

ANDHRA UNIVERSITY
DEPARTMENT OF CHEMISTRY
M.Sc. (PREVIOUS) CHEMISTRY SYLLABUS
SEMESTER-II
PAPER-I: GENERAL CHEMISTRY-II
(Effective from the admitted batch of 2021-2022)

Unit I

[12 Hours]

Wave equation – interpretation of wave function – properties of wave function – normalization and orthogonalisation, operators – linear and non-linear commutators of operators, Postulates of quantum mechanics, setting up of operators observables – Hermitian operator – Eigen values of Hermitian operator.

Unit-II

[12 Hours]

Wave mechanics of simple systems with constant potential energy, particle in one dimensional box – factors influencing colour – transition – dipole integral, symmetry arguments in deriving the selection rules-the concept of tunneling – particle in a three dimensional box, Rigid rotor, wave mechanics of systems with variable potential energy-simple harmonic oscillator-solution of wave equation-selection rules.

UNIT-III

[12 Hours]

Hydrogen atom-solution of $R(r)$, $\theta(\theta)$ and $\Phi(\phi)$ equations-probability density in orbitals-shapes of orbitals. Perturbation theory- time independent perturbation (only first order perturbation is to be dealt with) – application to ground state energy of hydrogen and helium atom

UNIT -IV

[12 Hours]

Variation principle-applications to hydrogen and helium atoms-calculation of zero point energy of harmonic oscillator-many electron atom- Comparison between Perturbation and variation theorems. Hartee-Fock self-consistent field method and introductory concepts of Density functional theory(DFT).

UNIT-V

[12 Hours]

Valence bond approach-directed valence-hybridization-covalent bond-calculation of ionic and covalent bond contributions in hydrogen molecule. Molecular orbital theory – LCAO approximation – hydrogen molecule ion – hydrogen molecule (fundamental concepts only) – The electronic transitions in the hydrogen molecule.

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UNIT-I **[12 Hours]**

Metal cluster compounds - definition – evidences for existence of M-M bonds - conditions favorable for formation of M-M bonds – preparation, structure and bonding of the following metal cluster compounds.

$\text{Re}_2\text{Cl}_8^{2-}$, $\text{Mo}_2\text{Cl}_8^{4-}$, $\text{Re}_2(\text{RCOO})_4\text{X}_2$, $\text{Mo}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cr}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cu}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cr}_2\text{Cl}_9^{3-}$, $\text{Mo}_2\text{Cl}_9^{3-}$, $\text{W}_2\text{Cl}_9^{3-}$, Re_3Cl_9 , $\text{Re}_3\text{Cl}_{12}^{3-}$, $\text{Mo}_6\text{Cl}_8^{4+}$, $\text{Nb}_6\text{X}_{12}^{2+}$ and $\text{Ta}_6\text{X}_{12}^{2+}$.

Polyatomic clusters – Zintl ions, Chevrel phases.

UNIT-II **[12 Hours]**

Organometallic compounds - 16 and 18 electron rules.

Isoelectronic relationship - Synthesis, structure, bonding and reactions of carbon monoxide, dinitrogen and nitric oxide complexes.

Isolobal relationship – H, Cl, CH_3 , $\text{Mn}(\text{CO})_5$; S, CH_2 , $\text{Fe}(\text{CO})_4$; P, CH, $\text{Co}(\text{CO})_3$

Synthesis, structure, bonding and reactions of metallocenes with special reference to ferrocene

UNIT-III **[12 Hours]**

Metal Ligand equilibria in solution:

Step wise and overall formation constants and their interaction. Trends in stepwise constants ((statistical effect and statistical ratio), factors affecting the stability of metal complexes; Stability correlations - Irving -William's series, Pearson's theory of hard and soft acids and bases (HSAB), Application of HSAB: Biological functions and toxicology of metals, and medicinal applications; chelate effect and its thermodynamic origin

UNIT-IV **[12 Hours]**

Determination of stability constants of complexes by spectrophotometric method ((Job's method) and pH –metric method(Bjerrum's).

Reactivity of metal complexes – inert and labile complexes. Explanation of lability on the basis of valence bond and crystal field theories.

UNIT- V **[12 Hours]**

Reaction Mechanisms of Metal Complexes:

Reactivity of metal complexes, inert and labile complexes, Kinetics and mechanisms of substitution reactions, kinetics of substitutions reactions in octahedral complexes, acid hydrolysis, Factors affecting acid hydrolysis, Base hydrolysis, Conjugate base mechanism, Anation reactions, substitution reactions in square planar complexes, Trans effect, Mechanism of trans effect, Electron transfer reactions— concept of complementary and non-complementary reactions with examples, inner sphere and outer sphere mechanisms, Marcus theory.

Text books:

1. Advanced Inorganic Chemistry by F.A. Cotton and R.G. Wilkinson, IV Edition, John, John Wiley and Sons, New York, 1980.
2. Inorganic Chemistry by J.E. Huheey, III edition, Harper International Edition, 1983.
3. Organometallic Chemistry-A unified approach by A. Singh and R.C. Mehrotra, Wiley Eastern Ltd.
4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999)
5. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press Pvt. Ltd., New Delhi.
6. Mechanisms of Inorganic reactions in solution by D.Benson, McGraw Hill, London, 1968.
7. Inorganic chemistry by K.F. Purcell and J.C.Kotz, W.B. Saunders company, New York, 1977.

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PAPER-III: ORGANIC CHEMISTRY-II

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UNIT-I

A) Aromaticity: Concept of Aromaticity, Aromaticity of five membered, six membered and fused systems -non-benzenoid aromatic compounds:- cyclopropenylcation, cyclobutadienyldication, cyclopentadienyl anion – tropyliumcation and cyclo octatetraenyl di anion – metallocenes, ferrocenes, azulenes, fulvenes, annulenes, fullerenes. Homo aromaticity, Anti aromaticity and Pseudo aromaticity.

B) Aromatic Nucleophilic Substitutions: The S_NAr, S_N1, benzyne and S_{RN}1 mechanisms. Reactivity: Effect of substrate, leaving group and attacking nucleophile. The Von- Richter ,Sommet- Hauser and Smiles rearrangements.

UNIT - II

A) Reactive Intermediates: Generation, structure, stability and reactivity of Reactive intermediates: carbanion, carbocation, free radicals, carbenes and nitrenes.

B) Name Reactions: - Wittig reaction, Grignard reaction, Stork enamine reaction, Michael addition, Mannich Reaction, Diel's-Alder reaction and Ene-reaction,

UNIT-III

Molecular Rearrangements:

Types of molecular rearrangements, migratory aptitude;

Rearrangements to electron deficient carbon: Pinacol-pinacolone, Wagner-Meerwein and Benzil-Benzilic acid,

Rearrangements to electron deficient nitrogen: Beckmann, Hofmann, Curtius, Schmidt and Lossen rearrangements;

Rearrangements to electron deficient oxygen: Baeyer-villiger, Dakin rearrangements;

Other rearrangements: Neber rearrangement and Favorskii rearrangements

UNIT - IV

A) UV Spectroscopy: Various electronic transitions, selection rules, effect of solvent on electronic transitions, the absorption laws, chromophores, auxochromes, bathochromic and hypso chromic shifts, hyperchromic and hypochromic effects, Woodward-Fieser rules for conjugated dienes and carbonyl compounds.

B) Infrared Spectroscopy: Basic principles: types of molecular vibrations, fingerprint region and identification of functional groups.

C) Nuclear Magnetic Resonance Spectroscopy (¹H-NMR): nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shifts, factors affecting the chemical shift, and assignment of chemical shifts.

D) Mass Spectroscopy: Basic principles, nitrogen rule and fragmentation pattern of carbonyl compounds and alcohols

B) Peptides and Proteins: α -Aminoacids, their general properties and synthesis, Synthesis of peptides by Merrifield solid phase synthesis. Primary, secondary and tertiary structures of proteins

C) Nucleic acids: Heterocyclic bases; Purines: Adenine and Guanine; Pyrimidines: Cytosine, Uracil and Thymine; nucleosides, nucleotides Basic concepts of the structures of RNA and DNA

Text books:

1. Organic Chemistry Vol. I (Sixth Edn.) and Vol. II (Fifth Ed.,) by I.L. Finar ELBS.
2. Organic Chemistry (fifth Edn.,) by Morrison and Boyd, PHI, India.
3. Organic Chemistry (fifth edition) by Francis A. Carey Tata McGraw Hill publishing Company Limited, New Delhi.
4. Reaction Mechanism in Organic Chemistry by Mukherjee Sirigh, N Ternitarr, Indiar
5. A guide book to mechanism in Organic Chemistry by Peter Sykes, ELBS.

REFERENCE BOOKS:

1. Advanced organic chemistry by Jerry March (4th Edition) Wiley Eastern. .
2. Stereochemistry of carbon compounds by E.Eliel, John Wiley & Sons, Inc.
3. Stereochemistry of Organic compounds by D. Nasipuri.
4. Chemistry of Natural products by R.S. Kalsi Kalyani Publishers. 1983.

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SEMESTER-II
PAPER-IV: PHYSICAL CHEMISTRY -II
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UNIT-I: **[12 Hours]**

Crystal structure of solids: Fundamental of lattices, unit cell, Bravais lattices, symmetry elements in crystals, packing efficiency, radius ratios; Miller indices. Structures and types of solids. Structure determination by X-ray diffraction (Bragg's equation). Magnetic properties of solids- classification of magnetic materials, Magnetic susceptibility, Measurement of magnetic susceptibility. Electric properties- Band theory, the band structure of metals, insulators, and semiconductors. The temperature dependence of the conductivity of extrinsic semiconductors. Superconductivity and occurrence. Meisner effect. Types of superconductors. Theories of superconductivity - BCS theory.

UNIT-II: **[12Hours]**

Classification of polymers - Free radical, ionic and Zeigler - Natta Polymerization - kinetics of free radical polymerization - Techniques of polymerization - Glass transition temperature - Factors influencing the glass transition temperature - Number average and Weight average, Molecular weights - molecular weights determination - End group analysis - Osmometry - Light scattering and ultra-centrifugation methods.

UNIT-III: **[12 Hours]**

Electrochemistry I: Ionic mobilities and conductivities - Debye-Huckel theory of strong electrolytes, Debye-Huckel onsagar equation-limitations- mean activity coefficient-Verification of Debye-Huckel limiting law. Electro chemical cell- Galvanic and electrolytic cell. Nernst equation-Concentration cell with and without transference- effect of complexation on redox potential- ferricyanide/ ferrocyanide couple, Iron (III) phenonhroline/ Iron(II) phenonhroline couple. Fuel Cells- construction-Various types- Examples.

UNIT-IV: **[12 Hours]**

Electrochemistry II: The electrode-electrolyte interface. The electrical double layer. The Helmholtz-Perrin parallel-plate model, the Gouy-Chapman diffuse-charge model and the Stern model. Electrodicts: Charge transfer reactions at the electrode-electrolyte interface.Derivation of Butler-Volmer equation. High field approximation, Tafel equation, Low field equilibrium, over voltage. Theories of over voltage- Corrosion - Concentration polarization - Polarography -Half wave potential and Ilkovic equation.

UNIT-V: **[12 Hours]**

Photochemistry: Electronic transitions in molecules, Franck-Condon principle. Electronically excited molecules- singlet and triplet states, spin-orbit interaction. Quantum yield and its determination. Actinometry. Derivation of fluorescence and phosphorescence quantum yields. Quenching effect- Stern Volmer equation. Photochemical equilibrium and delayed fluorescence- E-type and P-type. Photochemical primary processes, types of photochemical reactions-photodissociation, addition and isomerization reactions with examples.