

KAKATIYA UNIVERSITY - WARANGAL - TELANGANA
Under Graduate Courses (Under CBCS 2019–2022)
B.Sc. CHEMISTRY II Year
SEMESTER – III

Paper-III
Chemistry - III

Unit-I (Inorganic Chemistry)

15 h (1 hr/week)

S3-I-1: Chemistry of f-block elements:

5 h

Chemistry of Lanthanides: Position in periodic table, Electronic structure, oxidation state, ionic and atomic radii- lanthanide contraction- cause and consequences, anomalous behavior of post lanthanides-complexation- type of donor ligands preferred. Magnetic properties- paramagnetism. Colour and spectra, f-f transitions –occurrence and separation– ion exchange method, solvent extraction.

Chemistry of actinides- general features – electronic configuration, oxidation state, actinide contraction, colour and complex formation. Comparison with lanthanides.

S3-I-2: Coordination Compounds-I

6 h

Simple inorganic molecules and coordination complexes. Nomenclature – IUPAC rules, 1. Coordination number, coordination geometries of metal ions, types of ligands. 2. Brief review of Werner's theory, Sidgwick's electronic interpretation and EAN rule and their limitations. (Valence bond theory (VBT) – postulates and application to (a) tetrahedral complexes $[\text{Ni}(\text{NH}_3)_4]^{2+}$, $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ (b) Square planar complexes $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{PtCl}_4]^{2-}$ (c) Octahedral complexes $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{FeF}_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoF}_6]^{3-}$. Limitations of VBT. 3. Isomerism in coordination compounds, stereo isomerism – (a) geometrical isomerism in (i) square planar meta l complexes of the type $[\text{MA}_2\text{B}_2]$, $[\text{MA}_2\text{BC}]$, $[\text{M}(\text{AB})_2]$, $[\text{MABCD}]$. (ii) Octahedral metal complexes of the type $[\text{MA}_4\text{B}_2]$, $[\text{M}(\text{AA})_2\text{B}_2]$, $[\text{MA}_3\text{B}_3]$ using suitable examples, (b) Optical isomerism in (i). tetrahedral complexes $[\text{MABCD}]$, (ii). Octahedral complexes $[\text{M}(\text{AA})_2\text{B}_2]$, $[\text{M}(\text{AA})_3]$ using suitable examples. Structural isomerism: ionization, linkage, coordination ligand isomerism using suitable examples.

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S3-I-3: Metal carbonyls and Organometallic Chemistry**4 h**

Metal carbonyls: Preparation and properties of Ni(CO)₄. Structural features of Ni(CO)₄, Fe(CO)₅, Fe₂(CO)₉, Fe₃(CO)₁₂ and Cr(CO)₆ -18 valence electron rule.

Definition, nomenclature and classification of organometallic compounds. Methods of preparation, properties and applications of alkyl and aryl compounds of Li, Mg & Al.

Unit - II (Organic Chemistry)**15h(1 hr/week)****S3-O-1: Carboxylic acids and derivatives****5 h**

Preparation: a) Hydrolysis of Nitriles, amides and esters. b) Carbonation of Grignard reagents. Special methods of preparation of Aromatic Acids - Oxidation of Arenes. Physical properties- hydrogen bonding, dimeric association,. Chemical properties – Reactions involving H, OH and COOH groups -salt formation, anhydride formation, Acid halide formation, Esterification (mechanism) & Amide formation. Reduction of acid to the corresponding primary alcohol - via ester or acid chloride. Degradation of carboxylic acids by Huns Diecker reaction, Schmidt reaction (Decarboxylation). Arndt – Eistert synthesis, Halogenation by Hell – Volhard - Zelensky reaction. Carboxylic acid Derivatives – Hydrolysis and Amonolysis of acid halides, Acid anhydrides and esters (mechanism of ester hydrolysis by base and acid). Hydrolysis and dehydration of amides.

S3-O-2: Nitrohydrocarbons**3 h**

Preparation of Nitroalkanes. Reactivity - halogenation, reaction with HNO₂ (Nitrous acid), Nef reaction, reduction. Aromatic Nitrohydrocarbons: Preparation of Nitrobenzene by Nitration. Physical properties, chemical reactivity –Reduction of Nitrobenzenes in different media.

S3-O-3: Amines, Cyanides and Isocyanides**7 h**

Amines: classification into 1°, 2°, 3° Amines and Quarternary ammonium compounds. Preparative methods – Ammonolysis of alkyl halides, Gabriel synthesis, Hoffman's bromamide reaction (mechanism). Reduction of Amides and Schmidt reaction. Physical properties. Use of amine salts as phase transfer catalysts. Chemical Properties: a) Alkylation b) Acylation c) Carbylamine reaction d) Hinsberg separation. Reaction with Nitrous acid of 1°, 2°, 3° (Aliphatic and aromatic amines). Electrophilic substitutions of Aromatic amines – Bromination and Nitration, oxidation of aryl and 3° Amines, diazotisation. Diazonium salts: Preparation with mechanism. Synthetic importance – a) Replacement of diazonium group by – OH, X (Cl)- Sandmeyer and Gatterman reaction, by fluorine (Schiemann's reaction), by iodine, CN, NO₂, H and aryl groups. Coupling Reaction of diazonium salts. i) with phenols ii) with anilines. Reduction to phenyl hydrazines.

Cyanides and isocyanides: Structure. Preparation of cyanides from a) Alkyl halides b) from amides c) from aldoximes. Preparation of isocyanides from Alkyl halides and Amines. Properties of cyanides and isocyanides, a) hydrolysis b) addition of Grignard reagent iii)

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reduction iv) oxidation.

Unit III (Physical Chemistry)

15 h (1 hr/week)

S3-P-1: Thermodynamics -I

10 h

A brief review of - Energy, work and heat units, mechanical equivalent of heat, definition of system, surroundings. First law of thermodynamics statement- various forms mathematical expression. Thermodynamic quantities- extensive properties and intensive properties, state function and path functions. Energy as a state function and exact differential. Work of expansion and heat absorbed as path function.

Expression for work of expansion, sign convention problems on first law. Heat changes at constant pressure and heat changes at constant volume. Enthalpy. Heat capacities at constant pressure and constant volume. Derivation of $C_p - C_v = R$. Isothermal adiabatic processes. Reversible and irreversible processes. Reversible change and maximum work. Derivation of expression for maximum work for isothermal reversible process. Problems. Internal energy of an ideal gas. Joules experiment. Joule-Thompson coefficient. Adiabatic changes in ideal gas, derivation of equation, $PV^\gamma = \text{constant}$. P-V curves for isothermal and adiabatic processes. Heat of a reaction at constant volume and at constant pressure, relation between ΔH and ΔV .

Variation of heat of reaction with temperature. Kirchhoff's equation and problems. Limitations of first law and need for second law. Statement of second law of thermodynamics. Cyclic process. Heat engine, Carnot's theorem, Carnot's cycle. Derivation of efficiency of heat engine. Problems. Thermodynamic scale of temperature.

S3-P-2: Thermodynamics-II

5 h

Entropy: Definition from Carnot's cycle. Entropy as a state function. Entropy as a measure of disorder. Sign of entropy change for spontaneous and non-spontaneous processes & equilibrium processes. Entropy changes in i). Reversible isothermal process, ii). Reversible adiabatic process, iii). Phase change, iv). Reversible change of state of an ideal gas. Problems. Entropy of mixing of ideal gases. Free energy Gibbs function (G) and Helmholtz's function (A) as thermodynamic quantities. Concept of maximum work and maximum ΔG as Criteria for spontaneity. Derivation of equation $\Delta G = \Delta H - T\Delta S$. Significance of the equation. Gibbs equations and Maxwell relations. Variation of G with P, V and T.

Unit - IV (General Chemistry)

15 h (1 hr/week)

S3-G-1 Evaluation of analytical data

4 h

Significant figures, accuracy and precision. Errors-classification of errors- determinate and indeterminate errors, absolute and relative errors. Problems based on mean, median, range, standard deviation

S3-G-2: Carbanions-I

5 h

Introduction, acidic nature of α -hydrogens and tautomerism in carbonyl compounds, nitro hydrocarbons, ethyl acetoacetate, diethyl malonate. Terminal alkynes. Stability of carbanions Reactions : Aldol reaction, Perkin reaction, Benzoin condensation, haloform reaction, conversion of smaller alkynes to higher alkynes.

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S3-G-3: Phase Rule

6 h

Statement and meaning of the terms – Phase, Component and Degrees of freedom, Gibb's Phase rule, phase equilibria of one component system – water system. Phase equilibria of two-component system – Solid-Liquid equilibria, simple eutectic –Pb-Ag system, desilverisation of lead. Solid solutions – compound with congruent melting point – Mg-Zn system and incongruent melting point – NaCl-H₂O system.

References

General reference: B.Sc II Year Chemistry : Semester III, Telugu Academy publication, Hyd Unit- I

1. Analytical chemistry by G. L. David Krupadanam, D. Vijaya Prasad, K. Varaprasada Rao, K.L.N. Reddy and C. Sudhakar
2. Principles of Inorganic Chemistry by Puri, Sharma and Kalia Vishal Publications(1996).
3. Concise Inorganic Chemistry by J.D. Lee 3rd edn Van Nostrand Reinhold Company(1977)
4. Basic Inorganic Chemistry by F.A.Cotton, G.Wilkinson and Paul.L. Gaus 3rd edn Wiley Publishers (2001).
5. Inorganic Chemistry Principles of structure and reactivity by James E.Huhey, E.A. Keiter and R.L. Keiter 4th edn. (2006)
6. Chemistry of the elements by N.N.Greenwood and A. Earnshaw Pergamon Press(1989).
7. Inorganic Chemistry by Shriver and Atkins 3rd edn Oxford Press (1999).
8. Textbook of Inorganic Chemistry by R Gopalan(Universities Press(2012)
9. College Practical chemistry by V K Ahluwalia, Sunitha Dhingra and Adarsh Gulati Universities Press (India) Limited(2012)

Unit- II

1. Text book of organic chemistry by Soni. Sultan Chand & Sons; Twenty Ninth edition (2012)
2. General Organic chemistry by Sachin Kumar Ghosh. New Age Publishers Pvt Ltd (2008).
3. Text book of organic chemistry by Morrison and Boyd. Person(2009)
4. Text book of organic chemistry by Graham Solomons. Wiley(2015)
5. Text book of organic chemistry by Bruice Yuranis Powla. (2012)
6. Text book of organic chemistry by C N pillai CRC Press (2012)
7. Organic Chemistry by L. G. Wade Jr.
8. Organic Chemistry by M. Jones, Jr
9. Organic Chemistry by John McMurry.

Unit III

1. Principles of physical chemistry by Prutton and Marron. The MacmillanCompany; 4th Edn.(1970)
2. Text Book of Physical Chemistry by Soni and Dharmahara. Sulthan Chand and Sons.(2011)
3. Text Book of Physical Chemistry by Puri and Sharma. S. Nagin chand and Co.(2017)
4. Text Book of Physical Chemistry by K. L. Kapoor. (2012)
5. Colloidal and surface chemistry , M. Satake, Y. Hayashi, Y.Mido, S.A.Iqbal and M.S.sethi, Discovery Publishing Pvt.Ltd (2014)
7. Material science by Kakani & Kakani, New Age International(2016)
8. Physical Chemistry by Ira Levine (Author) McGraw-Hill Education; 6 edition (May 9, 2008)

Unit IV

1. Text book of organic chemistry by Morrison and Boyd, Person(2009)

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2. Text book of organic chemistry by Graham solomons, Wiley(2015)
3. Text book of organic chemistry by Sony, Sultan Chand & Sons; 29th edition (2012)
4. Text book of organic chemistry by Bruice yuranis Powla, (2012)
5. General Organic chemistry by Sachin kumar Ghosh, New Age Publishers Pvt Ltd (2008)

Laboratory Course

Paper III (Organic Synthesis)

45 h (3h/week)

1. Synthesis of Organic compounds:

Acetylation: Acetylation of salicylic acid, Benzoylation of Aniline.

Aromatic electrophilic substitution: Nitration: Preparation of nitro benzene and m-dinitro benzene.

Halogenation: Preparation of p-bromo acetanilide, Preparation of 2,4,6-tribromo phenol

Oxidation: Preparation of benzoic acid from benzyl chloride.

Esterification: Preparation of n-butyl acetate from acetic acid.

Methylation: Preparation of - naphthyl methyl ether.

Condensation: Preparation of benzilidene aniline and Benzaldehyde and aniline.

Diazotisation: Azocoupling of β -Naphthol.

2. Microwave assisted synthesis of Asprin – DEMO (demonstration only)

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