SEMESTER III

PHYSICAL AND ORGANIC CHEMISTRY -II THEORY

Program: B.Sc. Course Code: U20/CHE/DSC/301

Course: DSC-3 No. of Credits: 4 Max. Hours: 60 Hrs Hours per week: 4 Hrs Max. Marks: 100

COURSE OBJECTIVES:

- To understand the behavior of electrolytes in solution and to know the applications of electrode process
- To foster acquisition of knowledge on the concepts of solutions and phases of different systems.
- To understand the structure, sources, classification and inter conversions of carbohydrates.
- To learn about heterocyclic compounds, their preparation and properties.
- To introduce the basic principles of molecular spectroscopic techniques.

COURSE OUTCOMES:

- CO 1: Understand the theory of electrical conductance, transformation of chemical energy into electrical energy in Galvanic cells.
- CO 2: Differentiate between the different types of colloids and their properties and interpret the components from a phase diagram.
- CO 3: Distinguish between open chain and cyclic structures of simple sugars and write their inter conversions.
- **CO 4:** Understand the structure, and reactions of simple heterocyclic compounds.
- **CO 5:** Achieve knowledge about the basic principles and applications of rotational, vibrational and electronic spectroscopic techniques.

PHYSICAL CHEMISTRY

MODULE 1: ELECTRO CHEMISTRY AND EMF

(15 Hrs)

ELECTROCHEMISTRY AND EMF

Electrical transport – conduction in metals & in electrolyte solutions, specific conductance & equivalent conductance and measurement of equivalent conductance, variation of specific and equivalent conductance with dilution. Migration of ions and Kholrausch's law. Arrhenius theory of electrolytic dissociation and its limitation, weak and strong electrolytes, Ostwald's dilution law, its uses and limitations. Debye- Huckel- Onsagar's equation for strong electrolytes (elementary treatment only). Transport number, definition and determination by Hittorf method for attackable and non-attackable electrodes. Applications of conductivity measurements. Determination of degree of dissociation, determination of K_a of acids, determination of solubility product of sparingly soluble salt, conductometric titrations. Electrolytic and Galvanic cell – reversible and irreversible cells, conventional representation of electrochemical cell. EMF of a cell and its measurement. Computation of EMF. Types of reversible electrodes: gas electrode, metal - metal ion, metal - insoluble salt and redox electrode. Electrode reactions, Nernst equation, cell EMF and single electrode potential, standard Hydrogen electrode – reference electrodes (calomel electrode) – standard electrode potential, sign conventions, electrochemical series and its significance. Calculation of thermodynamic quantities of cell reaction – ΔG, ΔH and K .Determination of pH using Hydrogen electrode, Glass electrode, quinhydrone electrode, solubility product of AgCl. Potentiometric titrations.

MODULE 2: SOLUTIONS, COLLIGATIVE PROPERTIES & PHASE RULE (15 Hrs)

SOLUTIONS (5 Hrs)

Liquid- liquid mixtures – ideal liquid mixtures, Raoult's and Henry's law. Non – ideal systems. Azeotropes: HCl-H₂O, ethanol – water systems. Fractional distillation. Partially miscible liquids – phenol – water, trimethyl amine – water system, Nicotine - water

Lower and upper consolute temperature. Effect of impurity on consolute temperature. Immiscible liquids and steam distillation.

DILUTE SOLUTIONS AND COLLIGATIVE PROPERTIES (5 Hrs)

Dilute Solutions, Colligative Properties, Raoult's law, relative lowering of vapour pressure, molecular weight determination. Osmosis - laws of osmotic pressure, its measurement, determination of molecular weight from osmotic pressure. Elevation of boiling point and depression of freezing point. Derivation of relation between molecular weight and elevation in boiling point and depression in freezing point.

PHASE RULE (5 Hrs)

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.

MODULE 3: CARBOHYDRATES AND HETEROCYCLICS

(15 Hrs)

CARBOHYDRATES (10 Hrs)

Introduction: Nomenclature & Classification - Classification into mono, oligo & polysaccharides into pentoses, hexoses etc. into aldoses & ketoses.

Monosaccharides- All discussion to be confined to (+) glucose as an example of aldohexoses & (-) fructose as example of ketohexoses. Chemical properties & structural elucidation. Evidences for straight chain pentahydroxy aldehyde structure (acetylation, reduction to n-Hexane, cyanohydrin formation, reduction of Tollen's & Fehling's reagent & oxidation to gluconic & saccharic acids) Osazone formation of glucose. 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 (some negative aldehyde tests & mutarotation). Cyclic structure of glucose, proposition of cyclic structure (pyranose structure, anomeric carbon & anomers). Proof for ring size (methylation, hydrolysis & oxidation reactions). Different ways of writing pyranose structure (Haworth formula & chair conformational formula). Structure of fructose: Evidence of 2-Ketohexose structure (Formation of penta acetate, formation of cyanohydrin, its hydrolysis &reduction by HI to give 2-Carboxy-nhexane) Same osazone formation from glucose & fructose, Hydrogen bonding in osazone. Cyclic structure of fructose (furanose structure & Haworth formula). Inter conversion of Monosaccharides: Aldopentose to aldohexose-eg.arabinose to D-glucose, D-mannose (Kiliani-Fischer method). Epimers, Epimerisation. Lobry de bruyn van Ekenstein rearrangement. Aldohexose to Aldopentose eg. D-glucose to D-arabinose by Ruff's degradation. Aldohexose (+)(glucose) to Ketohexose (-)(fructose) & Ketohexose (fructose) to Aldohexose (+glucose).

HETEROCYCLIC COMPOUNDS

(5 Hrs)

Introduction & Definition: –Simple 5 membered ring compounds with one heteroatom, eg.-furan, thiophene & pyrrole. Importance of ring systems-presence in important natural products like haemoglobin & chlorophyll. Numbering the ring systems as per Greek letters & numbers. Aromatic character-6 electron system (4 electrons from 2 double bonds & a pair of non-bonded electrons from heteroatom), tendency to undergo substitution reactions.

Resonance structures: indicating electron surplus carbons & electron deficient heteroatom, explanation of feebly acidic character of pyrrole, electrophillic substitution at 2 or 5 position, halogenation, nitration & sulphonation under mild conditions. Reactivity of furan as 1,3-diene, Diels-Alder reaction (one example). Sulphonation of thiophene (purification of benzene obtained from coal tar), Preparation of furan, Pyrrole & thiophene from 1,4-dicarbonyl compounds only. Paal-Knorr synthesis.

Structure of pyridine, basicity, aromaticity, comparision with pyrrole, one method of preparation. Properties - reactivity towards nucleophilic substitution reactions- Chichibabin reaction.

MODULE 4: MOLECULAR SPECTROSCOPY I

(15 Hrs)

INTRODUCTION (2 Hrs)

Dipole moment. Introduction to electromagnetic radiation: different regions, wavelength, wave number, frequency and energy, interaction with molecules and types of molecular spectra.

ROTATIONAL SPECTROSCOPY (MICROWAVE SPECTROSCOPY) (2 Hrs)

Rotational axis, moment of inertia, classification of molecules (based on moment of inertia), rotational energies, selection rules, determination of bond length of rigid diatomic molecules eg. HCl.

INFRA RED SPECTROSCOPY

(5 Hrs)

Energy levels of simple harmonic oscillator, molecular vibration spectrum, selection rules. Determination of force constant. Qualitative relation of force constant to bond energies. Anharmonic motion of real molecules and energy levels. Modes of vibrations in polyatomic molecules. Characteristic absorption bands of various functional groups. Finger print nature of infrared spectrum.

ELECTRONIC SPECTROSCOPY

(4 Hrs)

Bonding and antibonding molecular orbitals, electronic energy levels of molecules (σ , π , n), types of electronic transitions: σ - σ *, n- σ *, n- π *, π - π * with suitable examples. Selection rules, Terminology of chromophore, auxochrome, bathochromic and hypsochromic shifts. Absorption of characteristic chromophores: diene, enone and aromatic chromophores. Representation of UV-visible spectra

RAMAN SPECTROSCOPY

(2 Hrs)

Raman spectroscopy: Raman effect, Rayleigh scattering, Stokes and anti-Stokes lines; their intensity difference, Effect of nuclear spin, rule of mutual exclusion.

Text Books:

- 1. Puri, B.R., Sharma L.R., and Pathania, M.S. (2003). *Elements of Physical Chemistry*. Jalandhar, Delhi: Vishal Publishing Co.
- 2 . Bahl, A, Bahl, B.S & Tuli (2009). Essentials of physical chemistry: A textbook for B. Sc. classes as per UGC model syllabus (Rev. multicoloured.). New Delhi: S. Chand.
- 2. Bahl, A. and Bahl, B.S.(2011). A Textbook of Organic Chemistry. Ram Nagar, New Delhi: S.
- 3. Chand and Company.4. Jain, M.K., and Sharma, S.C.(2011). *Modern Organic Chemistry*. Jalandhar, Delhi: Vishal Publishing Co.
- 4. Sharma, Y.R.(2012). *A Text Book of Complete Organic Chemistry*. Bangalore: Kalyani Publishers.
- 5. Sharma Y.R (2005) *Elementary Organic Spectroscopy; Principles and Chemical applications*: S.Chand & Company Ltd

Reference Books:

Soni, P. (1979). A textbook of physical chemistry (11th edn.). New York: Academic Press.

Prutton, C., & Maron, S. (1965). *Principles of physical chemistry* (4th edn.). New York: Macmillan

Morrison R.T., Boyd, R.N., and Bhattacharjee S.K. (2011). *Organic Chemistry*. Delhi, Chennai, Chandigarh: Pearson.

Ferguson, L. (1966). *The Modern Structural theory of Organic Chemistry*. New Delhi: Prentice-Hall of India Pvt.

Solomons, T., & Fryhle, C. (2008). Organic chemistry (9th edn.) Hoboken, NJ: John Wiley.

L. Pavia and Lampman Kriz Vyal, *Spectroscopy*: Singh Age Publications

Colin Banwell , Elaine McCash (1994) Fundamentals of Molecular Spectroscopy (West village U.S.A): Mcgraw Hill

PHYSICAL AND ORGANIC CHEMISTRY -II MODEL QUESTION PAPER THEORY

Course Code: U20/CHE/DSC/301 Max. Marks: 60 Credits: 4 Max. Time: 2 Hrs **SECTION - A** I. Answer the following 4X10=40 M 1. a) Describe the Hittorf method for the determination of transport number. (CO 1) 5M b) Explain Debye –Huckle's theory and explain the role of inter-ionic effect. (CO 1) 5M OR 2. a) Explain the working and construction of S.H.E. (CO 1) 5M b) State Kohlrausch law of independent migration of ions and list out its applications. (CO 1)5M a) What are azeotropes? Explain ethanol-water system. (CO 2) 5M b) State and explain Raoult's law with its limitation. (CO 2) 5M OR 4. a) Explain the term molal elevation constant. Derive the expression relating the molecular weight of solute with the elevation in boiling point.(CO 2) 5M 5M b) Illustrate one component system with a phase diagram (CO 2) 5. Prove that (+)-Glucose has a pyranose structure and draw the Haworth and chair conformational structures of α and β , D -Glucopyranose. (CO 3) 10M 6. a) Explain the synthesis of Furan, Pyrrole and Thiophene from 1,4-dicarbonyl compounds (CO 4)6M b) Electrophilic substitution in furan occurs preferentially at 2- or 5- position. Explain. (CO 4) 4M 7. a) What is dipole moment? Predict the structure of CO₂ and SO₂ based on dipole moment. 5M b) Explain the various molecular vibrations seen in IR spectroscopy. (CO 5) 5M

- 8. a) Describe in detail about the electronic transitions observed in UV-VIS spectroscopy. (CO 5)
 - b) Explain the basic principles of Raman spectroscopy. (CO 5) 5M

SECTION - B

II. Answer any FOUR.

4x5=20 M

- 9. Calculate the EMF of Cd,Cd $^{+2}$ //Cu $^{+2}$,Cu E 0 (Cu $^{+2}$,Cu) = 0.34V. E 0 (Cd $^{2+}$,Cd) = -0.488 V. (CO 1)
- 10. State and explain Henry's Law and its limitations. (CO 1)
- 11. Define terms a) component b) degrees of freedom c) eutectic point (CO 3)
- 12. Outline the structure and basic nature of pyridine. (CO 4)
- 13. How is Glucose converted to Fructose. (CO 4)
- 14. Explain the concept of chromophore and auxochrome. (CO 5)