
SEMESTER-IV

CEMACOR08T: PHYSICAL CHEMISTRY-III

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Application of Thermodynamics – II (20 lectures) Marks: 18

Colligative properties: Vapour pressure of solution; Ideal solutions, ideally diluted solutions and colligative properties; Raoult's law; Thermodynamic derivation using chemical potential to derive relations between the four colligative properties [(i) relative lowering of vapour pressure, (ii) elevation of boiling point, (iii) Depression of freezing point, (iv) Osmotic pressure] and amount of solute. Applications in calculating molar masses of normal, dissociated and associated solutes in solution; Abnormal colligative properties

Phase rule: Definitions of phase, component and degrees of freedom; Phase rule and its derivations; Definition of phase diagram; Phase diagram for water, CO₂, Sulphur

First order phase transition and Clapeyron equation; Clausius-Clapeyron equation - derivation and use; Liquid vapour equilibrium for two component systems; Phenol-water system

Three component systems, water-chloroform-acetic acid system, triangular plots

Binary solutions: Ideal solution at fixed temperature and pressure; Principle of fractional distillation; Duhem-Margules equation; Henry's law; Konowaloff's rule; Positive and negative deviations from ideal behavior; Azeotropic solution; Liquid-liquid phase diagram using phenol-water system; Solid-liquid phase diagram; Eutectic mixture

Electrical Properties of molecules (20 Lectures) Marks: 18

Ionic equilibria: Chemical potential of an ion in solution; Activity and activity coefficients of ions in solution; Debye-Huckel limiting law-brief qualitative description of the postulates involved, qualitative idea of the model, the equation (without derivation) for ion-ion atmosphere interaction potential. Estimation of activity coefficient for electrolytes using Debye-Huckel limiting law; Derivation of mean ionic activity coefficient from the expression of ion-atmosphere interaction potential; Applications of the equation and its limitations

Electromotive Force: Quantitative aspects of Faraday's laws of electrolysis, rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry; Chemical cells, reversible and irreversible cells with examples; Electromotive force of a cell and its measurement, Nernst equation; Standard electrode (reduction) potential and its application to different kinds of half-cells. Application of EMF measurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass and $\text{SbO/Sb}_2\text{O}_3$ electrodes

Concentration cells with and without transference, liquid junction potential; determination of activity coefficients and transference numbers; Qualitative discussion of potentiometric titrations (acid-base, redox, precipitation)

Dipole moment and polarizability: Polarizability of atoms and molecules, dielectric constant and polarisation, molar polarisation for polar and non-polar molecules; Clausius-Mosotti equation and Debye equation (both without derivation) and their application; Determination of dipole moments

Quantum Chemistry **(20 Lectures) Marks: 16**

Angular momentum: Commutation rules, quantization of square of total angular momentum and z-component; Properties of angular momentum operators; Eigenfunctions of L_Z and L_Z^2 ; Rigid rotator model of rotation of diatomic molecule and Schrödinger equation; Transformation to spherical polar coordinates; Separation of variables; Spherical harmonics; Discussion of solution

Qualitative treatment of hydrogen atom and hydrogen-like ions: Setting up of S.E. in spherical polar coordinates, radial part, quantization of energy (only final energy expression); Plots of polar parts and radial distributions; Wave –function of one electron atoms; Average and most probable distances of electron from nucleus; Setting up of Schrödinger equation for many-electron atoms (He, Li)

LCAO and HF-SCF: Born-Oppenheimer approximation; LCAO-MO treatment of H_2^+ ; Bonding and antibonding orbitals; Qualitative extension to H_2 ; Comparison of LCAOMO and VB treatments of H_2 and their limitations; Covalent bonding, valence bond and molecular orbital approaches, Hartree-Fock method development, SCF and configuration interaction (only basics)

Reference Books

1. Castellan, G. W. *Physical Chemistry*, Narosa
2. Atkins, P. W. & Paula, J. de *Atkins', Physical Chemistry*, Oxford University Press
3. McQuarrie, D. A. & Simons, J. D. *Physical Chemistry: A Molecular Approach*, Viva Press
4. Levine, I. N. *Physical Chemistry*, Tata McGraw-Hill
5. Moore, W. J. *Physical Chemistry*, Orient Longman

6. Mortimer, R. G. *Physical Chemistry*, Elsevier
7. Engel, T. & Reid, P. *Physical Chemistry*, Pearson
8. Levine, I. N. *Quantum Chemistry*, PHI
9. Atkins, P. W. *Molecular Quantum Mechanics*, Oxford
10. Engel, T. & Reid, P. *Physical Chemistry*, Pearson
11. Maron, S.H., Prutton, C. F., *Principles of Physical Chemistry*, McMillan
12. Klotz, I.M., Rosenberg, R. M. *Chemical Thermodynamics: Basic Concepts and Methods* Wiley
13. Rastogi, R. P. & Misra, R.R. *An Introduction to Chemical Thermodynamics*, Vikas
14. Glasstone, S. *An Introduction to Electrochemistry*, East-West Press

CEMACOR08P: PHYSICAL CHEMISTRY-III LAB

60 (Lectures/Contact Hours) Marks: 25

Experiment 1: Determination of solubility of sparingly soluble salt in water, in electrolyte with common ions and in neutral electrolyte (using common indicator)

Experiment 2: Potentiometric titration of Mohr's salt solution against standard $K_2Cr_2O_7$ solution

Experiment 3: Determination of K_{sp} for AgCl by potentiometric titration of $AgNO_3$ solution against standard KCl solution

Experiment 4: Effect of ionic strength on the rate of Persulphate – Iodide reaction

Experiment 5: Study of phenol-water phase diagram

Experiment 6: pH-metric titration of acid (mono- and di-basic) against strong base

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.

CEMACOR09T: INORGANIC CHEMISTRY-III**(Credits: Theory-04, Practicals-02)****Theory: 60 Lectures Marks: 50****General Principles of Metallurgy****(6 Lectures) Marks: 12**

Chief modes of occurrence of metals based on standard electrode potentials. Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent. Electrolytic Reduction, Hydrometallurgy. Methods of purification of metals: Electrolytic Kroll process, Parting process, van Arkel-de Boer process and Mond's process, Zone refining.

Chemistry of *s* and *p* Block Elements**(30 Lectures) Marks: 26**

Relative stability of different oxidation states, diagonal relationship and anomalous behaviour of first member of each group. Allotropy and catenation. Study of the following compounds with emphasis on structure, bonding, preparation, properties and uses. Beryllium hydrides and halides. Boric acid and borates, boron nitrides, borohydrides (diborane) and graphitic compounds, silanes, Oxides and oxoacids of nitrogen, phosphorus, sulphur and chlorine. Peroxo acids of sulphur, sulphur-nitrogen compounds, interhalogen compounds, polyhalide ions, pseudohalogens, fluorocarbons and basic properties of halogens.

Noble Gases:

Occurrence and uses, rationalization of inertness of noble gases, peculiar behaviour of liquid helium, Clathrates; preparation and properties of XeF₂, XeF₄ and XeF₆; Nature of bonding in noble gas compounds (Valence bond treatment and MO treatment for XeF₂ and XeF₄). Xenon-oxygen compounds. Molecular shapes of noble gas compounds (VSEPR theory).

Inorganic Polymers:

Types of inorganic polymers, comparison with organic polymers, synthesis, structural aspects and applications of silicones and siloxanes. Borazines, silicates and phosphazenes.

Coordination Chemistry-I**(24 Lectures) Marks: 12**

Coordinate bonding: double and complex salts. Werner's theory of coordination complexes, Classification of ligands, Ambidentate ligands, chelates, Coordination

numbers, IUPAC nomenclature of coordination complexes (up to two metal centers), Isomerism in coordination compounds, constitutional and stereo isomerism, Geometrical and optical isomerism in square planar and octahedral complexes.

Reference Books

1. Huheey, J. E.; Keiter, E.A. & Keiter, R.L. *Inorganic Chemistry, Principles of Structure and Reactivity 4th Ed.*, Harper Collins 1993, Pearson, 2006.
 2. Greenwood, N.N. & Earnshaw A. *Chemistry of the Elements*, ButterworthHeinemann, 1997.
 3. Cotton, F.A., Wilkinson, G., Murrillo, C. A., Bochmann, M., *Advanced Inorganic Chemistry 6th Ed.* 1999., Wiley.
 4. Miessler, G. L. & Donald, A. Tarr. *Inorganic Chemistry 4th Ed.*, Pearson, 2010.
 5. Purecell, K.F. and Kotz, J.C., *An Introduction to Inorganic Chemistry*, Saunders: Philadelphia, 1980.
 6. Mingos, D.M.P., *Essential trends in inorganic chemistry*. Oxford University Press (1998).
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CEMACOR09P: INORGANIC CHEMISTRY-III LAB
60 (Lectures/Contact Hours) Marks: 25

Complexometric titration

1. Zn(II)
2. Zn(II) in a Zn(II) and Cu(II) mixture.
3. Ca(II) and Mg(II) in a mixture.
4. Hardness of water.

Inorganic preparations

1. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6/\text{ClO}_4$
2. *Cis* and *trans* $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$
3. Tetraamminecarbonatocobalt (III) ion
4. Potassium tris(oxalato)ferrate(III)
5. Tris-(ethylenediamine) nickel(II) chloride.
6. $[\text{Mn}(\text{acac})_3]$ and $[\text{Fe}(\text{acac})_3]$ (acac= acetylacetonate)

Reference Books

1. Mendham, J., *A. I. Vogel's Quantitative Chemical Analysis* 6th Ed., Pearson, 2009.
 2. *Inorganic Synthesis*, Vol. 1-10.
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CEMACOR10T: ORGANIC CHEMISTRY-IV
(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Nitrogen compounds
(12 Lectures) Marks: 08

Amines: Aliphatic & Aromatic: preparation, separation (Hinsberg's method) and identification of primary, secondary and tertiary amines; reaction (with mechanism): Eschweiler-Clarke methylation, diazo coupling reaction, Mannich reaction; formation and reactions of phenylenediamines, diazomethane and diazoacetic ester.

Nitro compounds (aliphatic and aromatic): preparation and reaction (with mechanism): reduction under different conditions; Nef carbonyl synthesis, Henry reaction and conjugate addition of nitroalkane anion.

Alkyl nitrile and isonitrile: preparation and reaction (with mechanism): Thorpe nitrile condensation, von Richter reaction.

Diazonium salts and their related compounds: reactions (with mechanism) involving replacement of diazo group; reactions: Gomberg, Meerwein, Japp-Klingermann.

Rearrangements
(14 Lectures) Marks: 10

Mechanism with evidence and stereochemical features for the following

Rearrangement to electron-deficient carbon: Wagner-Meerwein rearrangement, pinacol rearrangement, dienone-phenol; Wolff rearrangement in Arndt-Eistert synthesis, benzilbenzilic acid rearrangement, Demjanov rearrangement, Tiffeneau–Demjanov rearrangement.

Rearrangement to electron-deficient nitrogen: rearrangements: Hofmann, Curtius, Lossen, Schmidt and Beckmann.

Rearrangement to electron-deficient oxygen: Baeyer-Villiger oxidation, cumene hydroperoxide-phenol rearrangement and Dakin reaction.

Aromatic rearrangements: Migration from oxygen to ring carbon: Fries rearrangement and Claisen rearrangement.

Migration from nitrogen to ring carbon: Hofmann-Martius rearrangement, FischerHepp rearrangement, *N*-azo to *C*-azo rearrangement, Bamberger rearrangement, Orton rearrangement and benzdine rearrangement.

Rearrangement reactions by green approach: Fries rearrangement, Claisen rearrangement, Beckmann rearrangement, Baeyer-Villiger oxidation.

The Logic of Organic Synthesis

(14 Lectures) Marks: 12

Retrosynthetic analysis: disconnections; synthons, donor and acceptor synthons; natural reactivity and *umpolung*; latent polarity in bifunctional compounds: consonant and dissonant polarity; illogical electrophiles and nucleophiles; synthetic equivalents; functional group interconversion and addition (FGI and FGA); C-C disconnections and synthesis: one-group and two-group (1,2- to 1,5-dioxygenated compounds), reconnection (1,6-dicarbonyl); protection-deprotection strategy (alcohol, amine, carbonyl, acid).

Strategy of ring synthesis: thermodynamic and kinetic factors; synthesis of large rings, application of high dilution technique.

Asymmetric synthesis: stereoselective and stereospecific reactions; diastereoselectivity and enantioselectivity (only definition); enantioselectivity: kinetically controlled MPV reduction; diastereoselectivity: addition of nucleophiles to C=O adjacent to a stereogenic centre: Felkin-Anh and Zimmermann-Traxler models.

Organic Spectroscopy

(20 Lectures) Marks: 20

UV Spectroscopy: introduction; types of electronic transitions, end absorption; transition dipole moment and allowed/forbidden transitions; chromophores and auxochromes; Bathochromic and Hypsochromic shifts; intensity of absorptions (Hyper/Hypochromic effects); application of Woodward's Rules for calculation of λ_{max} for the following systems: conjugated diene, α,β -unsaturated aldehydes and ketones (alicyclic, homoannular and heteroannular); extended conjugated systems (dienes, aldehydes and

ketones); relative positions of λ_{\max} considering conjugative effect, steric effect, solvent effect, effect of pH; effective chromophore concentration: keto-enol systems; benzenoid transitions.

IR Spectroscopy: introduction; modes of molecular vibrations (fundamental and nonfundamental); IR active molecules; application of Hooke's law, force constant; *fingerprint region* and its significance; effect of deuteration; overtone bands; vibrational coupling in IR; characteristic and diagnostic stretching frequencies of C-H, N-H, O-H, C-O, C-N, C-X, C=C (including skeletal vibrations of aromatic compounds), C=O, C=N, N=O, C≡C, C≡N; characteristic/diagnostic bending vibrations are included; factors affecting stretching frequencies: effect of conjugation, electronic effects, mass effect, bond multiplicity, ring-size, solvent effect, H-bonding on IR absorptions; application in functional group analysis.

NMR Spectroscopy: introduction; nuclear spin; NMR active molecules; basic principles of Proton Magnetic Resonance; equivalent and non-equivalent protons; chemical shift and factors influencing it; ring current effect; significance of the terms: up-/downfield, shielded and deshielded protons; spin coupling and coupling constant (1st order spectra); relative intensities of *first-order* multiplets: Pascal's triangle; chemical and magnetic equivalence in NMR; elementary idea about *non-first-order* splitting; anisotropic effects in alkene, alkyne, aldehydes and aromatics; NMR peak area, integration; relative peak positions with coupling patterns of common organic compounds (both aliphatic and benzenoid-aromatic); rapid proton exchange; interpretation of NMR spectra of simple compounds.

Applications of IR, UV and NMR spectroscopy for identification of simple organic molecules.

Reference Books

1. Finar, I. L. *Organic Chemistry (Volume 1)*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
2. Finar, I. L. *Organic Chemistry (Volume 2: Stereochemistry and the Chemistry of Natural Products)*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
3. Norman, R.O. C., Coxon, J. M. *Principles of Organic Synthesis*, Third Edition, Nelson Thornes, 2003.
4. Clayden, J., Greeves, N., Warren, S., *Organic Chemistry*, Second edition, Oxford University Press 2012.
5. Silverstein, R. M., Bassler, G. C., Morrill, T. C. *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, INC, Fifth edition.
6. Kemp, W. *Organic Spectroscopy*, Palgrave.
7. Pavia, D. L. *et al. Introduction to Spectroscopy*, 5th Ed. Cengage Learning India Ed. (2015).
8. Dyer, J. *Application of Absorption Spectroscopy of Organic Compounds*, PHI Private Limited
9. March, J. *Advanced Organic Chemistry*, Fourth edition, Wiley.
10. Harwood, L. M., *Polar Rearrangements*, Oxford Chemistry Primer, Oxford University Press.
11. Bailey, Morgan, *Organonitrogen Chemistry*, Oxford Chemistry Primer, Oxford University Press.

12. Ahluwalia, V. K. *Strategies for Green Organic Synthesis*, ANE Books Pvt. Ltd.
13. Warren, S. *Organic Synthesis the Disconnection Approach*, John Wiley and Sons.
14. Warren, S., *Designing Organic Synthesis*, Wiley India, 2009.
15. Carruthers, W. *Modern methods of Organic Synthesis*, Cambridge University Press.
16. Willis, C. A., Wills, M., *Organic Synthesis*, Oxford Chemistry Primer, Oxford University Press.

CEMACOR10P: ORGANIC CHEMISTRY-IV LAB

60 (Lectures/Contact Hours) Marks: 25

Quantitative Estimations: Each student is required to perform all the experiments.

1. Estimation of glycine by Sørensen's formol method
2. Estimation of glucose by titration using Fehling's solution
3. Estimation of sucrose by titration using Fehling's solution
4. Estimation of vitamin-C (reduced)
5. Estimation of aromatic amine (aniline) by bromination (Bromate-Bromide) method
6. Estimation of phenol by bromination (Bromate-Bromide) method
7. Estimation of formaldehyde (Formalin)
8. Estimation of acetic acid in commercial vinegar
9. Estimation of urea (hypobromite method)
10. Estimation of saponification value of oil/fat/ester

Reference Books

1. Arthur, I. V. *Quantitative Organic Analysis*, Pearson
2. *University Hand Book of Undergraduate Chemistry Experiments*, edited by Mukherjee, G. N., University of Calcutta