
SEMESTER-II

CEMACOR03T: INORGANIC CHEMISTRY-I

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Extra nuclear Structure of atom (18 Lectures) Marks: 14

Bohr's theory, its limitations and atomic spectrum of hydrogen atom; Sommerfeld's Theory. Wave mechanics: de Broglie equation, Heisenberg's Uncertainty Principle and its significance, Schrödinger's wave equation, significance of ψ and ψ^2 . Quantum numbers and their significance. Radial and angular wave functions for hydrogen atom. Radial and angular distribution curves. Shapes of *s*, *p*, *d* and *f* orbitals. Pauli's Exclusion Principle, Hund's rules and multiplicity, Exchange energy, Aufbau principle and its limitations, Ground state Term symbols of atoms and ions for atomic number upto 30.

Chemical periodicity (8 Lectures) Marks: 10

Modern IUPAC Periodic table, Effective nuclear charge, screening effects and penetration, Slater's rules, atomic radii, ionic radii (Pauling's univalent), covalent radii, lanthanide contraction. Ionization potential, electron affinity and electronegativity (Pauling's, Mulliken's and Allred-Rochow's scales) and factors influencing these properties, group electronegativities. Group trends and periodic trends in these properties in respect of s-, p- and d-block elements. Secondary periodicity, Relativistic Effect, Inert pair effect.

Acid-Base reactions (16 Lectures) Marks: 12

Acid-Base concept: Arrhenius concept, theory of solvent system (H_2O , NH_3 , SO_2 and HF), Bronsted-Lowry's concept, relative strength of acids, Pauling's rules. Lux-Flood concept, Lewis concept, group characteristics of Lewis acids, solvent levelling and differentiating effects. Thermodynamic acidity parameters, Drago-Wayland equation. Superacids, Gas phase acidity and proton affinity; HSAB principle. Acid-base equilibria in aqueous solution (Proton transfer equilibria in water), pH, buffer. Acidbase neutralisation curves; indicator, choice of indicators.

Redox Reactions and precipitation reactions (18 Lectures) Marks: 14

Ion-electron method of balancing equation of redox reaction. Elementary idea on standard redox potentials with sign conventions, Nernst equation (without derivation). Influence of complex formation, precipitation and change of pH on redox potentials; formal potential. Feasibility of a redox titration, redox potential at the equivalence point, redox indicators. Redox potential diagram (Latimer and Frost diagrams) of common elements and their applications. Disproportionation and comproportionation reactions.

Solubility product principle, common ion effect and their applications to the precipitation and separation of common metallic ions as hydroxides, sulfides, phosphates, carbonates, sulfates and halides.

Reference Books

1. Lee, J. D. *Concise Inorganic Chemistry*, 5th Ed., Wiley India Pvt. Ltd., 2008.
2. Douglas, B.E. and McDaniel, D.H. *Concepts & Models of Inorganic Chemistry* Oxford, 1970.
3. Day, M.C. and Selbin, J. *Theoretical Inorganic Chemistry*, ACS Publications, 1962.
4. Atkin, P. *Shriver & Atkins' Inorganic Chemistry*, 5th Ed., Oxford University Press (2010).
5. Cotton, F.A., Wilkinson, G. and Gaus, P.L., *Basic Inorganic Chemistry* 3rd Ed.; Wiley India.
6. Sharpe, A.G., *Inorganic Chemistry*, 4th Indian Reprint (Pearson Education) 2005.
7. Huheey, J. E.; Keiter, E.A. & Keiter, R.L. *Inorganic Chemistry, Principles of Structure and Reactivity* 4th Ed., Harper Collins 1993, Pearson, 2006.
8. Atkins, P.W. & Paula, J. *Physical Chemistry*, Oxford Press, 2006.
9. Mingos, D.M.P., *Essential trends in inorganic chemistry*. Oxford University Press (1998).
10. Winter, M. J., The Orbitron, <http://winter.group.shef.ac.uk/orbitron/> (2002). An illustrated gallery of atomic and molecular orbitals.
11. Burgess, J., *Ions in solution: basic principles of chemical interactions*. Ellis Horwood (1999).

CEMACOR01P: INORGANIC CHEMISTRY-I LAB

60 (Lectures/Contact Hours) Marks: 25

Acid and Base Titrations:

1. Estimation of carbonate and hydroxide present together in mixture
2. Estimation of carbonate and bicarbonate present together in a mixture.

3. Estimation of free alkali present in different soaps/detergents. **Oxidation-Reduction Titrimetric**

1. Estimation of Fe(II) using standardized KMnO_4 solution
2. Estimation of oxalic acid and sodium oxalate in a given mixture
3. Estimation of Fe(II) and Fe(III) in a given mixture using $\text{K}_2\text{Cr}_2\text{O}_7$ solution.
4. Estimation of Fe(III) and Mn(II) in a mixture using standardized KMnO_4 solution
5. Estimation of Fe(III) and Cu(II) in a mixture using $\text{K}_2\text{Cr}_2\text{O}_7$.
6. Estimation of Fe(III) and Cr(III) in a mixture using $\text{K}_2\text{Cr}_2\text{O}_7$ **Reference Books**

1. Mendham, J., A. I. Vogel's *Quantitative Chemical Analysis* 6th Ed., Pearson, 2009.

CEMACOR04T: ORGANIC CHEMISTRY-II

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Stereochemistry II

(20 Lectures) Marks: 16

Chirality arising out of stereoaxis: stereoisomerism of substituted cumulenes with even and odd number of double bonds; chiral axis in allenes, spiro compounds, alkylidenecycloalkanes and biphenyls; related configurational descriptors (R_a/S_a and P/M); atropisomerism; racemisation of chiral biphenyls; *buttressing* effect.

Concept of prostereoisomerism: prostereogenic centre; concept of $(pro)^n$ -chirality: topicity of ligands and faces (elementary idea); *pro-R/pro-S*, *pro-E/pro-Z* and *Re/Si* descriptors; *pro-r* and *pro-s* descriptors of ligands on propseudoasymmetric centre.

Conformation: conformational nomenclature: eclipsed, staggered, *gauche*, *syn* and *anti*; dihedral angle, torsion angle; Klyne-Prelog terminology; P/M descriptors; energy barrier of rotation, concept of torsional and steric strains; relative stability of conformers on the basis of steric effect, dipole-dipole interaction and H-bonding; *butane gauche* interaction; conformational analysis of ethane, propane, *n*-butane, 2methylbutane and 2,3-dimethylbutane; haloalkane, 1,2-dihaloalkanes and 1,2-diols (up to four carbons); 1,2-halohydrin; conformation of conjugated systems (*s-cis* and *s-trans*).

General Treatment of Reaction Mechanism II

(22 Lectures) Marks: 18

Reaction thermodynamics: free energy and equilibrium, enthalpy and entropy factor, calculation of enthalpy change via BDE, intermolecular & intramolecular reactions.

Concept of organic acids and bases: effect of structure, substituent and solvent on acidity and basicity; proton sponge; gas-phase acidity and basicity; comparison between nucleophilicity and basicity; HSAB principle; application of thermodynamic principles in acid-base equilibria.

Tautomerism: prototropy (keto-enol, nitro - aci-nitro, nitroso-oximino, diazo-amino and enamine-imine systems); valence tautomerism and ring-chain tautomerism; composition of the equilibrium in different systems (simple carbonyl; 1,2- and 1,3dicarbonyl systems, phenols and related systems), factors affecting keto-enol tautomerism; application of thermodynamic principles in tautomeric equilibria.

Reaction kinetics: rate constant and free energy of activation; concept of order and molecularity; free energy profiles for one-step, two-step and three-step reactions; catalyzed reactions: electrophilic and nucleophilic catalysis; kinetic control and thermodynamic control of reactions; isotope effect: primary and secondary kinetic isotopic effect (k_H/k_D); principle of microscopic reversibility; Hammond's postulate.

Substitution and Elimination Reactions **(18 Lectures) Marks: 16**

Free-radical substitution reaction: halogenation of alkanes, mechanism (with evidence) and stereochemical features; reactivity-selectivity principle in the light of Hammond's postulate.

Nucleophilic substitution reactions: substitution at sp^3 centre: mechanisms (with evidence), relative rates & stereochemical features: S_N1 , S_N2 , S_N2' , S_N1' (allylic rearrangement) and S_Ni ; effects of solvent, substrate structure, leaving group and nucleophiles (including ambident nucleophiles, cyanide & nitrite); substitutions involving NGP; role of crown ethers and phase transfer catalysts; [systems: alkyl halides, allyl halides, benzyl halides, alcohols, ethers, epoxides].

Elimination reactions: E1, E2, E1cB and Ei (pyrolytic *syn* eliminations); formation of alkenes and alkynes; mechanisms (with evidence), reactivity, regioselectivity (Saytzeff/Hofmann) and stereoselectivity; comparison between substitution and elimination; importance of Bredt's rule relating to the formation of C=C.

Reference Books

1. Clayden, J., Greeves, N., Warren, S. *Organic Chemistry*, Second edition, Oxford University Press 2012.
2. Sykes, P., *A guidebook to Mechanism in Organic Chemistry*, Pearson Education, 2003.
3. Smith, J. G. *Organic Chemistry*, Tata McGraw-Hill Publishing Company Limited.

- Carey, F. A. & Giuliano, R. M. *Organic Chemistry*, Eighth edition, McGraw Hill Education, 2012.
- Loudon, G. M. *Organic Chemistry*, Fourth edition, Oxford University Press, 2008.
- Eliel, E. L. & Wilen, S. H. *Stereochemistry of Organic Compounds*, Wiley: London, 1994.
- Nasipuri, D. *Stereochemistry of Organic Compounds*, Wiley Eastern Limited.
- Morrison, R. N. & Boyd, R. N. *Organic Chemistry*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
- Finar, I. L. *Organic Chemistry (Volume 1)* Pearson Education.
- Graham Solomons, T.W., Fryhle, C. B. *Organic Chemistry*, John Wiley & Sons, Inc.
- James, J., Peach, J. M. *Stereochemistry at a Glance*, Blackwell Publishing, 2003.
- Robinson, M. J. T., *Stereochemistry*, Oxford Chemistry Primer, Oxford University Press, 2005.
- Maskill, H., *Mechanisms of Organic Reactions*, Oxford Chemistry Primer, Oxford University Press.

CEMACOR04P: ORGANIC CHEMISTRY-II LAB

60 (Lectures/Contact Hours) Marks: 25

Organic Preparations

A. The following reactions are to be performed, noting the yield of the crude product:

- Nitration of aromatic compounds
- Condensation reactions
- Hydrolysis of amides/imides/esters
- Acetylation of phenols/aromatic amines
- Benzoylation of phenols/aromatic amines
- Side chain oxidation of aromatic compounds
- Diazo coupling reactions of aromatic amines
- Bromination of anilides using green approach (Bromate-Bromide method)
- Redox reaction including solid-phase method
- Green 'multi-component-coupling' reaction
- Selective reduction of *m*-dinitrobenzene to *m*-nitroaniline

Students must also calculate percentage yield, based upon isolated yield (crude) and theoretical yield.

B. Purification of the crude product is to be made by crystallisation from water/alcohol, crystallization after charcoal treatment, or sublimation, whichever is applicable.

C. Melting point of the purified product is to be noted.