P.G. 3rd SEMESTER SYLLABUS

DEPARTMENT OF CHEMISTRY

COTTON UNIVERSITY

PAPER : CHM 901C

INORGANIC CHEMISTRY- III

(Credits: 3+1+0=4)

Theory: 60 Lectures

Unit 1: Inorganic Chains, rings, cages and clusters (15 Lectures)

Catenation, Heterocatenation, Zeolites, Intercalation , Structure and bonding in borazine, phosphazenes, polyhedral boranes, carboranes, metalloboranes and metallocarboranes, Styx notation, Wade's rules, Synthesis and electron count in polyhedral boranes. Inorganic clathrates.

Synthesis and bonding in metal clusters. Metal-metal quadruple bonding in $Re_2Cl_8{}^{2-}$.

Unit 2: Bio Inorganic Chemistry (15 Lectures)

Active ion transport across cell membrane: Na^+/K^+ Pump, Oxygen: binding, transport and utilization, Photosynthesis, Nitrogen Fixation, Metalloenzymes: Haemoglobin, Myoglobin, Catalase, Peroxidase, Superoxide Dismutase, Cytochrome P-450. Nitrogenase, Chlorophyll, Carboxypeptidase, Carbonic anhydrase, Coenzyme Vitamin B_{12}, Xanthine Oxidase, Metal Complexes in Medicine.

Unit 3: Nuclear and Radio Chemistry (15 Lectures)

Radioactive decay processes, half-lives, auger effect. Nuclear reactions – notations, comparison with chemical reactions, types of nuclear reactions, reaction cross section, mechanism of nuclear reactions. Radiation detection & measurements, Geiger-Muller and Scintillation counters, applications of radioisotopes as tracers (reaction mechanism, structure determination, activation analysis, isotope dilution technique, age determination)

Unit 4: Inorganic materials (15 Lectures)

Superconducting materials: discovery, magnetic properties, theory, examples and uses of high temperature superconductors.

Nanomaterials: concept, novel optical and magnetic properties, synthesis, characterization techniques and applications.

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PAPER : CHM 902C

ORGANIC CHEMISTRY- III

(Credits: 3+1+0=4)

Theory: 60 Lectures

Unit1: Organic Photochemistry (10 Lectures)

Introduction to organic photochemical-photophysical processes, chemiluminescence, photosensitization.

Photochemistry of carbonyl compounds: α-cleavage, β-cleavage, intramolecular H-abstraction, addition to π-systems, Paterno-Buchi reaction; Photochemistry of olefins - photostereomutation of cis-trans isomers, optical pumping, cycloaddition, photochemistry of conjugated polyenes, photochemistry of vision

Photochemistry of enones; Photo-rearrangement reactions, di-π-methane rearrangement, Photo-rearrangement of cyclohexadienones, Barton rearrangement; Singlet oxygen photochemistry.

Unit 2: Oxidation Reactions (16 Lectures)

Metal based and non-metal based oxidations (Cr, Mn, Al, Ag, Os, Ru, Se, DMSO, hypervalent iodine and TEMPO based reagents). Reagents (Fremy's salt, silver carbonate, peroxides/per-acids, TPAP, Oxone).

Named reactions: Sharpless epoxidation and dihydroxylation, Baeyer-Villiger oxidation, Wacker oxidation, hydroboration-oxidation, Prevost reaction and Woodward modification, Oppenauer oxidation,.

Unit 3: Reduction Reactions (16 Lectures)

Catalytic hydrogenation (Pd/Pt/Rh/Ni/Ir). Wilkinson catalyst

Metal based reductions using Li/Na/Ca in liquid ammonia, Sodium, Magnesium, Zinc, Titanium and Samarium (Birch, Pinacol formation, McMurry, Acyloin formation, dehalogenation and deoxygenations);

Hydride transfer reagents from Group 13 and Group 14 in reductions (Borane, $NaBH_4$, $NaBH_3CN$, $LiBH_4$, Zn $(BH_4)_2$, triacetoxyborohydride, superhydride, selectrides, Luche reduction, $LiAlH_4$, DIBAL-H, and Red-Al, Diimide reduction, Trialkylsilanes and Trialkylstannane, Meerwein-Pondorff-Verley reduction)

Unit 4: Pericyclic Reactions (18 Lectures)

MO symmetry, FMO of conjugated polyenes. Woodward-Hoffmann principle of conservation of orbital symmetry, allowed and forbidden reactions, stereochemistry of pericyclic reactions, orbital symmetry correlation method, PMO method.

Cycloaddition reactions: [2+2], [4+2], [6+2] cycloadditions, [3+2] and [4+3] dipolar cycloadditions; stereoselectivity of the reactions, regioselectivity of [4+2] cycloaddition reaction.

Sigmatropic rearrangement: (m+n) sigmatropic rearrangement of hydrogen and chiral alkyl groups; Divinyl cyclopropane rearrangement, fluxional molecules, stereoselectivity in Cope, and Claisen rearrangement. Sommelet-Hauser rearrangement. Aza-Cope rearrangement, Overman rearrangement.

Electrocyclic reactions and cyclo-reversions: Conrotatory and disrotatory process, Stereoselectivity of the reactions.

Linear and nonlinear cheletropic rearrangement, theories of cheletropic reactions, stereoselectivity of the reactions.

Ene reactions of 1,7-dienes, carbonyl enophiles, simple problems, metallo-ene, Conia-ene reaction.

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PAPER : CHM 903C

ADVANCED QUANTUM CHEMISTRY

(Credits: 3+1+0=4)

Theory: 60 Lectures

Unit 1: Approximate Methods of Quantum Mechanics (10 Lectures)

(a) Time-independent first order perturbation theory for – (i) non-degenerate, and (ii) degenerate systems applications to the ground and first-excited states of the helium atom. Calculation of energy up to the second-order corrections.

(b) The variation theorem, linear variation function – secular equation.

Unit 2: Electronic Structure of Many-Electron Atoms (15 Lectures)

(a) Product wave functions- complete many-electron wave functions including electron spin. Pauli's anti-symmetry and exclusion principles. Spin states of a two-electron system- singlet and triplet states.

(b) Independent particle central field model of many-electron atoms- the helium atom. Atomic orbital theory – Slater type orbitals (STO); electron repulsion parameters (Racah and Condon-Shortly types).

(c) Spectroscopic term symbols for the s^1p^1, p^2 and d^2 configurations – splitting of term energies due to inter-electronic repulsion and spin orbit coupling, magnetic effects and Zeeman splitting.

Unit 3: Chemical Bonding (15 Lectures)

(a) The hydrogen molecule ion: linear combination of atomic orbital (LCAO)-molecular orbital (MO) theory- ground and excited electronic states.

(b) The hydrogen molecule: LCAO-MO and valence bond (VB) treatments. Equivalence of the MO and VB methods.

(c) Extension of the LCAO-MO method to homo- and heteronuclear diatomics-inclusion of hybridization.

(d) Term symbols for molecular electronic states, their symmetry classification. Correlation diagrams and the non-crossing rule.

(e) LCAO-MO theory of simple polyatomic molecules (e.g., the H_2O molecule).

(f) π-electron theory: Hückel molecular orbital (HMO) method for unsaturated carbon compounds showing chain and ring structures; introduction to extended Hückel theory.

Unit 4: General Theorems in Molecular Quantum Mechanics (10 Lectures)

(a) Born-Oppenheimer approximation, separation of electronic and nuclear motion.

(b) Hellmann-Feynman theorem and its chemical applications. The electrostatic theorem (derivation not required) and the force concept in chemistry, binding and anti-binding regions.

(c) Molecular electronic virial theorem, its simplified expression for diatomic molecules, resulting ideas about contribution of kinetic and potential energies to molecular bonding.

Unit 5: Introduction to Quantum Chemical SCF and Density-Functional Theories (10 Lectures)

(a) Review of the principles of quantum mechanics, Born-Oppenheimer approximation, separation of electronic and nuclear motion

(b) The self consistent field method, Hartree-Fock theory of closed shell electronic configurations of atoms and molecules, Coulomb and exchange integrals, Hartree-Fock equations, Koopman's theorem without derivation. Gaussian basis sets.

(c) Linear SCF LCAO-MO theory of molecules – the Roothan equations.

(d) Density-functional theories: basic ideas, Hohenberg-Kohn theorem and its derivation, Kohn-Sham formulation.

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Semester III: Special Papers

PAPER : CHM 904D

ORGANOMETALLICS AND PHOTO-INORGANIC CHEMISTRY

(Credits: 4+1+0=5)

Theory: 75 Lectures

Unit 1: Alkyls and Aryls of Transition Metals (8 Lectures)

Types, routes of synthesis, characteristics, stability, decomposition pathways, structure and bonding. Organocopper in organic synthesis.

Unit 2: Compounds of Transition Metal-Carbon Multiple Bonds (12 Lectures)

Alkylidenes, alkylidynes, low valent carbenes and carbynes- synthesis, nature of bond, structural, characteristics, nucleophilic and electrophilic reactions on the ligands, role in organic synthesis.

Unit 3: Transition Metal π – Complexes (8 Lectures) (15 Lectures)

Transition metal π-complexes with unsaturated organic molecules, alkenes, alkynes, allyl, diene, dienyl, arene and trienyl complexes, preparations, properties, nature of bonding and structural features. lmportant reactions relating to nucleophillc and electrophilic attack on ligands and to organic synthesis.

Unit 4: Organometallic Reactions and Catalysis (20 Lectures)

Organomettallic reactions for catalysis, Examples of catalysis: hydrogenation by Wilkinson's catalyst, Zeigler-Natta polymerization of olefins, hydrocarbonylation of olefins (oxo reaction), oxopalladation reactions (Wacker process), Monsanto acetic acid synthesis, activation of C-H bond.

Unit 5: Photo Inorganic Chemistry (20 Lectures)

Ligand field and charge transfer state (Thexi & DOSENCO states), Photo physical processes in electronically excited molecules, Types of excited states (radiative and non-radiative processes), Jablonski diagram. Photo substitution and photo redox reactions of chromium, cobalt and ruthenium compounds, Photo rearrangement reactions: Cis-trans isomerization, Linkage Isomerism. Photo catalysis and solar energy conservation by ruthenium complexes.

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PAPER : CHM 905D

ADVANCED ORGANIC SYNTHESIS

(Credits: 4+1+0=5)

Theory: 75 Lectures

Unit 1: C-C bond forming reactions (15 Lectures)

C-C bond formation reactions using organometallic compounds (orgnao Li, Mg, Zn, B, Sn, Si, Cu reagents). Pd catalyzed coupling reactions (Heck, Suzuki, Sonogashira, Stille and Negeshi coupling). Formation of C-C multiple bonds involving Csp2 and Csp carbon centers (with emphasis on important name reactions, e. g. Corey–Fuchs reaction, Horner–Wadsworth–Emmons reaction, Simmons−Smith Reaction), pyrolytic syn elimination reactions (Chugaev reaction and Cope reaction). Alkene from hydrazones, sulfones.

Unit 2: C-heteroatom bond forming reactions (10 Lectures)

Formation of carbon-heteroatom bonds: New methods for the construction of C-N, C-O, C-S and C-X bonds (including aspects related to the activation of C-H bonds), Ullmann reaction, Buchwald-Hartwig reaction, Ugi reaction, Stork-enamine reaction, hetero Diels-Alder reactions.

Unit 3: Asymmetric synthesis (16 Lectures)

Enantioselective synthesis (alkylation, allylation and crotylation reactions), use of chiral reagent; Chiral catalyst and chiral auxiliary; Use of chiral auxiliaries (Evans oxazolidones, Oppolzer sultams, Myers amides, Schöllkopf Chiral Auxiliaries), use of chiral pool.

Kinetic resolution (including enzymatic resolution), desymmetrization reactions.

Asymmetric reactions: Epoxidation (Sharpless, Jacobsen, Shi, Julia-Colonna), Dihydroxylation (Sharpless); Stereo/enantioselective reductions (Pfaltz catalyst, Chiral Boranes, Corey-Bakshi-Shibata catalyst, use of BINOL, BINAP, chiral phosphine ligands).

Unit 4: Construction of Ring Systems (12 Lectures)

Different approaches towards the synthesis of three, four, five and six-membered rings; photochemical approaches for the synthesis of four membered rings, oxetanes and cyclobutanes. Diels-Alder reaction (inter- and intra-molecular), ketene cycloaddition (inter- and intramolecular), Pauson-Khand reaction, Bergman cyclization; Nazarov cyclization, cation-olefin cyclization, radical-olefin cyclization, Hofmann- Loeffler- Freytag reactions, cyclization reactions of nitrenes,

Heterocyclic rings (with two or more heteroatoms): Pyrazoles, isoxazoles, thiazoles, triazoles and pyrimidines (Claisen synthesis, Fischer synthesis)

Inter-conversion of ring systems (contraction and expansion); construction of macrocyclic rings, ring closing metathesis.

Unit 5: Protecting Groups **(6 Lectures)**

Protection and deprotection of hydroxy, carboxyl, carbonyl, carboxy amino groups and carbon-carbon multiple bonds; chemo- and regioselective protection and deprotection. Illustration of protection and deprotection in peptide and carbohydrate synthesis.

Unit 6: Retrosynthetic Analysis **(8 Lectures)**

Basic principles and terminology of retrosynthesis, synthons and synthetic equivalents, synthesis of aromatic compounds, one group and two group C -X disconnections,

One group C-C and two group C-C disconnections, amine and alkene synthesis, important strategies of retrosynthesis, functional group transposition, important functional group interconversions, Umpolung of reactivity.

Unit 7: Synthesis of Complex Molecules **(8 Lectures)**

Total synthesis of Terpene (caryophylene) , alkaloid (morphine), and drug (efavirenz)

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PAPER : CHM 906D

CHEMICAL KINETICS AND ELECTROCHEMISTRY

(Credits: 4+1+0=5)

Theory: 75 Lectures

Unit 1: Chemical Kinetics – I **(25 Lectures)**

Drawbacks of Lindemann theory- Hinselwood modification, RRK theory, Slater's treatment, RRKM theory.

Effect of dielectric constant on reaction rate in solution, effect of pressure on rate, cage reactions, electron transfer reactions in solution, linear free energy relationship, Hammett equation, Taft equation, their applications.

Photochemical reactions: photophysical kinetics, state energy diagrams. Delayed fluorescence: the mechanism and kinetics of fluorescence quenching – Stern-Volmer equation.

Unit 2: Chemical Kinetics – II **(20 Lectures)**

Review of stopped flow technique, temperature and pressure jump methods. NMR studies in fast reactions, shock tube kinetics, relaxation kinetics. Linearised rate equation, relaxation time in single step fast reactions, determination of relaxation time.

Chemical kinetics in the elucidation of reaction mechanism: hydrolysis of lactones and aldol condensation, thermal decomposition of dinitrogen pentoxide and ligand replacement reactions of octahedral complexes.

Unit 3: Electrochemistry – I **(15 Lectures)**

Theories of electrical interface – Helmholtz-Perrin model, Gouy-Chapman model, Stern model. Electrocapillary phenomena – Lippmann equation. Electron transfer at interfaces – polarisable and non-polarisable interfaces, Butler-Volmer equation, Tafel Plots.

Unit 4: Electrochemistry – II **(15 Lectures)**

Electrochemical methods used in electrode kinetics: polarography, chronopotentiometric method, cyclic voltammetry. Convective diffusion, rotating disc electrode (RDE). Applications in electrode processes, electrodeposition on metals.

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Semester III: Open Elective Courses (OPE)

PAPER : CHM 907P

NANOSTRUCTURES AND NANOMATERIALS

(Credits: 3+1+0=4)

Theory: 60 Lectures

Unit 1: Introduction **(10 Lectures)**

Concept of nanosize, novel properties of nanomaterials, history of nanomaterials , nanomaterials in nature, scope and perspectives of nanoscience.

Unit 2: Synthesis and Stabilisation of Nanomaterials **(20 Lectures)**

Top Down and Bottom Up approaches of fabricating nanomaterials, Challenges in nano fabrication, Different physical and chemical methods of synthesizing nanoparticles, Ostwald ripening, electrostatic and steric stabilization, synthesis of metal, semiconducting and oxide nanoparticles. A brief introduction to dimensional control of nanoparticles.

Unit 3: Structural and Chemical Characterization **(20 Lectures)**

Electron Microscopy: Transmission Electron Microscopy/Selected Area Electron Diffraction Scanning Electron Microscopy/ Energy Dispersive X-Ray Analysis, Scanning Probe Microscopy: Surface Tunneling Microscopy and Atomic Force Microscopy, X-ray Diffraction. Miscellaneous Techniques.

Unit 4: Applications and Ethical Issues **(10 Lectures)**

Applications of Nanomaterials in enviromental, industrial and medical fields. Toxicity, Biosafety and Ethical issues in application of nanoparticles.

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