JYOTI NIVAS COLLEGE AUTONOMOUS
SYLLABUS FOR 2018 BATCH AND THEREAFTER

Programme: B.Sc. **Semester: IV**

CHEMISTRY PAPER IV

Course Code: 18IVCH4 **No. of Hours: 60**

COURSE OBJECTIVES: By the end of the course students should be able to:

- Write structures of Aldehydes, Ketones, Carboxylic Acids and their derivatives and active methylene compounds, discus synthesis and reactions of all the above and understand the concept of acid strength and effect of substituents on acid strength.
- Discuss the concepts in Nuclear and Radiochemistry pertaining to stability of nucleus, counters, applications of nuclear isotopes
- Draw and explain structures of typical Solids, and discuss the fundamental aspects of liquid crystalline state, discuss the advantages and applications of Powder Metallurgy
- Understand and explain Freundlich and Langmuir isotherms and the necessity for the BET isotherms as well as Phase diagram for one component and two component systems
- Appreciate the importance of green chemistry and green synthesis of a few compounds.
- Analyse the cations and anions present in a mixture of two simple inorganic salts (The laboratory component).

LEARNING OUTCOMES: On completion of the course the student should be able to:

- Outline theoretical reactions involving carbonyl compounds and carboxylic acids
- Use the chemistry of the above compounds as an aid in outlining synthesis involving active methylene compounds.
- Understand the principles of stability of the nucleus of an atom to apply them to radioactive reactions
- Have a foundation in basic crystallography
- Apply the phase rule to practical problems involving two components
- Perform qualitative analysis and identify the components of an inorganic salt mixture.

UNIT I

Chapter 1 - NUCLEAR AND RADIOCHEMISTRY **09 HRS**

Nucleus – structure and stability, binding energy, calculations on mass defect and binding energy. Radioactive decay law, half-life, radioactive equilibrium, radioactive series (four series), principle and construction: Geiger-Muller and Scintillation counter. Artificial radioactivity-nuclear reactions induced by α, n, p and D particles. Nuclear fission and fusion,

Nuclear reactors and Breeder reactors. Isotopes – use of radioactive isotopes as tracers in (i) studying reaction mechanism: O^{18} in reaction mechanism of photosynthesis and ester hydrolysis, (ii) agriculture: uptake of calcium, phosphorous by plants, (iii)medicine: as a diagnostic tool and as a therapeutic agent (iv) carbon dating (problems).

Chapter 2 - STATES OF MATTER AND STRUCTURE OF IONIC 09 HRS

Review: Structural differences between solids, liquids and gases.

Crystalline and amorphous solids – isotropy and anisotropy. Definition of space lattice, unit cell. Laws of crystallography. Symmetry elements in crystals. Miller indices, X–ray diffraction of crystals, Derivation of Bragg's equation. Determination of the structure of NaCl and KCl by rotating crystal method. Close packing of anions. Radius ratio rules (No derivation), structures of NaCl, CsCl, ZnS (Wurtzite and Zinc blende), CaF_2 and $CaTiO_3$. Extrinsic point defects: F –centers, gemstones.

Elementary discussions of the liquid crystalline state: Definition, Classification: Smectic, Nematic and Cholesteric and applications.

UNIT II

Chapter 3 - ADSORPTION 05 HRS

Adsorption: types, factors affecting and applications, Freundlich isotherm, desorption activation energy: life time, effect of temperature on life time, problems. Langmuir's isotherm and its derivation, experimental proof of Langmuir isotherm using adsorption of acetic acid on activated charcoal, BET Equation (derivation not required), problems on surface area, applications of surface area measurements in material research.

Chapter 4 - PHASE RULE 06 HRS

Statement (no derivation) and explanation of the terms with examples, one component systems: water, sulphur. Condensed phase rule, two component systems: KI–water; Pb-Ag system, desilverisation of lead by Pattinson's method. Eutectic temperature and composition. Freezing mixtures and their application.

UNIT III

Chapter 5 - POWDER METALLURGY, ALLOYS AND STEEL 09 HRS

Advantages of powder metallurgy, application techniques in production of metal powders, production of tungsten powder from wolframite. Characteristics of alloys, types of alloys, Hume-Rothery rule. Iron-Carbon phase diagram, austenite, ferrite, cementite and pearlite phases. Alloy steels : influence of Si, Mn, Cr, Ti and W on properties of steel. Ferro alloys : production of ferrochrome, ferromanganese and ferrosilicon. Carbon steel - classification, Heat treatment-hardening, case hardening; carburising and nitriding, tempering and annealing.

Chapter 6 - COMPOUNDS OF SOME NON-METALS 02 HRS

Synthesis, structure and applications of the following compounds: Boron – diborane, boron trifluoride. Nitrogen – Hydrazine, Hydroxylamine, hydrazide. Halogens- bleaching powder.

Chapter 7 - GREEN CHEMISTRY 04 HRS

Introduction, need of green chemistry, principles of green chemistry, green reactions: paracetamol, phenyl benzoate (solid state synthesis), butyraldehyde (ultra-sonication).

UNIT IV

Chapter 8 - ALDEHYDES AND KETONES 08 HRS

Review: nomenclature, general formula, physical properties of carbonyl compounds.

Preparation of carbonyl compounds: synthesis of aldehydes: (i) oxidation of primary alcohols: Swern oxidation and pyridinium chlorochromate (PCC), (ii) ozonolysis of alkenes, (iii) from acid chlorides and nitriles (using sterically hindered reducing agents: DIBAL–H), (iv) Rosenmund's reaction (v) Gatterman–Koch formylation (vi) Etard reaction.

Synthesis of Ketones: (i) ozonolysis of alkenes(ii) from carboxylic acids,(iii) from nitriles (Using Grignard reagents), (iv) Hoesch reaction.

Polarity of Carbonyl Group: General mechanism of neucleophilic addition across C–O bond (strong neucleophile only), relative reactivity of aldehydes and ketones (steric and electronic factors). Addition of alcohols: hemiacetal and acetal formation.

Acidity of α–hydrogen: formation and structure of enolates, (i)condensation reactions with mechanism: aldol condensation (aldol addition and dehydration), Cannizarro reaction and Benzoin condensation (ii) condensation reactions without mechanism- Perkin's condensation

and Knovenegel condensation (iii) reaction with ammonia: formation of aldimine and ketone-ammonia, synthesis of Urotropine from formaldehyde and hydrobenzamide from benzaldehyde (iv) Reaction with derivatives of ammonia: hydroxylamine, hydrazine, phenyl hydrazine (mention of reaction with 2,4–DNP and importance of the reaction) and semicarbazide.

Oxidation and reduction of carbonyl compounds: (i) Bayer–Villiger oxidation, (ii) Mannich reaction, (iii) Wolff – Kischener reduction, (iv) Clemmenson's reduction. (v) reduction to alcohols (using $LiAlH_4$ and $NaBH_4$)

UNIT V

Chapter 9 CARBOXYLIC ACIDS AND THEIR DERIVATIVES 06 HRS

Review: nomenclature, general formula, physical properties of carboxylic acids.

Introduction: acid strength: K_a and pK_a values, acidity of carboxylic acids based on delocalisation in conjugate base. Effect of substituents on acid strength: aliphatic acids (formic, acetic, monocloroacetic acid, dichloroacetic acid and trichloroacetic acids), aromatic acids (p– nitrobenzoic acid and p–aminobenzoic acids)

Synthesis of carboxylic acids by acid hydrolysis of nitriles with mechanism.

Reactions of carboxylic acids: (i) HVZ reaction, (ii) decarboxylation and (iii) reduction with $LiAlH_4$. Di and tricarboxylic acids: structure and action of heat: dicarboxylic acids from oxalic to adipic acid:tricarboxylic acids- tartaric acid and citric acid. Reduction of tartaric and citric acids with HI. Acid Derivatives: acid chlorides, esters, acid anhydrides and amides-synthesis from carboxylic acids. Relative reactivity of acid derivatives and explanation based on basicity of leaving groups. Reactions of acid derivatives: hydrolysis, alcoholysis, ammonolysis, Amides: reduction, Hoffmann rearrangement.

Chapter 10 - ACTIVE METHYLENE 02 HRS

Introduction. Preparation of diethyl malonate from acetic acid, synthetic applications: (i) preparation of monocarboxylic acid (butanoic acid), dicarboxylic acid (adipic acid), unsaturated acid (cinnamic acid). (ii) ketone (butanone), (iii) cyclic compound – barbituric acid.

Preparation of ethyl acetoacetate from ethyl acetate. Synthetic applications: (i) Preparation of monocarboxylic acids (butanoic acid). (ii) Dicarboxylic acid (succinic acid). (iii) unsaturated acid (crotonic acid). (iv) ketone (butanone).

REFERENCES:

1. 1. Puri B.R., Sharma L.R. and Pathania M.S., Principles of Physical Chemistry, 46th Edition, Vishal Publishing Co. 2013.
2. Barrow G.M., Physical Chemistry, 5th Edition, Tata McGraw Hill, 2013.
3. Bahl B.S., Bahl A., Tuli G.D., Essentials of Physical Chemistry, S. Chand Publ., 2008.
4. Atkins P.W. and DePaula J., Physical Chemistry, 7th Edition, Oxford University Press, 2008.
5. Azharoff L.V., Introduction to the Solid State. Wiley Publication. 2012.
6. Lee J.D., Concise Inorganic Chemistry, 5th Edition, Blackwell Publishing Co. 2013.
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10. Morrison R.T., Boyd R.N. and Bhattacharjee S.K., Organic Chemistry, 7th Edition, Pearson Publication., 2011.
11. Solomon G. And Fryhle C.B., Organic Chemistry, 10th Edition., Wiley Publication, 2014
12. Sanyal S.N., Reactions, Rearrangements and Reagents, harati Bhawan Publishers and Distributors, 2013.
13. Norman R.O.C and Coxon J.M, Principles of Organic Synthesis, 3rd Edition, CPP Publishers, 2017.
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16. March J. And Smith M.B., Advanced Organic Chemistry, 6th Edition., Wiley Publishing Co. 2009.

II B.Sc., IV Semester, Chemistry Practical – 4

DURATION: 3 HRS / **NO. OF UNITS: 15**

1. Systematic semi micro qualitative analysis of a mixture of two simple salts (with interfering radicals).

Repetition and Tests.

REFERENCES:

1. J Bassett, R.C.Denny,G.H.Jeffery and J.Menaham Qualitative chemical analysis. ELBS 1986.
2. V.V.Ramanujam Inorganic semimicro qualitative analysis. The National Pub.Co. 1974.
3. M.J.Sienko,R.A.Plane, S.T.Marcus Experimental Chemistry 6^{th} edition McGraw- Hill 1985.