
SEMESTER-VI

CEMACOR13T: INORGANIC CHEMISTRY-V

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Bioinorganic Chemistry

(24 Lectures) Marks: 20

Elements of life: essential and beneficial elements, major, trace and ultratrace elements. Basic chemical reactions in the biological systems and the role of metal ions (specially Na^+ , K^+ , Mg^{2+} , Ca^{2+} , $\text{Fe}^{3+/2+}$, $\text{Cu}^{2+/+}$, and Zn^{2+}). Metal ion transport across biological membrane Na^+/K^+ -ion pump. Dioxygen molecule in life. Dioxygen management proteins: Haemoglobin, Myoglobin, Hemocyanine and Hemerythrin. Electron transfer proteins: Cytochromes and Ferredoxins. Hydrolytic enzymes: carbonate bicarbonate buffering system and carbonic anhydrase and carboxyanhydrase A. Biological nitrogen fixation, Photosynthesis: Photosystem-I and Photosystem-II. Toxic metal ions and their effects, chelation therapy (examples only), Pt and Au complexes as drugs (examples only), metal dependent diseases (examples only)

Organometallic Chemistry

(24 Lectures) Marks: 20

Definition and classification of organometallic compounds on the basis of bond type. Concept of hapticity of organic ligands. 18-electron and 16-electron rules (pictorial MO approach). Applications of 18-electron rule to metal carbonyls, nitrosyls, cyanides. General methods of preparation of mono and binuclear carbonyls of 3d series. Structures of mononuclear and binuclear carbonyls. π -acceptor behaviour of CO, synergic effect and use of IR data to explain extent of back bonding. Zeise's salt: Preparation, structure, evidences of synergic effect. Ferrocene: Preparation and reactions (acetylation, alkylation, metallation, Mannich Condensation). Reactions of organometallic complexes: substitution, oxidative addition, reductive elimination and insertion reactions.

Catalysis by Organometallic Compounds

Study of the following industrial processes

1. Alkene hydrogenation (Wilkinson's Catalyst)
2. Hydroformylation
3. Wacker Process
4. Synthetic gasoline (Fischer Tropsch reaction)
5. Ziegler-Natta catalysis for olefin polymerization.

Reaction Kinetics and Mechanism
(12 Lectures) Marks: 10

Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, Trans- effect and its application in complex synthesis, theories of trans effect, Mechanism of nucleophilic substitution in square planar complexes, Thermodynamic and Kinetic stability, Kinetics of octahedral substitution, Ligand field effects and reaction rates, Mechanism of substitution in octahedral complexes.

Reference Books

1. Lippard, S.J. & Berg, J.M. *Principles of Bioinorganic Chemistry* Panima Publishing Company 1994.
2. Huheey, J. E.; Keiter, E.A. & Keiter, R.L. *Inorganic Chemistry, Principles of Structure and Reactivity 4th Ed.*, Harper Collins 1993, Pearson, 2006.
3. Greenwood, N.N. & Earnshaw A. *Chemistry of the Elements*, ButterworthHeinemann, 1997.
4. Cotton, F.A., Wilkinson, G., Murrillo, C. A., Bochmann, M., *Advanced Inorganic Chemistry 6th Ed.* 1999., Wiley.
5. Bertini, I., Gray, H. B., Lippard, S.J., Valentine, J. S., Viva, 2007.
6. Basolo, F, and Pearson, R.C. *Mechanisms of Inorganic Chemistry*, John Wiley & Sons, NY, 1967.
7. Purecell, K.F. and Kotz, J.C., *An Introduction to Inorganic Chemistry*, Saunders: Philadelphia, 1980.
8. Powell, P. *Principles of Organometallic Chemistry*, Chapman and Hall, 1988.
9. Collman, J. P. *et al. Principles and Applications of Organotransition Metal Chemistry*. Mill Valley, CA: University Science Books, 1987.
10. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*. New York, NY: John Wiley, 2000.

CEMACOR13P:: INORGANIC CHEMISTRY-V LAB

(60 Lectures/Contact Hours) Marks: 25

Qualitative semimicro analysis of mixtures containing four radicals. Emphasis should be given to the understanding of the chemistry of different reactions and to assign the most probable composition.

Cation Radicals: Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Cr^{3+} , $\text{Mn}^{2+}/\text{Mn}^{4+}$, Fe^{3+} , $\text{Co}^{2+}/\text{Co}^{3+}$, Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Bi^{3+} , $\text{Sn}^{2+}/\text{Sn}^{4+}$, $\text{As}^{3+}/\text{As}^{5+}$, $\text{Sb}^{3+}/\text{Sb}^{5+}$, NH_4^+ , Mg^{2+} .

Anion Radicals: F^- , Cl^- , Br^- , BrO_3^- , I^- , IO_3^- , SCN^- , S^{2-} , SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , AsO_4^{3-} , BO_3^{3-} , CrO_4^{2-} / $\text{Cr}_2\text{O}_7^{2-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$.

Insoluble Materials: $\text{Al}_2\text{O}_3(\text{ig})$, $\text{Fe}_2\text{O}_3(\text{ig})$, $\text{Cr}_2\text{O}_3(\text{ig})$, SnO_2 , SrSO_4 , BaSO_4 , CaF_2 , PbSO_4 .

Reference Books

1. Svehla, G., *Vogel's Qualitative Inorganic Analysis*, Pearson Education, 2012.
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CEMACOR14T: PHYSICAL CHEMISTRY- IV

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Molecular Spectroscopy

(25 Lectures) Marks: 20

Interaction of electromagnetic radiation with molecules; Transition between two states and time-dependent S.E.; Transition moment integral and selection rules; Various types of spectra

Rotation spectroscopy: Selection rules, intensities of spectral lines, determination of bond lengths of diatomic and linear triatomic molecules, isotopic substitution

Vibrational spectroscopy: Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies; Diatomic vibrating rotator, P, Q, R branches

Raman spectroscopy: Qualitative treatment of Rotational Raman effect; Effect of nuclear spin, Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion

Nuclear Magnetic Resonance (NMR) spectroscopy: Principles of NMR spectroscopy, Larmor precession, chemical shift and low resolution spectra, different scales, spin-spin coupling and high resolution spectra, interpretation of PMR spectra of organic molecules

Electron Spin Resonance (ESR) spectroscopy: Its principle, hyperfine structure, ESR of simple radicals

Photochemistry

(15 Lectures) Marks: 14

Lambert-Beer's law: Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients; Laws of photochemistry,

Stark-Einstein law of photochemical equivalence, quantum yield, actinometry, examples of low and high quantum yields

Photochemical Processes: Potential energy curves (diatomic molecules), Frank-Condon principle and vibrational structure of electronic spectra; Bond dissociation and principle of determination of dissociation energy (ground state); Decay of excited states by radiative and non-radiative paths; Pre-dissociation; Fluorescence and phosphorescence, Jablonskii diagram

Rate of Photochemical processes: Photochemical equilibrium and the differential rate of photochemical reactions, Photostationary state; HI decomposition, $\text{H}_2\text{-Br}_2$ reaction, dimerisation of anthracene; photosensitised reactions, quenching; Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence

Surface phenomenon (20 Lectures) Marks: 16

Surface tension and energy: Surface tension, surface energy, excess pressure, capillary rise and surface tension; Work of cohesion and adhesion, spreading of liquid over other surface; Vapour pressure over curved surface; Temperature dependence of surface tension

Adsorption: Physical and chemical adsorption; Freundlich and Langmuir adsorption isotherms; multilayer adsorption and BET isotherm (no derivation required); Gibbs' adsorption isotherm and surface excess; Heterogenous catalysis (single reactant); Zero order and fractional order reactions

Colloids: Lyophobic and lyophilic sols, Origin of charge and stability of lyophobic colloids, Coagulation and Schultz-Hardy rule, Zeta potential and Stern double layer (qualitative idea), Tyndall effect; Electrokinetic phenomena (qualitative idea only); Determination of Avogadro number by Perrin's method; Stability of colloids and zeta potential; Micelle formation

Reference Books

1. Castellan, G. W. Physical Chemistry, Narosa
2. Levine, I. N. Physical Chemistry, Tata McGraw-Hill
3. Atkins, P. W. & Paula, J. de Atkin's, Physical Chemistry, Oxford University Press
4. McQuarrie, D. A. & Simons, J. D. Physical Chemistry: A Molecular Approach, Viva Press
5. Mortimer, R. G. Physical Chemistry, Elsevier
6. Laidler, K. J. Chemical Kinetics, Pearson
7. Banwell, C. N. Fundamentals of Molecular Spectroscopy, Tata-McGraw-Hill
8. Barrow, G. M. Molecular Spectroscopy, McGraw-Hill
9. Hollas, J.M. Modern Spectroscopy, Wiley India
10. McHale, J. L. Molecular Spectroscopy, Pearson Education
11. Wayne, C. E. & Wayne, R. P. Photochemistry, OUP
12. Brown, J. M. Molecular Spectroscopy, OUP

13. Levine, I. N. Quantum Chemistry, PHI
14. Atkins, P. W. Molecular Quantum Mechanics, Oxford

CEMACOR14P: PHYSICAL CHEMISTRY- IV LAB
(60 Lectures/Contact Hours) Marks: 25

Experiment 1: Determination of surface tension of a liquid using Stalagmometer

Experiment 2: Determination of CMC from surface tension measurements

Experiment 3: Verification of Beer and Lambert's Law for KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ solution

Experiment 4: Study of kinetics of $\text{K}_2\text{S}_2\text{O}_8 + \text{KI}$ reaction, spectrophotometrically

Experiment 5: Determination of pH of unknown buffer, spectrophotometrically

Experiment 6: Spectrophotometric determination of CMC

Reference Books

1. Viswanathan, B., Raghavan, P.S. *Practical Physical Chemistry* Viva Books (2009)
2. Mendham, J., A. I. Vogel's Quantitative Chemical Analysis 6th Ed., Pearson
3. Harris, D. C. *Quantitative Chemical Analysis*. 6th Ed., Freeman (2007)
4. Palit, S.R., De, S. K. *Practical Physical Chemistry* Science Book Agency
5. *University Hand Book of Undergraduate Chemistry Experiments*, edited by Mukherjee, G. N., University of Calcutta
6. Levitt, B. P. edited *Findlay's Practical Physical Chemistry* Longman Group Ltd.
7. Gurtu, J. N., Kapoor, R., *Advanced Experimental Chemistry* S. Chand & Co. Ltd.

DISCIPLINE SPECIFIC ELECTIVE COURSE
(HONOURS) IN CHEMISTRY