
SEMESTER-V

CEMACOR11T: **INORGANIC CHEMISTRY-IV**

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Coordination Chemistry-II
(36 Lectures) Marks: 30

VB description and its limitations. Elementary Crystal Field Theory: splitting of d^n configurations in octahedral, square planar and tetrahedral fields, crystal field stabilization energy (CFSE) in weak and strong fields; pairing energy. Spectrochemical series. Jahn-Teller distortion. Octahedral site stabilization energy (OSSE). Metalligand bonding (MO concept, elementary idea), sigma- and pi-bonding in octahedral complexes (qualitative pictorial approach) and their effects on the oxidation states of transitional metals (examples). Magnetism and Colour: Orbital and spin magnetic moments, spin only moments of d^n ions and their correlation with effective magnetic moments, including orbital contribution; quenching of magnetic moment: super exchange and antiferromagnetic interactions (elementary idea with examples only); d-d transitions; L-S coupling; qualitative Orgel diagrams for $3d^1$ to $3d^9$ ions. Racah parameter. Selection rules for electronic spectral transitions; spectrochemical series of ligands; charge transfer spectra (elementary idea).

Chemistry of d- and f- block elements
(24 Lectures) Marks: 20

Transition Elements:
General comparison of 3d, 4d and 5d elements in term of electronic configuration, oxidation states, redox properties, coordination chemistry.

Lanthanoids and Actinoids:
General Comparison on Electronic configuration, oxidation states, colour, spectral and magnetic properties; lanthanide contraction, separation of lanthanides (ion-exchange method only).

Reference Books

1. Huheey, J. E.; Keiter, E.A. & Keiter, R.L. *Inorganic Chemistry, Principles ofStructure 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. Atkin, P. *Shriver & Atkins' Inorganic Chemistry* 5th Ed. Oxford University Press (2010).
5. Purecell, K.F. and Kotz, J.C., *An Introduction toInorganic Chemistry*, Saunders: Philadelphia, 1980.
6. Sinha, S. P., Ed., Lanthanide and Actinide Research (Journal, Vol. 1, 1986).
7. Wulfsberg, G., Principles of Descriptive Inorganic Chemistry, Brooks/Cole: Monterey, CA, 1987.

CEMACOR11P: INORGANIC CHEMISTRY-IV LAB

(60 Lectures/Contact Hours) Marks: 25

Chromatography of metal ions

Principles involved in chromatographic separations. Paper chromatographic separation of following metal ions:

1. Ni (II) and Co (II)
2. Fe (III) and Al (III)

Gravimetry

1. Estimation of Ni(II) using Dimethylglyoxime (DMG).
2. Estimation of copper as CuSCN.
3. Estimation of Al(III) by precipitating with oxine and weighing as $Al(oxine)_3$ (aluminium oxinate).
4. Estimation of chloride.**Spectrophotometry**

1. Measurement of 10Dq by spectrophotometric method.
2. Determination of λ_{max} of $[Mn(acac)_3]$ and $[Fe(acac)_3]$ complexes.

Reference Books

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

CEMACOR12T: **ORGANIC CHEMISTRY-V**

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Carbocycles and Heterocycles

(16 Lectures) Marks: 12

Polynuclear hydrocarbons and their derivatives: synthetic methods include Haworth, Bardhan-Sengupta, Bogert-Cook and other useful syntheses (with mechanistic details); fixation of double bonds and Fries rule; reactions (with mechanism) of naphthalene, anthracene, phenanthrene and their derivatives.

Heterocyclic compounds: 5- and 6-membered rings with one heteroatom; reactivity, orientation and important reactions (with mechanism) of furan, pyrrole, thiophene and pyridine; synthesis (including retrosynthetic approach and mechanistic details): pyrrole: Knorr synthesis, Paal-Knorr synthesis, Hantzsch synthesis; furan: Paal-Knorr synthesis, Feist-Benary synthesis and its variation; thiophenes: Paal-Knorr synthesis, Hinsberg synthesis; pyridine: Hantzsch synthesis; benzo-fused 5- and 6-membered rings with one heteroatom: reactivity, orientation and important reactions (with mechanistic details) of indole, quinoline and isoquinoline; synthesis (including retrosynthetic approach and mechanistic details): indole: Fischer, Madelung and Reissert; quinoline: Skraup, Doebner-Miller, Friedlander; isoquinoline: Bischler-Napieralski synthesis.

Cyclic Stereochemistry
(10 Lectures) Marks: 08

Alicyclic compounds: concept of I-strain; conformational analysis: cyclohexane, mono and disubstituted cyclohexane; symmetry properties and optical activity; topomerisation; ring-size and ease of cyclisation; conformation & reactivity in cyclohexane system: consideration of steric and stereoelectronic requirements; elimination (E2, E1), nucleophilic substitution (S_N1, S_N2, S_Ni, NGP), merged substitution-elimination; rearrangements; oxidation of cyclohexanol, esterification, saponification, lactonisation, epoxidation, pyrolytic *syn* elimination and fragmentation reactions.

Pericyclic reactions
(8 Lectures) Marks: 08

Mechanism, stereochemistry, regioselectivity in case of
Electrocyclic reactions: FMO approach involving 4π- and 6π-electrons (thermal and photochemical) and corresponding cycloreversion reactions.
Cycloaddition reactions: FMO approach, Diels-Alder reaction, photochemical [2+2] cycloadditions.

Sigmatropic reactions: FMO approach,sigmatropic shifts and their order; [1,3]- and [1,5]-H shifts and [3,3]-shifts with reference to Claisen and Cope rearrangements.

Carbohydrates
(14 Lectures) Marks: 10

Monosaccharides: Aldoses up to 6 carbons; structure of D-glucose & D-fructose (configuration & conformation); ring structure of monosaccharides (furanose and pyranose forms): Haworth representations and non-planar conformations; anomeric effect (including stereoelectronic explanation); mutarotation; epimerization; reactions (mechanisms in relevant cases): Fischer glycosidation, osazone formation, brominewater oxidation, HNO_3 oxidation, selective oxidation of terminal $–CH_2OH$ of aldoses, reduction to alditols, Lobry de Bruyn-van Ekenstein rearrangement; stepping–up (Kiliani-Fischer method) and stepping–down (Ruff's & Wohl's methods) of aldoses; end-group-interchange of aldoses; acetonide (isopropylidene) and benzylidene protections; ring-size determination; Fischer's proof of configuration of (+)-glucose.

Disaccharides: Glycosidic linkages, concept of glycosidic bond formation by glycosyl donor-acceptor; structure of sucrose, inversion of cane sugar.
Polysaccharides: starch (structure and its use as an indicator in titrimetric analysis).

Biomolecules
(12 Lectures) Marks: 12

Amino acids: synthesis with mechanistic details: Strecker, Gabriel, acetamido malonic ester, azlactone, Bücherer hydantoin synthesis, synthesis involving diketopiperazine; isoelectric point, zwitterions; electrophoresis, reaction (with mechanism): ninhydrin reaction, Dakin-West reaction; resolution of racemic amino acids.

Peptides: peptide linkage and its geometry; syntheses (with mechanistic details) of peptides using *N*-protection & C-protection, solid-phase (Merrifield) synthesis; peptide sequence: *C*-terminal and *N*-terminal unit determination (Edman, Sanger & 'dansyl' methods); partial hydrolysis; specific cleavage of peptides: use of CNBr.

Nucleic acids: pyrimidine and purine bases (only structure & nomenclature); nucleosides and nucleotides corresponding to DNA and RNA; mechanism for acid catalysed hydrolysis of nucleosides (both pyrimidine and purine types); comparison of alkaline hydrolysis of DNA and RNA; elementary idea of double helical structure of DNA (Watson-Crick model); complimentary base–pairing in DNA.

Reference Books

1. Clayden, J., Greeves, N., Warren, S. *Organic Chemistry,* Second edition, Oxford University Press 2012.

2. Eliel, E. L. & Wilen, S. H. *Stereochemistry of Organic Compounds*, Wiley: London.
3. Nasipuri, D. *Stereochemistry of Organic Compounds,* Wiley Eastern Limited.
4. Fleming, I. *Molecular Orbitals and Organic Chemical reactions*, Reference/Student Edition, Wiley, 2009.
5. Fleming, I. *Pericyclic Reactions*, Oxford Chemistry Primer, Oxford University Press.
6. Gilchrist, T. L. & Storr, R. C. *Organic Reactions and Orbital symmetry*, Cambridge University Press.
7. Finar, I. L. *Organic Chemistry (Volume 1)*, Dorling Kindersley (India) Pvt. Ltd.(Pearson Education).
8. Finar, I. L. *Organic Chemistry* (*Volume 2: Stereochemistry and the Chemistry of Natural Products*), Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
9. Morrison, R. T. & Boyd, R. N. *Organic Chemistry*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
10. Loudon, G. M. *Organic Chemistry*, Fourth edition, Oxford University Press.
11. James, J., Peach, J. M. *Stereochemistry at a Glance*, Blackwell Publishing, 2003.
12. Robinson, M. J. T., *Stereochemistry*, Oxford Chemistry Primer, Oxford University Press, 2005.
13. Davis, B. G., Fairbanks, A. J., *Carbohydrate Chemistry*, Oxford Chemistry Primer, Oxford University Press.
14. Joule, J. A. Mills, K. *Heterocyclic Chemistry*, Blackwell Science.
15. Acheson, R.M. *Introduction to the Chemistry of Heterocyclic compounds*, John Wiely & Sons (1976).
16. Gilchrist, T. L. *Heterocyclic Chemistry*, 3rd edition, Pearson.
17. Davies, D. T., *Heterocyclic Chemistry*, Oxford Chemistry Primer, Oxford University Press.

CEMACOR12P: ORGANIC CHEMISTRY-V LAB

(60 Lectures/Contact Hours) Marks: 25

A. Chromatographic Separations

1. TLC separation of a mixture containing 2/3 amino acids
2. TLC separation of a mixture of dyes (fluorescein and methylene blue)
3. Column chromatographic separation of leaf pigments from spinach leaves
4. Column chromatographic separation of mixture of dyes
5. Paper chromatographic separation of a mixture containing 2/3 amino acids
6. Paper chromatographic separation of a mixture containing 2/3 sugars

B. **Spectroscopic Analysis of Organic Compounds**

1. Assignment of labelled peaks in the ^{1}H NMR spectra of the known organic compounds explaining the relative δ-values and splitting pattern.

2. Assignment of labelled peaks in the IR spectrum of the same compound explaining the relative frequencies of the absorptions (C-H, O-H, N-H, C-O, C-N, C-X, C=C, C=O, N=O, C≡C, C≡N stretching frequencies; **characteristic bending vibrations are included**).

3. The students must record full spectral analysis of **at least 15 (fifteen)** compounds from the following list:

(i) 4′-Bromoacetanilide (ii) 2-Bromo-4'-methylacetophenone (iii) Vanillin (iv) 2′-Methoxyacetophenone (v) 4-Aminobenzoic acid (vi) Salicylamide (vii) 2′Hydroxyacetophenone (viii) 1,3-Dinitrobenzene (ix) *trans*-Cinnamic acid (x) *trans*-4Nitrocinnamaldehyde (xi) Diethyl fumarate (xii) 4-Nitrobenzaldehyde (xiii) 4′Methylacetanilide (xiv) Mesityl oxide (xv) 2-Hydroxybenzaldehyde (xvi) 4Nitroaniline (xvii) 2-Hydroxy-3-nitrobenzaldehyde (xviii) 2,3-Dimethylbenzonitrile (xix) Pent-1-yn-3-ol (xx) 3-Nitrobenzaldehyde (xxi) 3-Ethoxy-4-hydroxybenzaldehyde (xxii) 2-Methoxybenzaldehyde (xxiii) Methyl 4-hydroxybenzoate (xxiv) Methyl 3hydroxybenzoate (xxv) 3-Aminobenzoic acid (xxvi) Ethyl 3-aminobenzoate (xxvii) Ethyl 4-aminobenzoate (xxviii) 3-Nitroanisole (xxix) 5-Methyl-2-nitroanisole

(xxx) 3′-Methylacetanilide

Reference Books

1. *University Hand Book of Undergraduate Chemistry Experiments,* edited by Mukherjee, G. N. University of Calcutta, 2003.
2. *Practical Workbook Chemistry (Honours), UGBS, Chemistry*, University of Calcutta, 2015
3. Furniss, B.S.; Hannaford, A.J.; Smith, P.W.G.; Tatchell, A.R. *Practical Organic Chemistry, 5th Ed.,* Pearson (2012).
4. Mann, F.G. & Saunders, B.C. *Practical Organic Chemistry,* Pearson Education.