

## Course Title: Chemistry VIII

CHMC1622M

*Course Objectives*

1. To introduce the basic concepts of UV, IR and Rotational Spectroscopy.
2. To introduce the basic concepts of NMR, Raman, Electronic and Photoelectron spectroscopy.

*Course Outcomes*

Upon completion of the course students will be able to

1. Understand the application of UV, IR and Rotational spectroscopy in structural determination.
2. Learn the principle and application of NMR, Raman, Electronic and Photoelectronic spectroscopy in chemical characterization.

**Unit- I Spectroscopy-I****(16 Contact hours)**

Spectroscopy: Electromagnetic radiation, regions of the spectrum, Representation of molecular spectrum, Peak position, intensity and width. Types of peak broadening. Statement of Born-Oppenheimer approximation. Rotational spectrum: Moment of inertia, classification of molecules on the basis of moment of inertia. Energy of a rigid diatomic rotor, selection rules for rotational transition and associated spectrum, relative population of rotational levels and spectral intensity, determination of bond length in diatomic molecules.

**Unit-II Spectroscopy-II****(16 Contact hours)**

Vibrational Spectrum: Classical and quantum mechanical (qualitative) treatment of simple harmonic oscillator, selection rules for vibrational transition, pure vibrational spectrum of a diatomic molecule, determination and relation of force constant with bond length and bond energy. Molecular vibrations, IR transitions and selection rules. Group frequency and fingerprint regions and its significance. Effect of resonance, inductive effect and H-bonding on infrared absorptions. Characteristic absorptions of alkanes, alkenes, alkynes, alcohols, ethers, carbonyl compounds, amines and carboxylic acids and their derivatives.

**Unit- III Spectroscopy-III****(16 Contact hours)**

Photochemistry: Laws of photochemistry. Grothus-Drapper law, Stark-Einstein law. Beer-Lambert law, molar absorptivity. Jablonski diagram-fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing) quantum yield. Ultraviolet-visible spectroscopy: Presentation and analysis of electronic spectra. Types of electronic excitations. Chromophores and auxochromes. Bathochromic and hypsochromic shifts. Effects of conjugation and solvents on absorption bands. Ultraviolet spectra of enes and enones. Prediction of maxima of enes using Woodward's rules.

#### **Unit- IV Spectroscopy-IV**

**(16 Contact hours)**

Nuclear Magnetic Resonance Spectroscopy: Basic principles of NMR spectroscopy. Shielding and deshielding of protons. The chemical shift. Equivalent and non-equivalent protons. Spin-spin splitting, coupling constants for vicinal, geminal and long-range couplings. Characteristic functional group NMR absorptions. The <sup>1</sup>H NMR spectra of ethyl bromide, ethanol, acetaldehyde, ethyl acetate, methyl propionate, toluene and acetophenone.

#### **Books Recommended:**

1. Fundamentals of Molecular Spectroscopy; C. N. Banwell, E.M. McCash; 4th Edn. (Indian Edn.), Tata McGraw-Hill, 2017.
2. Principles of Physical Chemistry; B.R. Puri, L.R. Sharma and L.S. Pathania; 47th Edn. Vishal Pubs & Co, 2017.
3. Spectroscopy of Organic Compounds; P.S. Kalsi; 7<sup>th</sup> Edn, New Age International Pvt. Ltd., 2016.
4. Introduction to Spectroscopy; D.L. Pavia, G.M. Lampman, G.S. Kriz, J.R. Vyvyan; 5th Edn., Cengage Learning India Pvt. Ltd., 2015.
5. Organic Spectroscopy; L.D.S. Yadav; 1st Edn, Springer Netherlands, 2005.
6. Organic Spectroscopy; W. Kemp; 3rd Edn, Palgrave Macmillan, 2008.
7. Kakkar, R. Atomic & Molecular Spectroscopy: Concepts & Applications, Cambridge University Press; 2015.
8. John R. Dyer: Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall.
9. Spectrometric Identification of Organic Compounds; R. M. Silverstein, F. X. Webster, D. J. Kiemle, D. L. Bryce; 8th Edn., John Wiley & Sons, 2014.

#### **PART II: LAB COURSE**

**(64 hours)**

##### **Part I: Spectrophotometry (Attempt any three)**

1. To determine the  $\lambda_{\max}$  of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  and calculate the energies of two absorption bands in these molecules in different units.
2. Verify Lambert-Beer's law
3. Determination of unknown concentration of  $\text{CuSO}_4/\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$  in a solution using spectrophotometer.
4. Spectrophotometric determination of Fe (II), using 1, 10-Phenanthroline.

##### **Part II: Refractometry**

1. To determine refractive index of a liquid by using Abbe's refractometer.
2. To determine percentage composition of a mixture of two liquids by refractometry (Glycerol and water).

#### **Books Recommended:**

1. Advanced Practical Physical Chemistry; J.B. Yadav; Krishna Prakashan Media (P) Limited, 2015.

2. Senior Practical Physical Chemistry PB; B. D. Khosla; V. C. Garg; A. R. Gulati; R. Chand & Co, 2008.
3. Vogel's Qualitative Inorganic Analysis; G. Svehla; 7th Ed., Pearson Education. 2013.
4. Vogel's Textbook of Quantitative Inorganic Analysis; Bassett, G. H. Jeffery, J. Basset, J. Mendham, R. C. Denny, 6th ed., ELBS; 2007.
5. Experimental Physical Chemistry; A. M. Halpern, & G. C. Mc Bane; 3rd Ed.; W.H. Freeman & Co; 2006.
6. Experiments in Physical Chemistry; C. W.; Garland, J. W. Nibler, & D. P. Shoemaker, 8th Ed.; McGraw-Hill: New York, 2003.
7. Principles of Instrumental Analysis; D.A. Skoog, F.J. Holler & T.A. Nieman Cengage Learning India Ed.

## Course Title: Inorganic Chemistry-I (CHMC2622M)

### Course Objectives

1. To comprehend thermodynamic and kinetic aspects of metal ligand equilibria.
2. To understand CFT and MOT treatment of octahedral, tetrahedral and square planar complexes.
3. To understand metal ligand  $\pi$  back bonding and evidences for the same in light of various bonding theories.

### Course Outcomes

Upon completion of the course students will be able to:

1. have an understanding of stability and magnetic properties of complexes.
2. describe the bonding in coordination complexes in light of CFT sketch and justify molecular orbital diagram of various coordination complexes.
3. understand how  $\pi$  back bonding makes CO and phosphine type ligands unique and quantify the existence of  $\pi$  back bonding through IR spectroscopy.

### Unit-I Bonding in Coordination Compounds

(16 contact hours)

Crystal field theory splitting of d orbitals in octahedral, tetrahedral and square planar symmetries, factors affecting  $10Dq$ , crystal field stabilisation energy for high spin and low spin  $O_h$  and  $T_d$  complexes, Structural effects (Jahn-Teller distortion, Ionic radii) and Thermodynamics effects (Hydration and Lattice energies) of crystal field splitting. Spectrochemical series.

Ligand field theory. Molecular Orbital Theory and energy level diagrams: Sigma bonding in octahedral, square planar and tetrahedral complexes.

Evidences for existence of covalent bonding in transition metal complexes; Nephelauxetic effect.

*Spectral characteristics of complexes:* Term states for d ions, characteristics of d-d transitions, charge transfer spectra, selection rules for electronic spectra.

### Unit-II Metal-Ligand equilibria in Solutions

(16 contact hours)

*Stability of complexes:* Factors affecting stability of complexes, Thermodynamic aspects of complex formation, Stepwise and overall formation constants, Stability correlations, statistical factors and chelate effect, macrocyclic ligands. Crown ethers, cryptands.

*Determination of stability constant and composition of the complexes:* Formation curves and Bjerrum's half method, Potentiometric method, Spectrophotometric method, Ion exchange method, Polarographic method and Continuous variation method (Job's method)

*Magnetic property of complexes:* Spin-orbit coupling, effect of spin-orbit coupling on magnetic moments, quenching of orbital magnetic moments. Metal clusters (SMM, paramagnetism, antiferromagnetism)

### **Unit-III Organometallic Chemistry (16 contact hours)**

Definition and Classification of Organometallic compounds on the basis of bond type.

*Alkene Complexes:* Zeise's Salt and its structural features. Rhodium-ethylene complex, Metal-allyl complexes, Metal-acetylene complexes.

*Ferrocene :* Preparation and properties, structure and bonding in ferrocene. Metallocenes.

*Metal Carbonyls:* EAN rule, classification, preparation (Direct combination, High pressure synthesis, Disproportionation and Oxidation methods), Nature of bonding in metal carbonyls (C-O, M-C and M-M bonds), modes of ligation by CO. Carbonyl, Nitrosyl and Tertiary phosphine as  $\pi$  acid ligands. Mixed metal carbonyls.

*Organometallic Compounds as catalysts:* Conditions to be satisfied by metal to act as catalyst, Hydrogenation of olefins-Wilkinson's catalyst, Hydroformylation of olefins-The Oxo process, Oxidation of olefins-Wacker's process, Ziegler-Natta catalysis.

### **Unit –IV Reactions of Metal complexes. (16 contact hours)**

Labile and Inert Complexes (VBT and Taube's explanations).

*Ligand Substitution reactions:* dissociative, associative and  $SN_1CB$  mechanisms. Anation reaction.

*Electron Transfer reaction:* Outer sphere Mechanism and Inner Sphere Mechanism. Electron transfer reactions in Biological systems, Reactions of coordinated ligands.

*Isomerisation reactions :* Geometrical and Optical Isomers

*Substitution reactions in square planar complexes:* Eigen-Wilkins mechanism; Trans effect, theories of Trans effect and applications of Trans effect in synthesis of square planar compounds; Kurnakov test.

Stereochemical changes in octahedral substitution reactions. Substitution reactions without metal-ligand bond breaking.

#### ***Books Recommended***

1. Inorganic Chemistry, G L Meissler and D A.Tarr, 3rd Edition, Pearson Education Inc., 2008
2. Co-ordination Chemistry, D. Bannerjea, TATA Mcgraw Hill, 1993
3. Introduction to Ligand Fields, B. N. Figgis, Wiley Eastern Ltd, 1976.
4. Inorganic Chemistry– Principles of structure and reactivity, J.E. Huheey, E.A Keiter, R.L Keiter and O.K Medhi, 4 th Edition, Pearson Education Inc., 2006
5. Advanced Inorganic Chemistry; 5<sup>th</sup>. And 6th edn; F.A. Cotton, G. Wilkinson; Wiley; 1998/1999.
6. Chemistry of the Elements; 2<sup>nd</sup> edn; N. N. Greenwood, A. Earnshaw; Butterworth; 1997.
7. Inorganic Chemistry; 3<sup>rd</sup> edn; D. F. Shriver; P. W. Atkins; Oxford; 1999.
8. Principles of inorganic chemistry, B.R.Puri, L.R.Sharma and K.C.Kalia, Vishal publications, 33rd edition, 2016.
9. Advanced inorganic chemistry, S.K.Agarwal and Keemti Lal, Pragati Prakashan Educational publication, 5th edition,2016.
10. Magnetochemistry, R.L.Carlin, Springer Verlag,Berlin,Germany,1986.

## **PART II: LAB COURSE**

**(64 hours)**

### **I. Preparation of the following coordination compounds (any three):**

- i. Tris-thiourea copper(I) sulphate monohydrate.
- ii. Hexaamminecobalt(III) chloride
- iii. Trisethylenediaminecobalt(III) chloride
- iv. Ammonium dodecamolybdophosphate

### **II. Potentiometric Titrations (any two) :**

- i. Titration of a mixture of HCl and CH<sub>3</sub>COOH potentiometrically and hence the composition of a mixture using Quinhydrone electrode.
- ii. Titration of ferrous ammonium sulphate against potassium dichromate potentiometrically and hence the formal redox potential of Fe (II) to Fe (III) system.
- iii. Titration of pure solutions of KCl, KBr and KI and their mixtures with standard AgNO<sub>3</sub> Solution.

### **Books Recommended**

1. Svehla, G. Vogel's Qualitative Inorganic Analysis, Pearson Education, 2012.
2. Mendham, J. Vogel's Quantitative Chemical Analysis, Pearson, 2009.
3. J. B. Yadav, Advanced Practical Physical Chemistry ; ; Edition, 16 ; Goel Pub., 2006.
4. Advanced Practical Organic Chemistry; N. K. Vishnoi; 3rdEdn; Vikas Publishing, 2009.
5. Comprehensive Practical Organic Chemistry: Qualitative analysis Ahluwalia, V.K. & Sunita Dhingra; Universities Press, India, 2004.

**Course Title: Physical Chemistry I (CHMC3622M)****Course Objectives**

To introduce the concepts of fast reactions and kinetic investigations of fast reactions.

1. To make students to understand the reason for need and role of solvent and solvent characteristics on the kinetics of solution phase reactions.
2. To introduce the basic concepts of enzyme kinetics.
3. To introduce students to basic concepts of statistical thermodynamics and learn how to use of concepts for estimation of thermodynamic parameters of simple systems.
4. To introduce the basic concepts of X-Ray crystallography and interpretation of the X-Ray diffractograms

**Course Outcomes****Upon completion of the course students will be able to**

Students shall learn what fast reactions are and how the kinetic investigations are carried out for such reactions.

1. Students will learn about the ways a solvent shall affect the kinetics of reactions in solution.
2. Students shall appreciate the difference between the solution and gas phase reactions.
3. Learn how to use the activated complex theory for the estimation of rate constants for gas phase, solution phase and surface reactions.
4. Students shall understand how reaction kinetics of ionic reactions can be changed through use of salt addition and solvent change.
5. Students shall learn the basic concepts of statistical thermodynamics and how to use these concepts for the estimation of thermodynamic parameters of simple systems.
6. Students learn the basic concepts of X-Ray crystallography and how to interpret X-Ray diffractograms of simple crystalline solids

**Unit-I: Advanced Chemical Kinetics****(16 hours)**

Kinetics of Fast Reactions: General features of fast reactions, study of fast reactions by flow method, relaxation method (Temperature Jump Method) and flash photolysis.

Theories of Chemical Reactions: Collision theory of bimolecular chemical reactions for similar and dissimilar molecules. (Derivation of expression of Pre-exponential factor, rate constant and rate of reaction. Limitations of collision theory. Activated complex theory of reaction rates (thermodynamic formulation), comparison with collision theory.

## **Unit-II: Catalysis**

**(16 hours)**

*Homogenous Catalysis:* Characteristics of Catalysis, Acid Base Catalysis, kinetics of Acid-Base catalysed reactions.

*Heterogeneous Catalysis:* Kinetics of Surface Reactions, unimolecular & bimolecular surface reactions viz. Fischer-Tropsch synthesis. Langmuir-Hinshelwood & Langmuir- Riedel mechanism.

*Enzyme Catalysis:* Introduction to enzyme-catalyzed reactions, Characteristics . Michaelis-Menton equation, effect of temperature and pH. Enzyme inhibition.

*Photocatalysis:* General characteristics, photocatalytic breakdown of water.

## **Unit-III: Statistical Thermodynamics**

**(16 hours)**

*Distribution:* Introduction and types(Combinatorial Problems). Basics of Probability: Laws of Probability (addition and multiplication), Stirling approximation, Microstates, Macrostates and thermodynamic probability.

*Distribution Laws:* Boltzmann, Bose-Einstein and Fermi- Dirac distribution . Limitations of distribution laws.

*Partition function:* Meaning & its significance, Translational, Rotational, Vibrational partition functions.

Concept of Ensemble and its types( elementary idea only).

## **Unit-IV: X-Ray Diffraction of Solids**

**(16 hours)**

*Crystallography:* Introduction, Laws of Crystallography (Law of interfacial angles, rational indices and symmetry), Symmetry elements in sodium chloride. Lattice Planes and Miller indices; Interplanar distance,

*X-Ray diffraction:* Bragg equation, Debye-Scherrer method of X-ray structural analysis of crystals, Systematic absences, identification of cubic, body centered and face centered unit cells from systematic absences in diffraction pattern.

Structure factor and its relation to intensity. Calculation of structure factor for rock salt, and cesium chloride structures.

### **Books Recommended:**

- 1) Physical Chemistry –P. W. Atkins, 9th Edition, ELBS , Oxford, 2009.
- 2) Elements of Physical Chemistry, Peter Atkins and Julio de Paula, 7th Edition, Oxford University Press, 2016.
- 3) Physical Chemistry, Concepts and Models, Volume II, Nabakumar Bera, Subhasree Ghosh, Paulami Ghosh, Techno world.
- 4) Atkins' Physical Chemistry, Peter Atkins, Julio de Paula & James Keeler, 11th Edition, Oxford University Press, 2018.
- 5) Chemical Kinetics, K. J. Laidler, 3rd Edition, Pearson, 1987.

- 6) Chemical Kinetics and Reaction Dynamics, Paul L. Houston, Dover Publications, INC., Mineola, New York, 2001.
- 7) Chemical Kinetics and Dynamics, J. I. Steinfeld, J. S. Francisco, W.L. Hase, Prentice Hall, 1989
- 8) Chemical Kinetics and Catalysis, R.I. Masel, Wiley, 2001
- 9) Chemical Kinetics: From Molecular Structure to Chemical Reactivity, Luis G Arnaut, Sebastiao Jose Formosinho, Hugh Burrows, Elsevier, 2007.
- 10) An Introduction to Chemical Thermodynamics, R. P. Rastogi and R. R Misra, 6th Edition, Vikas Publishing House Pvt. Ltd. 2018.
- 11) A systematic Approach to Statistical Thermodynamics, Vakil Poddar, Pragati Prakashan, 2019.
- 12) Statistical Thermodynamics, M.C.Gupta, New Age International, 1993.
- 13) Chemical Thermodynamics, Classical, Statistical, and Irreversible, Pearson, 2013.
- 14) Solid-state Chemistry and its Applications, West, Wiley, 2014. 5.
- 15) The Physical Chemistry of Solids, Borg, Biens, Academic press, 1992.

**PART II: Tutorials**

**(2 credits)**

A: Use of following software in Chemistry.

1. Microsoft Excel
2. Origin
3. Chemdraw/Gaussian

B: Lab Visit