

 Finar, I.L. Organic Chemistry (Vol. I & II), E.L.B.S.

 Morrison, R.T. & Boyd, R.N. Organic Chemistry, Pearson, 2010.

 Bahl, A. & Bahl, B.S. Advanced Organic Chemistry, S. Chand, 2010.

Evaluation Criteria:

1) Mid Term Examination [50 marks/25% weightage]

2) End Term Examination [100 marks/50% weightage]

3) Internal Assessment [25% weightage]: Aassignments/Problems solving/Quizzes.

Course Code: CCS 102 L (For Physics Honour's)

Course Name: CHEMISTRY LAB II

Practical: 40 Lectures

Faculty will plan the experiments as per convenience and availability of instruments and other materials.

Section A: Inorganic Chemistry - Volumetric Analysis

1. Estimation of sodium carbonate and sodium hydrogen carbonate present in a mixture.

2. Estimation of oxalic acid by titrating it with KMnO4.

3. Estimation of water of crystallization in Mohr's salt by titrating withKMnO4.

4. Estimation of Fe (II) ions by titrating it with K2Cr2O7 using internal indicator.

Section B: Organic Chemistry

1. Separation of mixtures by Chromatography: Measure the Rf value in each case (combination of two compounds to be given)

(b) Identify and separate the components of a given mixture of 2 amino acids (glycine, aspartic acid, glutamic acid, tyrosine or any other amino acid) by paper chromatography

(c) Identify and separate the sugars present in the given mixture by paper chromatography.

Reference Books:

- Svehla, G. Vogel's Qualitative Inorganic Analysis, Pearson Education, 2012.

 Mendham, J. Vogel's Quantitative Chemical Analysis, Pearson, 2009.

 Vogel, A.I., Tatchell, A.R., Furnis, B.S., Hannaford, A.J. & Smith, P.W.G., Textbook of Practical Organic Chemistry, Prentice-Hall, 5th edition, 1996.

 Mann, F.G. & Saunders, B.C. Practical Organic Chemistry Orient-Longman, 1960.

HUMAN MAKING COURSE

CCS 538- BIOCHEMISTRY-I (Credit-2)

UNIT I: Proteins: Classification, Amino acid, property, primary, secondary, tertiary and quaternary structure of protein. Determination of primary structure. Enzyme: Classification, nomenclature, Kinetic of enzyme action, comparative, uncooperative and non comparative inhibition, allo enzyme, isozymes.

UNIT III: Vitamins and Hormones: Fat soluble and water soluble vitamins .Vitamins as co enzymes and co-factor.NAD, FAD, TPP, Folic acid, Vit.B6, Vit.B2, Lipoic acid, Co ASH, Epinephrine, nor epinephrine, Steroid hormones.

UNIT III: Chemistry of lipids: Structure and function of bio membranes. Structure and function of lipids. Chemistry of carbohydrates: Classification and importance constitution plants and bacterial cell wall. Animal cell coat.

UNIT IV: Bioenergetics: The ATP cycle. Nucleic Acids: DNA and RNA. Type of RNA and their function. Property of DNA in solution. Watson - Crick Model of DNA structure. Replication, Transcription and translation, (in detail). Regulation of gene expression.

SKILL DEVELOPMENT COURSE

CCS 549- ELECTRONIC SPECTROSCOPY (ABSORPTION AND EMISSION) (Credit-2)

UNIT I: Qualitative treatment of Born-Oppenheimer separation, Frank-Condon principle, selection rules, characteristics of π-π^*, n-π^*, d-d transitions and their intensities. Apparent violation of selection rule (vibrational and spin-orbit couplings). Potential energy curves, mirror-image symmetry, deactivation – internal conversion and intersystem crossing, radiationless deactivation, fluorescence and phosphorescence.

UNIT II: Quenching of fluorescence, Life-time variation in presence of quencher. Excimers and exciplexes. Intermolecular energy transfer (FRET). Energy transfer and conformation distributions of biopolymers, protein fluorescence. Excited state proton transfer. Einstein theory – A, B coefficients, Principles of LASER and characteristic features.

CCS 409- PHYSICAL CHEMISTRY II [Credit -4]

UNIT I: **Quantum Mechanics**

Time independent Schrödinger equation, probability concept, concept of stationary state. Linear operators in quantum mechanics, Eigen value equation. Properties of the Hermitian operator, canonical commutation relations. Applications: Particle-in-a box (1-, 2-, 3-dimensional), different potential functions and barrier problems, degeneracy, density of states. Simple harmonic oscillator: Ladder operator, properties of the eigen functions. Rigid rotor: Angular momentum operator, spherical harmonics. Hydrogen atom: Details of the solution, shapes of the orbitals. Approximate method: Elementary perturbation theory, Variation theorem, Simple applications.

UNIT II: **Atomic structure and Spectroscopy**

Motion under central force: Conservation of angular momentum and its consequence. Motion of angular momentum under magnetic field. Larmor precession. Quantization rule and quantum numbers. Zeeman effect. Stern Gerlach experiment. Spin-orbit interaction, conservation of total angular momentum J, Vector atom model. Anomalous Zeeman effect, Paschen-Beck effect. Multielectron system- Pauli exclusion principle. Term symbols for simple multi-electron system. Magnetic moment and Lande's g factor. Schrödinger equation for hydrogen atom (only qualitative idea), separation of radial and angular part. Orbits and Orbitals. Shape of orbitals.

UNIT III: **Chemical Kinetics and Reaction Dynamics-I**

Reaction Dynamics: Rates and mechanisms of photochemical, chain and oscillatory reactions (hydrogen-bromine, hydrogen – chlorine reactions, pyrolysis of acetaldehyde, decomposition of ethane and Belousov- Zhabotinsky reaction as examples), dynamics of barrier less chemical reactions in solutions, dynamics of uni molecular reactions (Lindemann- Hinselwood and Rice-Ramsperger- Kasel-Marcus [RRKM] theories). Enzyme catalysis; Michaelis-Menten equation

UNIT IV: **Chemical Kinetics and Reaction DynamicsII**

Fast Ractions: Luminescence and energy transfer processes. Study of kinetics by stopped flow and relaxation methods, flash photolysis and magnetic resonance method. Statistical formulation of chemical kinetics reaction dynamics: Intermolecular collision and its consequence. Role of intermolecular potential, elastic and inelastic collision. Thermodynamics of reaction rates. Activation energy- Experimental and zero point activation energy. Rate constant expression for chemical reaction based on Eyring equation with examples. Physical rate processes –viscosity and diffusion.

Course name: INORGANIC CHEMISTRY II
Course code: CCS 408
Credit -4

UNIT I: Organometallic Chemisty-I
The 18- electron rule for organometallic compounds of transition metals: Classification based on 18- electron rule: complexes of two, three, four, five six, seven, eight-electron pi-ligands: nomenclature. Exceptions to 18 electron rule: the 16-electron rule. Agostic interaction, Isolobal and isoelectronic relationship of complexes,.

UNIT II: Organometallic Chemisty-II
Elementary idea about homoleptic and non-homoleptic compounds: oxidative addition and reductive elimination reaction: insertion. Direct combination of carbon monoxide and metal . Reductive carbonylation of transition metal salts . Synthesis using [Fe $(CO)_6$] . Photolysis of lower metal carbonyls Thermolysis of lower metal carbonyls Abstraction of CO from organic compounds

UNIT III: Molecular Clusters
Metal-carbonyl clusters, structures, capping. Molecular clusters in catalysis, boron-carbides and metal borides. . Synthesis of heteronuclear metal carbonyls

UNIT IV: **Bioinorganic Chemistry**
Reversible oxygenation in life process O2-uptake proteins, myoglobin, hemoglobin, hemeerythrin, hemocyanin, electron transport proteins, Fe-S proteins, ferridoxin, rubredoxin, respiratory electron transport chains: cytochromes, photosynthetic electron transport chain, chlorophyll, PS-I and PS-II, Biological nitrogen fixation (Nitrogenase) and a biological nitrogen fixation; metalloenzymes: superoxide dismutase (SOD), cytochrome P 450, cytochrome C oxidase, carbonic anhydrase, carboxypeptidase; molybdoenzymes.
Metal dependent diseases Wilsons, Alzheimer, vitamin B12 -enzyme, Chelation therapy Metal complexes in therapeutic use of chelated and non chelated compounds,

CCS 546- ADVANCED BIOINORGANIC CHEMISTRY (Credit-2)

UNIT I: Metal ions in biology:

Essential and trace elements in the biological systems, metal of life, basic reactions in the biological systems and the roles of metal ions in biological process. Ion transport (active) across biological membrane and its significance, mechanism of Na+ K+ -ion pump.

UNIT II:

Bioenergetic principle and role of ATP, chemistry of respiration, DNA polymerization, metal ion interaction with nucleoside and nucleotide, metal ion transport and storage proteins, ferritin, transferrin, ceruloplasmin. Metal ion transport across biological membrane, enzymatic and ionophoric transport.

UNIT III: Study of metalloprotein and metalloenzyme: catalase, peroxidase, superoxide dismutase, ceruloplasmin, cytochrome oxidases, Ascorbate oxidase, Role of metal ions in different hydrolytic enzymes: Carbonic anhydrase, Carboxypeptidase, Urease.

UNIT IV: Toxicity and drugs: Toxic effects of metal ions (metals) and non metals. Specific examples of Pb, As, Hg, F. Detoxification by chelation therapy, metal dependent diseases and metal complexes as drugs, Pt, Ru, Rh and Au drugs.