KAKATIYA UNIVERSITY: WARANGAL

B.Sc. III YEAR CHEMISTRY SYLLABUS

PAPER – III **90 hrs (3h/w)**

UNIT – I (Inorganic Chemistry –III) 30 hrs (1 h / w)

1. **Coordination Chemistry: (10 h)**
   IUPAC nomenclature, bonding theories – review of Werner's theory and Sidgwick's concept of coordination, Valence bond theory, geometries of coordination numbers, 4-tetrahedral and square planar and 6-octahedral and its limitations, crystal field theory, splitting of d-orbitals in octahedral, tetrahedral and square planar complexes – low spin and high spin complexes – factors affecting crystal field splitting energy, merits and demerits of crystal field theory. Isomerism in coordination compounds – structural isomerism and stereo isomerism, stereochemistry of complexes with 4 and 6 coordination numbers.

2. **Spectral and magnetic properties of metal complexes** : **(4 h)**
   Electron absorption spectrum of $[Ti(H_2O)_6]^{3+}$ ion. Types of magnetic behaviour, spin-only formula, calculation of magnetic moments, experimental determination of magnetic susceptibility – Gouy method.

3. **Reactivity of metal complexes : (4 h)**
   Labile and inert complexes, ligand substitution reactions – S_N1 and S_N2 substitution reactions of square planar complexes – Trans effect and applications of trans effect.

4. **Stability of metal complexes : (4 h)**
   Thermodynamic stability and kinetic stability, factors affecting the stability of metal complexes, chelate effect, determination of composition of complex by Job's method and mole ratio method.

5. **Hard and soft acids bases (HSAB) : (4 h)**
   Classification, Pearson's concept of hardness and softness, application of HSAB principles – Stability of compounds / complexes, predicting the feasibility of a reaction.

6. **Bioinorganic chemistry : (4 h)**
   Essential elements, biological significance of Na, K, Mg, Ca, Fe and chloride (Cl^-). Metalloporphyrins – haemoglobin, structure and function, Chlorophyll, structure and role in photosynthesis.

UNIT – II (Organic Chemistry – III) 30 hrs (1 h / w)

1. **Nitrogen Compounds: (9 h)**

Nitro hydrocarbons: Nomenclature and classification – nitro hydrocarbons – structure. Tautomerism of nitroalkanes leading to acid and keto form. Preparationof Nitroalkanes. Reactivity – halogenation, reaction with HONO (Nitrous acid), Nef reaction and Mannich reaction leading to Michael addition and reduction.

Amines(Aliphatic and Aromatic) : Nomenclature, Classification into 1^0,2^0,3^0 Amines and Quaternary ammonium compounds. Preparative methods – (1). Ammonolysis of alkyl halides (2). Gabriel synthesis (3). Hoffman's bromamide reduction reaction(mechanism). (4). Reduction of Amides and Schmidt reaction. Physical properties and basic character – Comparative basic strength of Ammonia, methyl amine, dimethyl amine, trimethyl amine and aniline - Comparative basic strength of aniline, *N*-methyl aniline and *N*,*N*-dimethyl aniline (in aqueous and non-aqueous medium), steric effects and substituent effects. Use of amine salts as phase transfer catalysts. Chemical properties : a) Alkylation b) Acylation c) Carbylamine reaction d) Hinsberg separation e) Reaction with Nitrous acid of 1^0,2^0,3^0 (Aliphatic and aromatic amines). Electrophilic substitutions of Aromatic amines – Bromination and Nitration. Oxidation of aryl and 3^0 amines. Diazotization. Cyanides and isocyanides : Nomenclature (aliphatic and aromatic) structure. Preparation of cyanides: a) from 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 c) reduction d) oxidation.

2. **Heterocyclic Compounds: (5 h)**

Introduction and definition: Simple 5 membered ring compounds with one hetero atom Ex. Furan, Thiophene and Pyrrole. Importance of ring system – presence in important natural procducts like haemoglobin and chlorophyll. Numbering the ring systems as per Greek letter and Numbers. Aromatic character – 6-electron system (four-electrons from two double bonds and a pair of non-bonded electrons from the hetero atom). Tendency to undergo substitution reactions. Resonance structure : Indicating electron surplus carbons and electron deficient hetero atom. Explanation of feebly acidic character of pyrrole, electrophilic substitution at 2 or 5 position, halogenation, nitration and sulphonation under mild conditions. Reactivity of furan as 1,3-diene, Diels Alder reactions (one example). Sulphonation of thiophene, purification of Benzene (obtained from coal tar). Preparation of furan, Pyrrole and thiophene from 1,4-dicarbonyl compounds only. Paul-Knorr synthesis, structure of pyridine, Basicity – Aromaticity – Comparision with pyrrole – one method of preparation and properties – Reactivity towards Nucleophilic substitution reaction –Chichibabin reaction.

3. **Carbohydrates: (6 h)**

Monosaccharides : All discussion to be confined to (±) glucose as an example of aldo hexoses and D(-) fructose as example of ketohexoses. Chemical properties and structural elucidation: Evidences for straight chain pentahydroxy aldehyde structure (Acetyaltion, readuction to n-hexane, cyanohydrin formation, reduction of Tollen's and Fehling's

reagents and oxidation to gluconic and saccharic acid). Number of optically active isomers possible for the structure, configuration of glucose based on D-glyceraldehyde as primary standard (no proof for configuration is required). Evidence for Cyclic structure of glucose – Decomposition of cyclic structure (Pyranose structure, anomeric carbon and anomers). Proof for the ring size (methylation, hydrolysis and oxidation reactions). Different ways of writing pyranose structure (Haworth formula and chair conformation formula). Structure of fructose : Evidence of 2-ketohexose structure (formation of penta acetate, formation of cyanohydrine its hydrolysis and reduction by HI to give 2-Carboxy-n-hexane). Same osazone formation from glucose and fructose, Hydrogen bonding in osazones, cyclic structure for fructose (Furanose structure and Haworth formula).

Interconversion of Monosaccharides : Aldopentose to aldo hexose – eg : Arabinose to D-glucose, D-mannose (Kilinai – Fischer method). Epimers, Epimerisastion – Lobry de bruyn van Ekenstein rearrangement. Aldohexose to Aldopentose eg: D-glucose to D-arabinose by Ruff's degradation. Aldohexose (+) (glucose) to ketohexose (-) (fructose) and Ketohexose (Fructose) to aldohexose (Glucose).

4. Amino acids and proteins : (5 h)

Introduction : Definition of Amino acids, classification of Amino acids into alpha, beta, and gama amino acids. Natural and essential amino acids – definition and examples, classification of alpha amino acids into acidic, basic and neutral amino acids with examples. Methods of synthesis : General methods of synthesis of alpha amino acids (specific examples –Glysine, Alanine, Valine and Leucine) by following methods : a) from halogenated carboxylic acid b) Malonic ester synthesis c) Strecker's synthesis.

Physical properties : Optical activity of naturally occurring amino acids: L-configuration irrespective of sign rotation, Zwitter ion structure – salt like character – solubility, melting points, amphoteric character, definition of isoelectric point.

Chemical properties : General reactions due to amino and carboxyl groups – lactams from gamma and delta amino acids by heating peptide bond (amide linkage). Structure and nomenclature of peptides and proteins.

5. Mass Spectrometry : (5 h)

Basic principles – Molecular ion / parent ion, fragment ions / daughter ions. Theory – formation of parent ions. Representation of mass spectrum. Identification of parent ion, (M+1), (M+2), base peaks (relative abundance 100%) – Mass spectra of ethylbenzene, acetophenone, n-butyl amine and 1-proponol.

UNIT-III (Physical Chemistry-III) 30 hrs (1 h / w)

1. Chemical Kinetics : (9 h)

Rate of reaction, factors influencing the rate of a reaction – Concentration, temperature, pressure, solvent, light, catalyst . Experimental methods to determine the rate of reaction. Definition of order and molecularity. Derivation of rate constants for first, second and zero order reactions and examples. Derivation for time half change. Methods to determine the order of reactions. Effect of temperature on rate of reaction, Arrhenius equation, concept of activation energy. Theories of reaction rates – collision theory – derivation of rate constant for bimolecular reaction. The transition state theory (elementary treatment).

2. Photochemistry: (5 h)

Difference between thermal and photochemical processes. Laws of photochemistry – Grothus-Draper's law and Stark-Einstein's law of photochemical equivalence. Quantum yield. Photochemical hydrogen-chlorine, hydrogen-bromine reaction. Jablsonski diagram-depicting various processes occurring in the excited state,qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing). Photosensitized reactions – energy transfer processes (simple example).

3. Thermodynamics: (16 h)

The first law of thermodynamics - statement, definition of internal energy and enthalpy. Heat capacities and their relationship. Joule – Thomson effect and Joule-Thomson coefficient. Calculation of w, q, dE and dH for the expansion of perfect gas under isotherm and adiabatic conditions for reversible processes. State function. Temperature dependence of enthalpy of formation- Kirchoff's equation.

Second law of thermodynamics. Different statements of the law – Carnot Cycle and its efficiency. Carnot theorem. Thermodynamic scale of temperature – Concept of entropy, entropy as a state function, entropy changes in cyclic, reversible and irreversible processes and reversible phase change. Calculation of entropy changes with changes in V & T and P & T. Entropy changes in spontaneous and equilibrium processes.

The Gibb's (G) and Helmholtz (A) energies - A & G as criteria for thermodynamic equilibrium and spontaneity – advantage over entropy change. Gibbs equation and the variation of G with P & T.

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Paper - IV Chemistry and industry 90 hrs (3 h)

UNIT – I (Physico chemical methods of analysis) 30 hrs (1 h /w)

1. **Separation techniques: (12 h)**

1. Chromatography : Classification of chromatography methods, principles of differential migration adsorption phenomenon, Nature of adsorbents, solvent systems, R_f values, factors effecting R_f values.

a) **Paper Chromatography :** Principles, R_f values, experimental procedures, choice of paper and solvent systems, developments of chromatogram – ascending, descending and radial. Two dimensional chromatography, applications.

b) **Thin layer Chromatography (TLC) :** Advantages, principles, factors effecting R_f values. Experimental procedures. Adsorbents and solvents. Preparation of plates. Development of the chromatogram. Detection of the spots. Applications.

c) **Column Chromatography :** Principles, experimental procedures, stationary and mobile phases, separation technique. Applications.

2. **Spectrophotometry: (4 h)**

General features of absorption – spectroscopy, Beer-Lambert's law and its limitations, transmittance, Absorbance and molar absorptivity. Double beam spectrophotometer. Application of Beer-Lambert's law for quantitative analysis of

1) Chromium in $K_2Cr_2O_7$
2) Manganese in $KMnO_4$
3) Iron(III) with thiocyanate

3. **Molecular Spectroscopy: (14 h)**

i) Electronic spectroscopy:

Interaction of electromagnetic radiation with molecules and types of molecular spectra. Potential enrgy curves for bonding and antibonding molecular orbitals. Energy levels of molecules (σ, π, n). Selection rules for electronic spectra. Types of electronic transitions in molecules, effect of conjugation. Concept of chromophore.

ii) Infrared Spectroscopy:

Energy levels of simple harmonic oscillator, molecular vibration spectrum, selection rules. Determination of force constant. Qualitative relation of force constant to bond energies. Modes of vibration in CO, CO_2 and H_2O molecules. Characteristic absorption bands of various functional groups. Finger print nature of infrared spectrum.

iii)Proton magnetic resonance spectroscopy (^{1}H-NMR):

Principles of nuclear magnetic resonance, equivalent and non-equivalent protons, position of signals. Chemical shift, NMR splitting of signals – spin-spin coupling, coupling constants. Applications of NMR with suitable examples- ethyl

bromide, ethanol, acetaldehyde, 1,1,2-tribromo ethane, ethyl acetate, toluene and acetophenone.

iv)Spectral interpretation:

Interpretation of IR, UV-Visible, ^{1}H-NMR and mass spectral data of the following compounds 1) Phenyl acetylene 2) Acetophenone 3) Cinnamic acid 4) Paranitro aniline.

UNIT – II (Drugs, Formulations, pesticides and green chemistry) 30 hrs(1 h/ w)

1. Drugs: (20 h)

1. **Introduction:** Drug, disease (definition), Historical evolution, Sources – plant, Animal synthetic, Biotechnology and human gene therapy.
2. **Terminology:** Pharmacy, Pharmacology, Pharmacophore, Pharmacodynamics, Pharmaco kinetics (ADME, Receptors – brief treatment) Metabolites and Anti Metabolites.
3. **Nomenclature :** Chemical name, Generic name and trade names with examples
4. **Classification :** Classification based on structures and therapeutic activity with one example each.
5. **Synthesis :** Synthesis and therapeutic activity of the following drugs, L-Dopa, Chloroquin, Omeprazole, Albuterol and ciprofloxacin.
6. **Drug development:** Penicillin, Seperation and isolation,structure of the different penicillines.
7. **Monographs of drugs:** Eg: Paracetamol, Sulpha methoxazole (Tablets).

2. Formulations: (3 h)

1. Need of conversion of drugs into medicine. Additives and their role (brief account only)
2. Different types of formulations.

3. Green Chemistry: (7 h)

Introduction: Definition of green chemistry, need of green chemistry, basic principles of green chemistry.

Green synthesis: Evaluation of the type of the reaction i) Rearrangements (100% atom economic), ii) Addition reaction (100% atom economic), Pericyclic reactions (no by-product).

Selection of solvent:

i) Aqueous phase reactions ii) Reactions in ionic liquids iii) Solid supported synthesis iv) Solvent free reactions (solid phase reactions)

Microwave and Ultrasound assisted green synthesis:

1. Aldol condensation
2. Cannizzaro reaction
3. Diels-Alder reaction
4. Strecker synthesis
5. Williamson synthesis
6. Dieckmann condensation

UNIT-III (Polymers, material Science and catalysis) 30 hrs (1h /w)

1. **Polymers: (14 h)**
   Classification of polymers, chemistry of polymerisation, chain polymerisation, step polymerisation, coordination polymerisation – tacticity (isotactic, syndiotactic and atactic polypropylene). Molecular weight of polymers. Number average and weight average molecular weights, degree of polymerisation, determination of molecular weight of polymers by Viscometry, Osmometry: Mechanism of free radical polymerization – Preaparation and industrial application of polyethylene, PVC, Teflon, Polyacrylonitrile, Terylene and Nylon-66.

2. **Material Science: (2h)**
   Properties and applications of nano-materials.

3. **Catalysis : (14h)**
   Homogeneous and heterogenous catalysis, comparision with examples. Kinetics of specific acid catalysed reactions, inversion of cane sugar. Kinetics of specific base catalysed reactions, base catalysed conversion of acetone to diacetone alcohol. Acid and base catalysed reactions – hydrolysis of esters, mutarotation of glucose.
   Enzyme catalysis: Classification, characteristics of enzyme catalysis. Kinetics of enzyme catalysed reactions-Michaelis Menten law, significance of Michaelis constant (Km) and maximum velocity (*V* max). Factors affecting enzyme catalysis-effect of temperature, *p*H, concentration and inhibitor. Catalytic efficiency. Mechanism of oxidation of ethanol by alcohol dehydrogenase.

LABORATORY COURSE – III

Practical Paper – III (Organic Chemistry) 90 hrs (3 h / w)

1. Synthesis of Organic Compounds:

i) Aromatic electrophilic substitution Nitration: Preparation of nitro benzene and *p*-nitro acetanilide, Halogenation; Preparation of *p*-bromo acetanilide – preparation of 2,4,6-tribromo phenol.
ii) Diazotization and coupling : Preparation of phenyl azo β-naphthol
iii) Oxidation: Preparation of benzoic acid from benzoyl chloride.
iv) Reduction: Preparation of *m*-nitro aniline from *m*-dinitro benzene.
v) Esterification: Preparation of methyl *p*-nitro benzoate from *p*-nitro benzoic acid.
vi) Methylation : Preparation of β-naphthyl methyl ether
vii) Condensation: Preparation of benzilidine aniline and Benzoyl aniline.

2. Thin Layer Chromatography and Column Chromatography:

i) Preparation of the TLC plates. Checking the purity of compounds by TLC.
ii) Separation of ortho and para nitro aniline mixture by column chromatography

3. Organic Qualitative Analysis :

i) Identification of an organic compound through the functional group analysis, determination of melting point and preparation of suitable derivatives.
ii) Separation of two component mixtures
a) Aniline + Naphthalene b) Benzoic acid + Benzophenone c) *p*-Cresol + Chlorobenzene.

4. Demonstration experiments:

(1) Steam distillation experiment: separation of ortho and paranitrophenols (2) Microwave assisted Green synthesis, two examples: (a) Hydrolysis of Benzamide (b) Oxidation of Toluene.

LABORATORY COURSE – IV

Practical Paper IV (Physical Chemistry) 90 hrs (3 h / w)

1. **Chemical Kinetics:**
   (i) Kinetic study of acid catalysed hydrolysis of methyl acetate and determination of rate constant–Graphical method.
   (ii) Kinetic study of acid catalysed Acetone–Iodine reaction and determination of rate constant–Graphical method.
   (iii) Kinetic study of Persulphate–Iodide reaction and determination of rate constant–Graphical method.

2. **Distribution law:**
   i) Determination of distribution coefficient of iodine between water and Carbon tetrachloride.
   ii) Determination of molecular state and partition coefficient of benzoic acid in Toluene and Water.
3. **Electrochemistry:**
   i) Determination of concentration of HCl conductometrically using standard NaOH solution.
   ii) Determination of concentration of acetic acid conductometrically using standard NaOH solution.
   iii) Determination of solubility and solubility product of $BaSO_4$.
   iv) Determination of concentration of Fe^{2+} by potentiometric titration of ferrous ammonium sulphate vs potassium dichromate.
4. ***p*H metry**:

   i) Preparation of phosphate buffer solutions
   ii) P^H metric titration of a weak acid (acetic acid) with a strong base (NaOH) and calculation of dissociation constant.

5. **Colorimetry:**
   i) Verification of Beer-Lambert law for $KMnO_4$, $K_2Cr_2O_7$ and determination of concentration of the given solution.
   ii) Verification of Beer-Lambert law for $CuSO_4$ and determination of concentration of the given solution.

6. **Adsorption :**
   i) Surface tension and viscosity of liquids.
   ii) Adsorption of acetic acid on animal charcoal, verification of Freundlich isotherm.

7. **Project Work :**
   Collection of spectral data of a minimum of six compounds belonging to different functional groups (other than those included in the syllabus) and submission of the report.

NOTE: Apart from the experiments (1 to 6) the project work (7) shall be included in the University Examiantion.

Recommended Text Books and Reference Books

Inorganic Chemistry

1. Concise Inorganic Chemistry by J.D.Lee
2. Basic Inorganic Chemistry by Cotton and Wilkinson
3. Advanced Inorganic Chemistry Vol-I by Satyaprakash, Tuli, Basu and Madan
4. Inorganic Chemistry by R R Heslop and P.L. Robinson
5. Modern Inorganic Chemistry by C F Bell and K A K Lott
6. University Chemistry by Bruce Mahan
7. Qualitative Inorganic analysis by A.I.Vogel
8. A textbook of qualitative inorganic analysis by A.I. Vogel
9. Inorganic Chemistry by J.E.Huheey
10. Inorganic Chemistry by Chopra and Kapoor
11. Coordination Chemistry by Basalo and Johnson
12. Organometallic Chemistry – An introduction by R.C.Mehrotra and A.Singh
13. Inorganic Chemistry by D.F.Shriver, P.W.Atkins and C.H.Langford
14. Inorganic Chemistry by Philips and Williams, Lab Manuals
15. Introduction to inorganic reactions mechanisms by A.C.Lockhart
16. Theoretical inorganic chemistry by McDay and J.Selbin
17. Chemical bonding and molecular geometry by R.J.Gillepsy and P.L.Popelier
18. Advanced Inorganic Chemistry By Gurudeep Raj
19. Analytical chemistry by Gary D Christian, Wiley India
20. Analytical Chemistry by G.L.David Krupadanam, et al, Univ. Press
21. Selected topics in inorganic chemistry by W.D.Malik, G..D.Tuli, R.D.Madan
22. Concepts and models of Inorganic Chemistry by Bodie Douglas, D.McDaniel ar J.Alexander
23. Modern Inorganic Chemistry by William L. Jolly
24. Concise coordination chemistry by Gopalan and Ramalingam
25. Satyaprakash's modern inorganic chemistry by R.D.Madan.

Recommended Text Books and Reference Books

Organic Chemistry

1. Organic Chemistry By R T Morrison and R.N.Boyd
2. Organic Chemistry by T.J.Solomons
3. Organic Chemistry by L.G.Wade Sr
4. Organic Chemistry by D.Cram, G.S.Hammond and Herdricks
5. Modern Organic Chemistry by J.D.Roberts and M.C.Caserio
6. Text book of Organic Chemistry by Ferguson
7. Problems and their solutions in organic Chemistry by I.L.Finar
8. Reaction mechanisms in Organic Chemistry by S.M.Mukherji and S.P.Singh
9. A guide book to mechanisms in Organic Chemistry by Peter Sykes
10. Organic spectroscopy by J.R.Dyer
11. Organic Spectroscopy by William Kemp
12. Fundamentals of organic synthesis amd retrosynthetic analysis by Ratna Kumar Kar
13. Comprehensive practical organic qualitative analysis by V.K.Ahluwalia & Sumta Dhingra
14. Comprehensive practical organic chemistry: Preparation and quantitative analysis by V.K.Ahluwalia and Reena Agarwal.
15. Organic Chemistry by Janice Gorzynski
16. Organic Chemistry by Stanley H Pine
17. Fundamentals of Organic Chemistry by John Mc Murray, Eric Simanek
18. Organic Chemistry by Francis A Carey
19. Text book of Organic Chemistry by K.S.Mukherjee
20. Organic Chemistry by Bhupinder Meha & Manju Mehta
21. Organic Chemistry by L.G.Wade Jr, Maya Shankar Singh
22. Elementary organic spectroscopy by Y.R. Sharma
23. Chemistry & Industry by Gurdeep R. Chatwal
24. Applied Chemistry by Jayashree Ghosh
25. Drugs by David Krupadanam
26. Pharmacodynamics by R.C.Srivastava, Subit Ghosh
27. Analytical Chemistry by David Krupadanam
28. Green Chemistry – V.K.Ahluwalia
29. Organic Synthesis by V.K.Ahluwalia and R.Agarwal
30. New trends in Green Chemistry –by V.K.Ahluwalia & M.Kidwai
31. Industrial Chemistry by B.K.Sharma
32. Industrial Chemistry by Banerji
33. Industrial Chemistry byM.G.Arora
34. Industrial Chemistry by O.P.Veramani & A.K.Narula
35. Synthetic Drugs by O.D.Tyagi & M.Yadav
36. Medicinal Chemistry by Ashutoshkar
37. Medicinal Chemistry by P.Parimoo
38. Pharmacology & Pharmacotherapeutics by R.S Satoshkar & S.D.Bhandenkar
39. Medicinal Chemistry by Kadametal P-I & P.II
40. European Pharmacopoeia
41. Vogel's Qualitative organic analysis.
42. Laboratory manual of Organic Chemistry by Raj K Bansal