

CEMADSE01T:

ADVANCED PHYSICAL CHEMISTRY (Credits: Theory-04, Practicals-02)

Theory

(60 Lecturers)

Crystal Structure

(20 Lectures) Marks: 18

Bravais Lattice and Laws of Crystallography: Types of solid, Bragg's law of diffraction; Laws of crystallography; Permissible symmetry axes in crystals; Lattice, space lattice, unit cell, crystal planes, Bravais lattice. Packing of uniform hard sphere, close packed arrangements (fcc and hcp); Tetrahedral and octahedral voids. Void space in p-type, F-type and I-type cubic systems

Crystal planes: Distance between consecutive planes [cubic, tetragonal and orthorhombic lattices]; Indexing of planes, Miller indices; calculation of d_{hkl} ; Relation between molar mass and unit cell dimension for cubic system; Laue's diffraction; Bragg's law (derivation)

Determination of crystal structure: Powder method; Structure of NaCl and KCl crystals

Statistical Thermodynamics

(20 Lectures) Marks: 16

Configuration: Macrostates, microstates and configuration; calculation of microstates with harmonic oscillator and tossing of coins; variation of W with E ; equilibrium configuration

Boltzmann distribution: Thermodynamic probability, entropy and probability, Boltzmann distribution formula (with derivation); Applications to barometric distribution; Concept of ensemble - canonical ensemble and grand canonical ensembles

Partition function: molecular partition function and thermodynamic properties (U , H , S , C_v , q , P); Partition function correlating – Chemical equilibrium and Maxwell's speed distribution; Gibbs' paradox; Ideal gas equation

Special selected topics

(20 Lectures) Marks: 16

Specific heat of solid: Coefficient of thermal expansion, thermal compressibility of solids; Dulong –Petit's law; Perfect Crystal model, Einstein's theory – derivation from partition function, limitations; Debye's T^3 law – analysis at the two extremes

3rd law: Absolute entropy, Plank's law, Calculation of entropy, Nernst heat theorem
Adiabatic demagnetization: Approach to zero Kelvin, adiabatic cooling, demagnetization, adiabatic demagnetization – involved curves

Polymers: Classification of polymers, nomenclature, Molecular forces and chemical bonding in polymers, Texture of Polymers; Criteria for synthetic polymer formation; Relationships between functionality, extent of reaction and degree of polymerization; Mechanism and kinetics of step growth and copolymerization; Conducting polymers

Reference Books

1. Castellan, G. W. *Physical Chemistry*, Narosa
2. Levine, I. N. *Physical Chemistry*, Tata McGraw-Hill
3. Moore, W. J. *Physical Chemistry*, Orient Longman
4. Atkins, P. W. & Paula, J. de *Atkins', Physical Chemistry*, Oxford University Press
5. McQuarrie, D. A. & Simons, J. D. *Physical Chemistry: A Molecular Approach*, Viva Press
6. Engel, T. & Reid, P. *Physical Chemistry*, Pearson
7. Nash, L. K. *Elements of Statistical Thermodynamics*, Dover
8. Rastogi, R. P. & Misra, R.R. *An Introduction to Chemical Thermodynamics*, Vikas
9. Zemansky, M. W. & Dittman, R.H. *Heat and Thermodynamics*, Tata-McGraw-Hill
10. Billmeyer, F. W. *Textbook of Polymer Science*, John Wiley & Sons, Inc.
11. Seymour, R. B. & Carraher, C. E. *Polymer Chemistry: An Introduction*, Marcel Dekker, Inc.
12. Odian, G. *Principles of Polymerization*, Wiley
13. Billmeyer, F. W. *Textbook of Polymer Science*, Wiley Interscience, 1971.

CEMADSE01P: ADVANCED PHYSICAL CHEMISTRY LAB (60 Lectures/Contact Hours) Marks: 25

Computer programs based on numerical methods for

Programming 1: Roots of equations: (e.g. volume of van der Waals gas and comparison with ideal gas, pH of a weak acid)

Programming 2: Numerical differentiation (e.g., change in pressure for small change in volume of a van der Waals gas, potentiometric titrations)

Programming 3: Numerical integration (e.g. entropy/ enthalpy change from heat capacity data), probability distributions (gas kinetic theory) and mean values

Programming 4: Matrix operations (Application of Gauss-Siedel method in colourimetry)

Programming 5: Simple exercises using molecular visualization software

Reference Books

1. McQuarrie, D. A. *Mathematics for Physical Chemistry* University Science Books (2008)
2. Mortimer, R. *Mathematics for Physical Chemistry*. 3rd Ed. Elsevier (2005)
3. Yates, P. *Chemical Calculations*. 2nd Ed. CRC Press (2007)
4. Harris, D. C. *Quantitative Chemical Analysis*. 6th Ed., Freeman (2007) Chapters 3-5
5. Noggle, J. H. *Physical Chemistry on a Microcomputer*. Little Brown & Co. (1985)

CEMADSE02T: ANALYTICAL METHODS IN CHEMISTRY

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Qualitative and quantitative aspects of analysis:

(05 Lectures) Marks: 06

Sampling, evaluation of analytical data, errors, accuracy and precision, methods of their expression, normal law of distribution if indeterminate errors, statistical test of data; F, Q and t test, rejection of data, and confidence intervals.

Optical methods of analysis:

(25 Lectures) Marks: 16

Origin of spectra, interaction of radiation with matter, fundamental laws of spectroscopy and selection rules, validity of Beer-Lambert's law.

UV-Visible Spectrometry: Basic principles of instrumentation (choice of source, monochromator and detector) for single and double beam instrument;

Basic principles of quantitative analysis: estimation of metal ions from aqueous solution, geometrical isomers, keto-enol tautomers. Determination of composition of metal complexes using Job's method of continuous variation and mole ratio method.

Infrared Spectrometry: Basic principles of instrumentation (choice of source, monochromator & detector) for single and double beam instrument; sampling techniques.

Structural illustration through interpretation of data, Effect and importance of isotope substitution.

Flame Atomic Absorption and Emission Spectrometry: Basic principles of instrumentation (choice of source, monochromator, detector, choice of flame and Burner designs. Techniques of atomization and sample introduction; Method of background

correction, sources of chemical interferences and their method of removal. Techniques for the quantitative estimation of trace level of metal ions from water samples.

Thermal methods of analysis:
(05 Lectures) Marks: 06

Theory of thermogravimetry (TG), basic principle of instrumentation.

Techniques for quantitative estimation of Ca and Mg from their mixture.

Electroanalytical methods:
(10 Lectures) Marks: 08

Classification of electroanalytical methods, basic principle of pH metric, potentiometric and conductometric titrations. Techniques used for the determination of equivalence points. Techniques used for the determination of pK_a values.

Separation techniques:
(15 Lectures) Marks: 14

Solvent extraction: Classification, principle and efficiency of the technique.

Mechanism of extraction: extraction by solvation and chelation.

Technique of extraction: batch, continuous and counter current extractions.

Qualitative and quantitative aspects of solvent extraction: extraction of metal ions from aqueous solution, extraction of organic species from the aqueous and nonaqueous media.

Chromatography: Classification, principle and efficiency of the technique.

Mechanism of separation: adsorption, partition & ion exchange.

Development of chromatograms: frontal, elution and displacement methods.

Qualitative and quantitative aspects of chromatographic methods of analysis: IC, GLC, GPC, TLC and HPLC.

Stereoisomeric separation and analysis: Measurement of optical rotation, calculation of Enantiomeric excess (ee)/ diastereomeric excess (de) ratios and determination of enantiomeric composition using NMR, Chiral solvents and chiral shift reagents. Chiral chromatographic techniques using chiral columns (GC and HPLC).

Role of computers in instrumental methods of analysis.

Reference Books

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

- 2009.
2. Willard, H.H. *et al.*: *Instrumental Methods of Analysis*, 7th Ed. Wardsworth Publishing Company, Belmont, California, USA, 1988.
3. Christian, G.D. *Analytical Chemistry*, 6th Ed. John Wiley & Sons, New York, 2004.
4. Harris, D.C.: *Exploring Chemical Analysis*, 9th Ed. New York, W.H. Freeman, 2016.
5. Khopkar, S.M. *Basic Concepts of Analytical Chemistry*. New Age International Publisher, 2009.
6. Skoog, D.A. Holler F.J. & Nieman, T.A. *Principles of Instrumental Analysis*, Cengage Learning India Ed.
7. Mikes, O. *Laboratory Hand Book of Chromatographic & Allied Methods*, Elles Harwood Series on Analytical Chemistry, John Wiley & Sons, 1979.
8. Ditts, R.V. *Analytical Chemistry; Methods of separation*, van Nostrand, 1974.
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CEMADSE02P: ANALYTICAL METHODS IN CHEMISTRY LAB
(60 Lectures/Contact Hours) Marks: 25

I. Separation Techniques

Chromatography:

- (a) Separation of mixtures

Separation and identification of the monosaccharides present in the given mixture (glucose & fructose) by paper chromatography. Reporting the R_f values.

- (b) Separate a mixture of Sudan yellow and Sudan Red by TLC technique and identify them on the basis of their R_f values.
- (c) Chromatographic separation of the active ingredients of plants, flowers and juices by TLC

II. Solvent Extractions:

To separate a mixture of Ni^{2+} & Fe^{2+} by complexation with DMG and extracting the Ni^{2+} -DMG complex in chloroform, and determine its concentration by spectrophotometry.

Analysis of soil:

- (i) Determination of pH of soil.

- (ii) Estimation of calcium, magnesium, phosphate

Ion exchange:

Determination of exchange capacity of cation exchange resins and anion exchange resins.

III. Spectrophotometry

1. Determination of pKa values of indicator using spectrophotometry.
2. Determination of chemical oxygen demand (COD).
3. Determination of Biological oxygen demand (BOD).

Reference Books

1. Mendham, J., *A. I. Vogel's Quantitative Chemical Analysis 6th Ed.*, Pearson, 2009.
2. Willard, H.H. *et al.: Instrumental Methods of Analysis, 7th Ed.* Wardsworth Publishing Company, Belmont, California, USA, 1988.
3. Christian, G.D. *Analytical Chemistry, 6th Ed.* John Wiley & Sons, New York, 2004.
4. Harris, D.C. *Exploring Chemical Analysis, 9th Ed.* New York, W.H. Freeman, 2016.
5. Khopkar, S.M. *Basic Concepts of Analytical Chemistry.* New Age International Publisher, 2009.
6. Skoog, D.A. Holler F.J. and Nieman, T.A. *Principles of Instrumental Analysis*, Cengage Learning India Edition.
7. Mikes, O. & Chalmes, R.A. *Laboratory Handbook of Chromatographic & Allied Methods*, Elles Harwood Ltd. London.
8. Ditts, R.V. *Analytical Chemistry: Methods of separation.* Van Nostrand, New York, 1974.

CEMADSE03T: INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

**Introduction to spectroscopic methods of analysis:
(04 Lectures) Marks: 04**

Recap of the spectroscopic methods covered in detail in the core chemistry syllabus: Treatment of analytical data, including error analysis. Classification of analytical methods and the types of instrumental methods. Consideration of electromagnetic radiation.

Molecular spectroscopy:**(16 Lectures) Marks: 12***Infrared spectroscopy:*

Interactions with molecules: absorption and scattering. Means of excitation (light sources), separation of spectrum (wavelength dispersion, time resolution), detection of the signal (heat, differential detection), interpretation of spectrum (qualitative, mixtures, resolution), advantages of Fourier Transform (FTIR). Samples and results expected. Applications: Issues of quality assurance and quality control, Special problems for portable instrumentation and rapid detection.

UV-Visible/ Near IR – emission, absorption, fluorescence and photoacoustic. Excitation sources (lasers, time resolution), wavelength dispersion (gratings, prisms, interference filters, laser, placement of sample relative to dispersion, resolution), Detection of signal (photocells, photomultipliers, diode arrays, sensitivity and S/N), Single and Double Beam instruments, Interpretation (quantification, mixtures, absorption vs. fluorescence and the use of time, photoacoustic, fluorescent tags).

Separation techniques:**(16 Lectures) Marks: 12**

Chromatography: Gas chromatography, liquid chromatography, supercritical fluids, Importance of column technology (packing, capillaries), Separation based on increasing number of factors (volatility, solubility, interactions with stationary phase, size, electrical field), Detection: simple vs. specific (gas and liquid), Detection as a means of further analysis (use of tags and coupling to IR and MS), Electrophoresis (plates and capillary) and use with DNA analysis.

Elemental analysis:**(08 Lectures) Marks: 06**

Mass spectrometry (electrical discharges).

Atomic spectroscopy: Atomic absorption, Atomic emission, and Atomic fluorescence.

Excitation and getting sample into gas phase (flames, electrical discharges, plasmas), Wavelength separation and resolution (dependence on technique), Detection of radiation (simultaneous/scanning, signal noise), Interpretation (errors due to molecular and ionic species, matrix effects, other interferences).

NMR spectroscopy:**(04 Lectures) Marks: 04**

Principle, Instrumentation, Factors affecting chemical shift, Spin-coupling, Applications.

Electroanalytical Methods:

(04 Lectures) Marks: 04

Potentiometry & Voltammetry

Radiochemical Methods:

(04 Lectures) Marks: 04

Elementary idea

X-ray analysis and electron spectroscopy (surface analysis):

(04 Lectures) Marks: 04

Elementary idea

Reference books

1. D.A. Skoog, F.J. Holler & S. Crouch (ISBN 0-495-01201-7) *Principles of Instrumental Analysis*, Cengage Learning India Edition, 2007.
2. Willard, Merritt, Dean, Settle, *Instrumental Methods of Analysis*, 7th ed, IBH Book House, New Delhi.
3. Atkins, P.W & Paula, J.D. *Physical Chemistry*, 10th Ed., Oxford University Press (2014).
4. Kakkar, R. *Atomic and Molecular Spectroscopy: Concepts and Applications*. Cambridge University Press, 2015.
5. Castellan, G. W. *Physical Chemistry* 4th Ed., Narosa (2004).
6. Banwell, C. N. & McCash, E. M. *Fundamentals of Molecular Spectroscopy* 4th Ed.
7. Smith, B.C. *Infrared Spectral Interpretations: A Systematic Approach*. CRC Press, 1998.
8. Moore, W.J., *Physical Chemistry* Orient Blackswan, 1999.

CEMADSE03T: INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS LAB

(60 Lectures/Contact Hours) Marks: 25

1. Safety Practices in the Chemistry Laboratory
2. Determination of the isoelectric pH of a protein.
3. Titration curve of an amino acid.
4. Determination of the void volume of a gel filtration column.
5. Determination of a Mixture of Cobalt and Nickel (UV/Vis spec.)
6. Study of Electronic Transitions in Organic Molecules (i.e., acetone in water)
7. IR Absorption Spectra (Study of Aldehydes and Ketones)
8. Determination of Calcium, Iron, and Copper in Food by Atomic Absorption

9. Quantitative Analysis of Mixtures by Gas Chromatography (i.e., chloroform and carbon tetrachloride)
10. Separation of Carbohydrates by HPLC
11. Determination of Caffeine in Beverages by HPLC
12. Potentiometric Titration of a Chloride-Iodide Mixture
13. Cyclic Voltammetry of the Ferrocyanide/ Ferricyanide Couple
14. Nuclear Magnetic Resonance
15. Use of fluorescence to do “presumptive tests” to identify blood or other body fluids.
16. Use of “presumptive tests” for anthrax or cocaine
17. Collection, preservation, and control of blood evidence being used for DNA testing
18. Use of capillary electrophoresis with laser fluorescence detection for nuclear DNA (Y chromosome only or multiple chromosome)
19. Use of sequencing for the analysis of mitochondrial DNA
20. Laboratory analysis to confirm anthrax or cocaine
21. Detection in the field and confirmation in the laboratory of flammable accelerants or explosives
22. Detection of illegal drugs or steroids in athletes
23. Detection of pollutants or illegal dumping
24. Fibre analysis

At least 10 experiments to be performed.

Reference Books

1. Skoog, D.A. Holler F.J. & Nieman, T.A. *Principles of Instrumental Analysis*, Cengage Learning India Ed.
 2. Willard, H.H., Merritt, L.L., Dean, J. & Settoe, F.A. *Instrumental Methods of Analysis*, 7th Ed. Wadsworth Publishing Company Ltd., Belmont, California, USA, 1988
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CEMADSE04T: GREEN CHEMISTRY

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Introduction to Green Chemistry:

(04 Lectures) Marks: 06

What is Green Chemistry? Need for Green Chemistry. Goals of Green Chemistry. Limitations/ Obstacles in the pursuit of the goals of Green Chemistry

Principles of Green Chemistry and Designing a Chemical synthesis:
(30 Lectures) Marks: 22

Twelve principles of Green Chemistry with their explanations and examples and special emphasis on the following:

- Designing a Green Synthesis using these principles; Prevention of Waste/ byproducts; maximum incorporation of the materials used in the process into the final products , Atom Economy, calculation of atom economy of the rearrangement, addition, substitution and elimination reactions. Prevention/ minimization of hazardous/ toxic products reducing toxicity. $\text{risk} = (\text{function}) \text{hazard} \times \text{exposure}$; waste or pollution prevention hierarchy.
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- Green solvents– supercritical fluids, water as a solvent for organic reactions, ionic liquids, fluorinated biphasic solvent, PEG, solventless processes, immobilized
- solvents and how to compare greenness of solvents.
- Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy. □
- Selection of starting materials; avoidance of unnecessary derivatization – careful □ use of blocking/protecting groups. □
- Use of catalytic reagents (wherever possible) in preference to stoichiometric reagents; catalysis and green chemistry, comparison of heterogeneous and
- homogeneous catalysis, biocatalysis, asymmetric catalysis and photocatalysis. □
- Prevention of chemical accidents designing greener processes, inherent safer design, principle of ISD “What you don’t have cannot harm you”, greener alternative to Bhopal Gas Tragedy (safer route to carbaryl) and Flixborough accident (safer route to cyclohexanol) subdivision of ISD, minimization,
- simplification, substitution, moderation and limitation. □
- Strengthening/ development of analytical techniques to prevent and minimize the generation of hazardous substances in chemical processes. □

Examples of Green Synthesis/ Reactions and some real world cases:
(16 Lectures) Marks: 12

1. Green Synthesis of the following compounds: adipic acid, catechol, disodium iminodiacetate (alternative to Strecker synthesis)
2. Microwave assisted reactions in water: Hofmann Elimination, methyl benzoate to benzoic acid, oxidation of toluene and alcohols; microwave assisted reactions

- in organic solvents Diels-Alder reaction and Decarboxylation reaction
3. Ultrasound assisted reactions: sonochemical Simmons-Smith Reaction
(Ultrasonic alternative to Iodine)
 - 4 Surfactants for carbon dioxide – replacing smog producing and ozone depleting solvents with CO₂ for precision cleaning and dry cleaning of garments.
 - 5 Designing of Environmentally safe marine antifoulant.
 - 6 Rightfit pigment: synthetic azopigments to replace toxic organic and inorganic pigments.
 - 7 An efficient, green synthesis of a compostable and widely applicable plastic (poly lactic acid) made from corn.
 - 8 Healthier Fats and oil by Green Chemistry: Enzymatic Inter esterification for production of no Trans-Fats and Oils
 - 9 Development of Fully Recyclable Carpet: Cradle to Cradle Carpeting

Future Trends in Green Chemistry:
(10 Lectures) Marks:10

Oxidation reagents and catalysts; Biomimetic, multifunctional reagents; Combinatorial green chemistry; Proliferation of solventless reactions; co crystal controlled solid state synthesis (C²S³); Green chemistry in sustainable development.

Reference Books

1. Anastas, P.T. & Warner, J.K.: *Green Chemistry - Theory and Practical*, Oxford University Press (1998).
 2. Matlack, A.S. *Introduction to Green Chemistry*, Marcel Dekker (2001).
 3. Cann, M.C. & Connely, M.E. *Real-World cases in Green Chemistry*, American Chemical Society, Washington (2000).
 4. Ryan, M.A. & Tinnesand, M. *Introduction to Green Chemistry*, American Chemical Society, Washington (2002).
 5. Lancaster, M. *Green Chemistry: An Introductory Text* RSC Publishing, 2nd Edition, 2010.
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CEMADSE04P: GREEN CHEMISTRY LAB
(60 Lectures/Contact Hours) Marks: 25

1. Safer starting materials

- Preparation and characterization of nanoparticles of gold using tea leaves.