

CHEMISTRY

DSC-3:Analytical and Organic Chemistry-II

Contact Hours: 56

Work load: 4 Hours/Week.

Credit Points :4

Evaluation: Continuous Internal Assessment-40 Marks

Semester End Examination -60 Marks

Course Objectives:

- 1) Interrelationship among frequency, wavelength and wave number and importance of validation parameters of an instrumental method will be taught
- 2) Principle, instrumentation and applications of spectrophotometry, nephelometry and turbidometry will be taught
- 3) Fundamentals of separation methods and principles of paper, thin layer and column chromatography will be taught
- 4) Principle, types and applications of solvent extraction will be taught
- 5) Principle and mechanism of ion-exchange, types of resins and domestic and industrial applications of ion-exchange chromatography will be taught
- 6) The concept of mechanism and its importance will be taught to the student
- 7) Concept and importance of intermediates in organic chemistry will be taught taking proper examples
- 8) The various techniques for identification of reaction mechanism will be taught to the student taking proper examples
- 9) Concept of stereochemistry and its importance will be taught.
- 10) The various projection formulae and the techniques of designating the molecules into R, S, D, L will be taught taking proper examples
- 11) The theory and concept of Cis-, Trans- isomerism and its importance and the techniques to differentiate between them will be taught taking examples

Course Specific Outcomes

After the completion of this course, the student would be able to

- 1) Understand the importance of fundamental law and validation parameters in chemical analysis
- 2) Know how different analytes in different matrices (water and real samples) can be determined by spectrophotometric, nephelometric and turbidometric methods.
- 3) Understand the requirement for chemical analysis by paper, thin layer and column chromatography.

- 4) Apply solvent extraction method for quantitative determination of metal ions in different samples
- 5) Utilize the ion-exchange chromatography for domestic and industrial applications
- 6) Explain mechanism for a given reaction.
- 7) Predict the probable mechanism for an reaction
Explain the importance of reaction intermediates, its role and techniques of generating such intermediates
- 8) Explain the importance of Stereochemistry in predicting the structure and property of organic molecules.
- 9) Predict the configuration of an organic molecule and able to designate it.
- 10) Identify the chiral molecules and predict its actual configuration

Unit-I

Quantitative analysis-Instrumental methods

Electromagnetic spectrum, absorption of electromagnetic radiation, Definition and units of frequency, wavelength, wave number, Beer's law, Beer-Lambert law derivation, deviations from Beer's law, limitations, construction of calibration graph (Plot of absorbance versus concentration), Evaluation Procedures- standard addition, Internal standard addition, validation parameters-detection limits, sensitivity, dynamic/linearity range, Instrumentation, single beam and double beam spectrophotometers, quantitative applications of colorimetry (determination of Fe, Mo, Cu, Ti and PO_4^{3-}) and numerical problems on application of Beer's law. **10 hrs**

Nephelometry and Turbidimetry: Introduction, principle, instrumentations of nephelometry and turbidimetry; effects of concentration, particle size and wavelength on scattering; choice between nephelometry, applications of nephelometry and turbidimetry (determination of SO_4^{2-} and PO_4^{3-}) **4 hrs**

Unit-II

Separation methods

Fundamentals of chromatography: General description, definition, terms and parameters used in chromatography, classification of chromatographic methods, criteria for selection of stationary and mobile phase and nature of adsorbents. Principles of paper, thin layer, column chromatography. Column efficiency, factors affecting the column efficiency, van Deemter's equation and its modern version. **3hrs**

Paper chromatography: Theory and applications

Thin layer chromatography (TLC): Mechanism, R_f value, efficiency of TLC plates, methodology—selection of stationary and mobile phases, development, spray reagents, identification and detection, qualitative applications. **4 hrs**

Solvent Extraction: Types- batch, continuous, efficiency, selectivity, distribution coefficient, Nernst distribution law, derivation, factors affecting the partition, relationship between % extraction and volume fraction, Numerical problems on solvent extraction. Solvent extraction of iron and copper. **4hrs**

Ion exchange

chromatography: resins, types with examples- cation exchange and anion exchange resins, mechanism of cation and anion exchange process and applications of ion-exchange chromatography (softening of hard water, separation of lanthanides, industrial applications). **03Hrs**

Unit-III

Reaction Intermediates: Generation, Stability and Reactions of,

- i) Carbocations: Dienone-phenol; and Pinacol-Pinacolone Rearrangement.
- ii) Carbanions :PerkinReaction,Aldolcondensation,Claisen-Schmitt condensation.
- iii) Free Radicals : Sandmeyer Reaction
- iv) Carbenes and Nitrenes: Singlet and Triplet states, their relative stability and reactions
- v) Arynes: Formation,detection etc. **8 hrs**

Methods for Identifying Reaction Mechanism:

Product analysis, Isolation and Identification of Intermediates, Stereochemical Evidences,Effect of Catalyst,crossover Experiments,Isotopic studies,Kinetic Studies.

6 hrs

Unit-IV

Stereochemistry of Organic Compounds:

Fischer projection,Newmann and Sawhorse projection formulae and their interconversions.

Geometrical isomerism : Cis-trans and syn-anti isomerism, E/Z notations with C.I.P rules. Optical Isomerism :Optical activity, Specific rotation, Chirality/Asymmetry, Enantiomers, Molecules with two or more chiral centres, Diastereoisomers, meso structures, Racemic mixtures and Resolution, Relative and absolute configuration, D/L and R/S designations

14 hrs

References :

- 1) Fundamental of Analytical Chemistry, D.A. Skoog, D.M. West, Holler and Crouch, 8th edition, Saunders College Publishing, New York (2005).
- 2) Analytical Chemistry, G.D. Christian, 6th edition, Wiley-India (2007).

- 3) Quantitative Analysis, R.A. Day and A.L. Underwood, 6th edition, PHI Learning Pvt Ltd. New Delhi (2009).
- 4) Vogel's Textbook of Quantitative Chemical Analysis, J. Mendham, R.C. Denney, J.D. Barnes and M.J.K. Thomas, 6th edition, Third Indian Reprint, Pearson Education Pvt. Ltd. (2007).
- 5) Organic Reaction Mechanism by V.K. Ahluwalia and R.K. Parashar (Narosa Publishers)
- 6) Organic Chemistry by S.M. Mukherji, S.P. Singh and R.K. Kapoor (Narosa Publishers)
- 7) Morrison R.N and Boyd R.N, Organic Chemistry, Darling Kindersley (India) Pvt. Ltd. (Pearson Education)
- 8) Finar I.L, Organic Chemistry (Volume I); Finar I.L (Volume II) Stereochemistry and the Chemistry of Natural Products., Dorling Kindersley (India) Pvt. Ltd. (Pearson Education)
- 9) Kalsi P.S. Stereochemistry, conformation and Mechanism, New age International
- 10) Eliel E.L and Wilen S.H, Stereochemistry of Organic Compounds, Wiley, (London)

PRACTICALS

Credit Points: 2

Teaching Hours: 4 hrs

Evaluation : Continuous Internal Assessment-20 marks

Semester End Examination : 30 marks

Course Objectives

- 1) To impart skills related to preparation of stock and working solutions and handling of instrumental methods
- 2) To know the principle of colorimetric analysis and construction of calibration plot
- 3) To understand the chemistry involved in colorimetric determination of metal ions and anions
- 4) To determine R_f values of different metal ions present in a mixture
- 5) To impart knowledge on the importance of functional groups in organic compounds.
- 6) Techniques to identify the functional groups in a compound by performing physical and chemical tests
- 7) To record its melting point/boiling point.
- 8) To prepare suitable derivative for that compound and to characterize it.

Course Specific outcomes

After the completion of this course, the student would be able to

- 1) Understand the importance of instrumental methods for quantitative applications

- 2) Apply colorimetric methods for accurate determination of metal ions and anions in water or real samples
- 3) Understand how functional groups in a compound is responsible for its characteristic property
- 4) Learn the importance of qualitative tests in identifying functional groups.
- 5) Learn how to prepare a derivative for particular functional groups and how to purify it'

PART-A (Analytical Chemistry)

- 1) Colorimetric determination of copper using ammonia solution
- 2) Colorimetric determination of iron using thiocyanate solution
- 3) Colorimetric determination of nickel using DMG solution
- 4) Colorimetric determination of titanium using hydrogen peroxide
- 5) Colorimetric determination of nitrite in a water sample (diazo coupling Reaction/Griess reagent)
- 6) Colorimetric determination of phosphate as ammonium phosphomolybdate
- 7) Determination of R_f values of two or three component systems by TLC
- 8) Separation of different metal ions by paper chromatography/ Solvent extraction of iron using oxine solution (**demonstration**)

PART-B(Organic Chemistry)

Qualitative analysis of bifunctional Organic compounds such as 1)Salycilic acid ,p-Nitro benzoic acid,Antranilicacid,p-Chloro benzoic acid 2) o-Cresol,p-Cresol,Resorcinol,o-Nitrophenol,p-nitrophenol 3)o-Nitro aniline,p-Nitroaniline,p-Toluidine,p-Chloroaniline,p-Bromoaniline, 4)Ethyl Salicylate, Salicylaldehyde, Acetophenone,p-Dichlorobenzene,p-Nitro toluene,,Benzamide etc.(Atleast 6-8 compounds to be analysed in a semester)

References

- 1)Vogel's Textbook of Quantitative Chemical Analysis, J. Mendham, R.C. Denney, J.D.Barnes and M.J.K. Thomas, 6th edition, Third Indian Reprint, Pearson Education Pvt.Ltd.(2007)
- 2) Vogels Text Book of Qualitative Chemical Analysis,ELBS

CHEMISTRY

DSC-4: Inorganic and Physical Chemistry-II

Contact Hours: 56

Work load: 4 Hours/Week.

Credit Points :4

Evaluation: Continuous Internal Assessment-40 Marks

Semester End Examination -60 Marks

Course Objectives:

Students learn about

1. Different types of bonding in molecules/compounds/ions
2. The structures of molecules/compounds/ions based on different models/theories
3. Properties of compounds based on bonding and structure
4. The fundamentals of thermodynamics including the laws, the concept of entropy and free energy functions and their applications.
5. The concepts of surface chemistry, catalysis and their applications.
6. The theoretical and experimental aspects of chemical kinetics including basic theories of reaction rates and methods of determining order.
7. Electrochemistry dealing with electrolytes in solution. Conductance measurements and applications. Concept of ionic mobility and their determination.

Course outcomes: After the completion of this course, the student would be able to

1. Predict the nature of the bond formed between different elements
2. Identify the possible type of arrangements of ions in ionic compounds
3. Write Born - Haber cycle for different ionic compounds
4. Relate different energy parameters like, lattice energy, entropy, enthalpy and solvation energy in the dissolution of ionic solids
5. Explain covalent nature in ionic compounds
6. Write the M.O. energy diagrams for simple molecules
7. Differentiate bonding in metals from their compounds
8. Learn important laws of thermodynamics and their applications to various thermodynamic systems
9. Understand adsorption processes and their mechanisms and the function and purpose of a catalyst

10. Apply adsorption as a versatile method for waste water purification.
11. Understand the concept of rate of a chemical reaction, integrated rate equations, energy of activation and determination of order of a reaction based on experimental data
12. Know different types of electrolytes, usefulness of conductance and ionic mobility measurements
13. Determine the transport numbers

Unit - I

Structure and Bonding -I

The ionic bond :Structures of ionic solids

Radius ratio rules, Calculation of some limiting radius ratio values, Coordination number 3 (planar triangle), Coordination number 4 (tetrahedral and square planar), Coordination number 6 (octahedral), Close packing. **3hrs**

Classification of ionic structures:

Ionic compounds of the type AX (ZnS, NaCl, CsCl)

Ionic compounds of the type AX₂ (Calcium fluoride (fluorite) and Rutile structure

Layer structures CdI₂ , Cadmium iodide structure

Limitations of radius ratio concept

2 hrs

Lattice energy and Born-Haber cycle, Derivation of Born-Landé equation and its drawbacks, Kapustinskii equation, solvation energy and solubility of ionic solids, polarizing power and polarizability, Fajan's rules with applications.

Numerical problems

5 hrs

Covalent bond: Valence bond theory, The Lewis theory, The octet rule, Exceptions to the octet rule, Sidgwick- Powell theory. Valence shell electron pair repulsion (VSEPR) theory, Effect of lone pairs, electronegativity, isoelectronic principle, Examples using VSEPR theory: BF₃ and BF₄⁻, NH₃ and NH₄⁺, H₂O, PCl₅, ClF₃, SF₄, I₃⁻ and I₃⁺, SF₆, and IF₇. Limitations of VSEPR. **4 hrs**

Unit - II

Structure and Bonding -II

Concept of resonance, resonance energy, hybridisation, types of hybridization, sp, sp², sp³ dsp² dsp³, d²sp³, sp³d² with one example each, and energetics of hybridization. Bent's rule, Limitations of Valence Bond Theory. **3 hrs**

Molecular Orbital theory:

LCAO concept: s-s, s-p, p-p, p-d and d-d combinations of orbitals, bonding, nonbonding and antibonding molecular orbitals, non-bonding combinations of orbitals, Rules for linear combination of atomic orbitals

Examples of molecular orbital treatment for homonuclear diatomic molecules

H₂ molecule, H₂⁺, He₂ molecule, He₂⁺ molecule ion, Li₂ molecule, Be₂ molecule

B₂ molecule, C₂ molecule, N₂ molecule, N₂⁺, O₂ molecule, O₂⁻ and O₂²⁻.

M.O. energy diagrams of heteronuclear diatomic molecules with examples (NO, NO⁺, CO and HCl). Calculation of bond order, relationship between bond order, bond energy and bond length, magnetic properties based on MOT. **7 hrs**

Metallic Bonding:

General properties of metals : Conductivity, Lustre, Malleability and cohesive force

Crystal structures of metals and Bond lengths

Theories of bonding in metals:

Free electron theory, Valence bond theory, Molecular orbital or band theory of solids

Prediction of conducting properties of conductors, insulators and semiconductors, extrinsic and intrinsic semiconductors using M.O. theory. **4 hrs**

UNIT III

First Law of Thermodynamics

Thermodynamic Processes, Reversible and Irreversible Processes, Nature of Heat and Work, Internal Energy, First Law of Thermodynamics, Enthalpy of a System, Work done in isothermal and adiabatic expansion of an ideal gas, Numerical problems, Joule-Thomson Expansion, Relation between Joule-Thomson coefficient and other thermodynamic parameters.

Second law of Thermodynamics

Concept of entropy, thermodynamic scale of temperature, Statements of the Second Law of Thermodynamics, molecular and statistical interpretation of entropy, Calculation of entropy change for reversible and irreversible processes, Free Energy Functions: Gibbs and Helmholtz energy, Variation of S, G, A with T, V and P, Numerical problems, Free energy change and spontaneity, Gibbs-Helmholtz equation.

Third Law of Thermodynamics

Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules. **10 Hrs**

Surface Chemistry

Adsorption

Types of adsorption isotherms. Freundlich adsorption isotherm (only equation), its limitations. Langmuir adsorption isotherm (derivation to be done) and BET equation (derivation not included).

Catalysis

Types of Catalysis and theories with examples (intermediate compound theory and adsorption theory), Theory of acid base catalysis, Michaelis-Menten mechanism. Heterogeneous catalysis: surface reactions, unimolecular, bimolecular surface reactions. Autocatalysis with examples. Applications: Design process to removal of toxic compounds from industrial wastewater and treatment of portable water requirements.

4Hrs

UNIT IV

Chemical Kinetics

Differential and integrated form of rate expressions up to second order reactions, Derivation of expression of rate constant of second order reaction ($a=b$ and $a \neq b$), Problems on rate constant ($a=b$), Methods of determination of order of a reaction, temperature dependence of reaction rates; Arrhenius equation, activation energy, Numerical problems on Arrhenius equation in calculating energy of activation and rate constants. Collision theory of reaction rates, Lindemann's mechanism, qualitative treatment of the theory of absolute reaction rates. Experimental determination of kinetics of (i) inversion of cane sugar by polarimetric method (ii) spectrophotometric method for the reaction between potassium persulphate and potassium iodide. **7 Hrs**

Electrochemistry – I

Arrhenius theory of electrolytic dissociation. Merits and Demerits, Conductance, Specific conductance, equivalent and molar conductivity and their variation with dilution. Molar conductivity at infinite dilution. Numerical problems.

Kohlrausch's law of independent migration of ions and its applications, Debye-Hückel-Onsager equation. Ionic mobilities and their determinations, transference numbers and their relation to ionic mobility's, determination of transference numbers using Hittorf and Moving Boundary methods.

Applications of conductance measurement: (i) degree of dissociation of weak electrolytes (ii) ionic product of water (iii) solubility and solubility product of sparingly soluble salts (iv) conductometric titrations (acid base titrations only) and (v) Hydrolysis constants of salts. Numerical problems. **7 Hrs**

Reference Books

1. Peter Atkins & Julio De Paula, Physical Chemistry, 9th Ed., Oxford University Press (2010)
2. G W Castellan, Physical Chemistry, 4th Ed., Narosa (2004)
3. R G Mortimer, Physical Chemistry 3rd Ed., Elsevier: Noida, UP (2009)
4. B R Puri, L R Sharma and M S Pathania, Principal of Physical Chemistry, Vishal Publishing Co.
5. B S Bahl, G D Tuli and Arun Bahl, Essentials of Physical chemistry, S Chand & Company Ltd.
6. A S Negi and S C Anand, A textbook of Physical Chemistry, New Age International Publishers.
7. B N Bajpai, Advanced Physical chemistry, S Chand and Company Ltd.
8. R L Madan, Chemistry for Degree Students, Semester I, II, III and IV, S Chand and Company Ltd.
9. P L Soni, O P Dharmarha and U N Dash, Textbook of Physical Chemistry, Sultan Chand and Sons.

PRACTICALS

Credit Points: 2

Teaching Hours:4Hrs

Evaluation : Continuous Internal Assessment-20 marks

Semester End Examination : 30 marks

Course objective:

To attain practical knowledge about:

1. Analytical skills in detecting the constituents present in unknown samples by systematically carrying out the qualitative analysis.
2. The methods of determining rates of chemical reactions.
3. Designing electrochemical cells and making measurements related to it.
4. Determination of physical characteristics of electrolytes using conductivity measurements in solution.
5. Adsorption phenomenon, mechanism and basic models to explain adsorption.
6. Simple techniques like conductometry to obtain physicochemical parameters of electrolytes.

Course outcomes: At the end of the course student would be able to

1. Understand the chemical reactions involved in the detection of cations and anions.
2. Explain basic principles involved in classification of ions into groups in semi-micro qualitative analysis of salt mixture
3. Carryout the separation of cations into groups and understand the concept of common ion effect.

4. Understand the choice of group reagents used in the analysis.
5. Analyse a simple inorganic salt mixture containing two anions and cations
6. Use instruments like conductivity meter to obtain various physicochemical parameters.
7. Apply the theory about chemical kinetics and determine the velocity constants of various reactions.
8. Learn about the reaction mechanisms.
9. Interpret the behaviour of interfaces, the phenomena of physisorption and chemisorptions and their applications in chemical and industrial processes.
10. Learn to fit experimental data with theoretical models and interpret the data

Part A- Inorganic Chemistry Practicals

Qualitative semi-micro analysis of mixtures containing 2 anions and 2 cations. Emphasis should be given to the understanding of different reactions.

The following cations and anions are suggested.

Cations: NH_4^+ , Pb^{2+} , Bi^{3+} , Cu^{2+} , Al^{3+} , Fe^{3+} , Co^{2+} , Cr^{3+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Ba^{2+} , Ca^{2+} , Sr^{2+} , Mg^{2+} , Na^+ , K^+ and Li^+ .

Anions: CO_3^{2-} , CH_3COO^- , Cl^- , Br^- , I^- , NO_3^- , BO_3^{3-} , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$ and PO_4^{3-}

Spot tests and flame tests to be carried out wherever possible.

Part B- Physical Chemistry Practicals

1. Determination of the enthalpy of neutralization of a strong acid with strong base.
2. Verification of Freundlich and Langmuir isotherms for adsorption of acetic acid on activated charcoal.
3. The study of kinetics of potassium persulphate and potassium iodide volumetrically.
4. Determination of velocity constant for acid catalyzed hydrolysis of methyl acetate.
5. Determination of velocity constant for the saponification of ethyl acetate ($a = b$) volumetrically.
6. Determination of equivalent conductivity of strong electrolyte and verification of DHO equation.
7. Determination of dissociation constant of weak acid by conductivity method.
8. Conductometric titration of strong acid and strong base.
9. Conductometric titration of weak acid and strong base.
10. Determination of the hydrolysis constant of aniline hydrochloride conductometrically.
11. Determination of solubility product of sparingly soluble salt conductometrically.

References

1. Vogel's Qualitative analysis, Revised by G. Svehla, Pearson education, 2002
2. J B Yadav, Advanced Physical Chemistry, Krishna Prakashan Media (P) Ltd, Meerut.
3. Khosla, B. D.; Garg, V. C. & Gulati, A. Senior Practical Physical Chemistry, R. Chand & Co.: New Delhi (2011).
4. Garland, C. W.; Nibler, J. W. & Shoemaker, D. P. Experiments in Physical Chemistry 8th Ed.; McGraw-Hill: New York (2003).
5. Halpern, A. M. & McBane, G. C. Experimental Physical Chemistry 3rd Ed.; W.H. Freeman & Co.: New York (2003).