M.Sc.

CHEMISTRY

2nd SEMESTER

SPRING 2019

CCS 407-ORGANIC CHEMISTRY II [Credit -4](Core Compulsary)

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 408- INORGANIC CHEMISTRY II [Credit -4] (Core Compulsory)

UNIT I: **Organometallic Chemistry-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. Isolobal and isoelectronic relationship of complexes, Agostic interaction.
Metal-carbon-bonded compounds (compounds of the sigma electron ligands), Metal-alkyl, -allyl, -carbene, -carbonyl, -carbide and cyclopentadienyl complexes structure and bonding in η^2- ethylene and η^3- allylic compounds with typical examples, structure and bonding of $K[PtC_4H_4Cl_3]$, $[(Ph_3P)_2Pt(Ph\text{-}C{\equiv}C\text{-}Ph)]$, $[Co_2(CO)_6(Ph\text{-}C{\equiv}C\text{-}Ph)]$

UNIT II: **Organometallic Chemisty-II**

Elementary idea about homoleptic and non-homoleptic compounds: synthesis, reactivity, oxidative addition and reductive elimination reaction: insertion reactions and elimination; electrophilic and nucleophilic reactions; instability (decomposition pathway) and stabilization. Metallacycles.

UNIT III: **Molecular Clusters**

Main-group clusters: Geometric and electronic structure, three-, four- and higher connect clusters, the closo-, nido-, arachno-borane structural paradigm, styx No. of neutral and boron hydrides, Wade-Mingos and Jemmis electron counting rules, clusters with nuclearity 4-12 and beyond 12. Structure, synthesis and reactivity. Transition-metal clusters: Capping rules, metal-ligand complexes vs heteronuclear cluster. Main-group Transition-metal clusters: Isolobal analogs of p-block and d-block clusters, limitations and exceptions. Clusters having interstitial main group elements, cubane clusters and naked or Zintl clusters. Metal-carbonyl clusters, structures, capping and electron counting. Molecular clusters in catalysis, clusters to materials, boron-carbides and metal borides. [Lipscomb topological diagrams, polyhedral skeletal electron pair theory (PSEPT); Illustrative examples from recent literature-*not in details*].

UNIT IV: **Bioinorganic Chemistry**

Reversible oxygenation in life process O_2-uptake proteins, myoglobin, hemoglobin, hemeerythrin, hemocyanin and model systems, electron transport proteins, Fe-S proteins, ferridoxin, rubredoxin and model systems, respiratory electron transport chains: cytochromes, photosynthetic electron transport chain, chlorophyll, PS-I and PS-II, Biological nitrogen fixation (Nitrogenase) and abiological nitrogen fixation; metalloenzymes: – catalase, peroxidase, urease, superoxide dismutase (SOD), cytochrome P 450, cytochrome C oxidase, carbonic anhydrase, carboxypeptidase; molybdoenzymes.

Metal dependent diseases Wilsons, Alzheimer, vitamin B_{12} and B_{12} -enzyme, Metal complexes in therapeutic use of chelated and non chelated compounds, Chelation therapy.

CCS 409- PHYSICAL CHEMISTRY II [Credit -4] (Core Compulsory)

UNIT I: **Quantum Mechanics**

Time independent Schrödinger equation, probability concept, concept of stationary state. Linear operators in quantum mechanics, Eigen value equation. Formal derivation of Heisenberg uncertainty principle: commutability and compatibility. Properties of the Hermitian operator, canonical commutation relations, Ehrenfest theorem. 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 prescision. 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). Correlation between Kinetics and mechanism & vice-varsa. Enzyme catalysis; Michaelis-Menten equation

UNIT IV: **Chemical Kinetics and Reaction Dynamics-II**

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.

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

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

CCS 102 (B.Sc.) CHEMISTRY –II (for Physics Honours students) Credit 4

CCS 102L (B.Sc.) CHEMISTRY LAB-II (for Physics Honours) Credit 2

CCS 544- STRUCTURE AND PROPERTIES OF SOLIDS (Credit-2)(Core Open)

UNIT I: Defects in solids, point, line and plane defects. Determination of equilibrium concentration of Schotky and Frenkel defects. Stoichiometric imbalance in crystals and non stoichiometric phases, color center in ionic crystals, band theory, band gap, metals and insulators, semiconductors, hoping semiconductors rectifiers and transistors, Bonding in metals; free electron theory, electronic specific heat, Hall effect, electrical and thermal conductivity of metals, superconductors; meissner effect, elementary concepts of BCS theory, ferroelectricity, antiferroelectricity, piezoelectricity, liquid crystals, cooperative magnetism.

UNIT II: Illustrative examples of ionic, covalent and hydrogen bonded solids; perovskite, ilmenite and rutile; spinel and inverse spinel, silicates: pyroxene, amphibole, talc, mica, clay, zeolite, ultramarine;