# Semester –V: Inorganic Chemistry II (3L-0T-1P)

**Graduate Attributes**

i. ***Course Objective:***

This course focuses on further extending the concepts of coordination chemistry along with the chemistry of main group elements, noble gases and introduction to organometallics. Intermediate level quantitative analysis of metal ions is included to give a hands-on experience to the students.

ii. ***Learning outcome:***

Students shall learn about electronic and magnetic properties of coordination complexes. They shall understand the preparation, structure and properties compounds of main group elements and noble gases. Students will also learn about organometallic compounds, comprehend their bonding, stability and reactivity. The laboratory experiments shall enable the learners to separate and estimate individual ions in multicomponent systems.

No. of Required Classes: 45 (Theory) + 30 (Practical)

No. of Contact Classes: 45 (Theory) + 30 (Practical)

No. of Non-Contact Classes:

iii. ***Particulars of Course Designer*** (Name, Institution, email id):

1) Dr. Apurba Kalita, B Barooah College, apurbakalitabbc@gmail.com

2) Dr. Sanchay Jyoti Bora, Pandu College, sanchay.bora@gmail.com

3) Dr. Sonit Kumar Gogoi, Gauhati University, skgogoi@gauhati.ac.in

## Semester –V: Inorganic Chemistry II (3L-0T-1P)

| Unit | Content | Contact Hrs |
|---|---|---|
| Unit I: Coordination Chemistry IV | Electronic spectra and magnetism of coordination compounds: microstates, free ion term symbols and their splitting in tetrahedral and octahedral fields, Racah parameters, selection rules and relaxation mechanisms (vibronic coupling and spin orbit coupling), Orgel diagrams and prediction of spectral transitions, Jahn-Teller effect on electronic spectra, charge-transfer spectra, calculation of spin only and orbital contribution to magnetic moments. Spin crossover. | 12 |
| Unit II: Main Group elements | Relative stability of different oxidation states, inert pair effect, diagonal relationship, and anomalous behaviour of main group elements.<br>a) Preparation and properties of ortho and para hydrogen.<br>b) Preparation, structure and properties of borane (bonding in diborane, brief idea of styx number, Wade's rule), boric acid, borax, borazine, phosphazine, $S_4N_4$.<br>c) Preparation and properties of oxides, superoxides, peroxides, hydrides, hydroxides, halides and carbonates of alkali and alkaline earth metals. Reactions of alkali and alkaline earth metals with liquid ammonia.<br>d) Allotropes of carbon, phosphorus, and sulphur.<br>e) Oxides and oxoacids of nitrogen, phosphorus, sulphur, and chlorine.<br>f) Interhalogen compounds, polyhalides, pseudo halogen<br>g) Hydrates, clathrates and inclusion compounds.<br>h) Preparation, structure and properties of silicates, aluminosilicates. | 15 |
| Unit III:Noble Gases | Occurrence and uses, rationalisation of inertness of noble gases, clathrates; preparation and properties of $XeF_2$, $XeF_4$ and $XeF_6$; Nature of bonding in noble gas compounds (Valence bond treatment and MO treatment for $XeF_2$). Molecular shapes of noble gas compounds (VSEPR theory). | 6 |

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| Unit IV: Organometallics I | Definition and classification of organometallic compounds on the basis of bond type. Concept of hapticity of organic ligands, 18 electron rule.<br>Metal carbonyls: electron count of mononuclear, polynuclear and substituted metal carbonyls of 3d series.<br>General methods of preparation (direct combination, reductive carbonylation, thermal and photochemical decomposition) of mono and binuclear carbonyls of 3d series.<br>Structures of mononuclear and binuclear carbonyls of Cr, Mn, Fe, Co and Ni. Pi -acceptor behaviour of CO (MO diagram of CO to be discussed), synergic bonding effect and use of IR data to explain the extent of back bonding.<br>Zeise's salt: preparation and structure, evidence of synergic effect and comparison of synergic effect with that in carbonyls. | 12 |
| **Laboratory:** Inorganic quantitative analysis | 1. Estimation by volumetric method of any two of the following:<br>a. Fe(III)- By standard $KMnO_4$ solution<br>b. Fe(III) – By standard $K_2Cr_2O_7$ solution<br>c. Cu(II) – By Iodometric method.<br>2. Estimation of Ni(II) by gravimetric method.<br>3. Separation and estimation of individual ions in two-component systems of<br>a. Cu and Fe<br>b. Fe and Ca<br>c. Ca and Mg<br>d. Cu and Ni and<br>e. $Cl^-$ and $SO_4^{2-}$. | 30 |
| **Text/ reference Books** | 1. Inorganic Chemistry (Principles of Structure and Reactivity), J. E. Huheey, E. A. Keiter, R. L. Keiter, O. K. Medhi, 5th edition, Pearson Education.<br>2. Principles of Inorganic Chemistry, 7th edition, Puri, Sharma, Kalia, Vishal Publishing Co.<br>3. Concepts and Models of Inorganic Chemistry, 3rd edition, Bodie Douglas, Darl Mcdaniel, John Alexander, Wiley.<br>4. Advanced Inorganic Chemistry, F. Albert Cotton, Geoffrey Wilkinson, Carlos A. Murillo, Manfred Bochmann, Wiley.<br>5. Vogel's Quantitative Chemical Analysis 6th edition, J. Mendham, R. C. Denney, J. D. Barnes, M. Thomas, B. Sivsankar, Pearson. | |

# Semester-V: Organic Chemistry II (3 L- 0 T- 1 P)

## Graduate Attributes

i. ***Course Objective:***

This course aims at introducing students to stereo-chemical aspects of organic reactions and their mechanisms. Students will also learn the chemical aspects of carbohydrates and terpenoids.

Familiarize the students with qualitative analysis of carbohydrates and small organic compounds with functional groups. Further, to teach students methods for identifying functional groups using IR spectroscopy.

ii. ***Learning outcome:***

Students will be able to predict and recognize reactivity of organic molecules by their functional groups, and utilize this understanding for the construction of complex molecules.

Learners will be able to qualitatively analyse organic molecules and identify the functional groups by interpreting the IR spectra.

No. of Required Classes: 45 (Theory) + 30 (Practical)

No. of Contact Classes: 45 (Theory) + 30 (Practical)

No. of Non-Contact Classes:

iii. ***Particulars of Course Designer*** (Name, Institution, email id):

1) Prof. Rupam Jyoti Sarma, Gauhati University, rjs@gauhati.ac.in

2) Dr. Diganta Choudhury, B Barooah College, digantachoudhury2008@gmail.com

# Semester-V: Organic Chemistry II (3 L- 0 T- 1 P)

| Unit | Content | Contact Hours |
|---|---|---|
| Unit I: Formation of carbon-carbon and carbon-heteroatom bonds | Wurtz Reaction, Wurtz-Fittig reaction, Simmons-Smith reaction; Free radical substitutions; Saytzeff and Hofmann eliminations; reagents of phosphorus, sulfur and boranes; stereospecific and stereoselective reactions; stereoselective reactions of alkenes: epoxidation reaction using mCPBA. | 10 |
| Unit II: Reactions of active methylene compounds | Active methylene compounds (keto-enol tautomerism): preparation and synthetic applications of diethyl malonate and ethyl acetoacetate. | 8 |
| Unit III: Reactions of enolates and enamines | Formation and stability of enolates and enamines; alkylation of enolates and enamines; aldol reaction: aldol and benzoin condensation; Claisen reaction, Claisen-Schmidt reaction, Knoevenagel condensation, Perkin reaction; Cannizzaro reaction, Wittig reaction, Favorskii reaction, Beckmann rearrangement, Benzil-Benzilic acid rearrangement; addition reactions of unsaturated carbonyl compounds; Michael addition, Wolff rearrangement. | 8 |
| Unit IV: Nucleophilic reactions on the C=O groups | Nucleophilic attack at the carbonyl group (geometrical aspects); concept of prochirality; stereoselective additions to carbonyl groups: Crams rule, Felkin-Anh model. | 4 |
| Unit V: Carbohydrate chemistry | Classification of monosaccharides; absolute configuration of glucose and fructose, epimers and anomers; mutarotation; determination of ring size of glucose and fructose; conformations of glucose (Fischer, Haworth and stereoscopic projections); interconversions of aldoses and ketoses; Killiani Fischer synthesis and Ruff degradation; disaccharides: structure elucidation of maltose, lactose and sucrose. Polysaccharides -structures of starch, cellulose and glycogen. | 9 |
| Unit VI: Terpenes | Occurrence of terpenes; structure and classification of terpenes, isoprene rule; synthesis of citral, neral and α-terpineol; biosynthesis of limonene, pinene, carvone (*via* isopentenyl pyrophosphate). | 6 |

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| Lab Course | 1. Qualitative analysis of carbohydrates: aldoses and ketoses, reducing and non-reducing sugars.<br>2. (a) Qualitative analysis of unknown organic compounds containing simple functional groups (alcohols, phenols, amines, nitro, carboxylic acids and carbonyl compounds).<br>(b) Interpretation of infrared (IR) spectra of simple organic compounds.<br>*The student is required to learn about identification of functional groups of simple organic compounds by interpreting the IR spectra. The spectra may be recorded and/or provided to the students from literature.* | 30 |
| Recommended books | 1. Organic Chemistry, Jonathan Clayden, Nick Greeves, Stuart Warren, 2nd Edition.<br>2. Principles of Organic Synthesis, R. O. C. Norman, J. M. Coxon, 3rd Edition.<br>3. Advanced Organic Chemistry, R. Bruckner.<br>4. Organic Chemistry, G. M. Loudon, 4th Edition.<br>5. Organic Chemistry, R. T. Morrison, R. N. Boyd, S. K. Bhattacharjee, 7th Edition.<br>6. Organic Chemistry, Volume 2, I. L. Finar, 5th Edition.<br>7. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, Vogel's Textbook of Practical Organic Chemistry, Pearson, 2012.<br>8. V. K. Ahluwalia, S. Dhingra, Comprehensive Practical Organic Chemistry, University Press.<br>9. F. G. Mann, B. C. Saunders, Practical Organic Chemistry, 3rd Edition Longman, 1978. | |

# Semester-V: Reaction Dynamics (3L-0T-1P)

**Graduate Attributes**

i. ***Course Objective:***
The aim of this course is to teach students reaction dynamics with emphasis on order and molecularity of reactions, rate laws and rate equations, equilibrium and steady states, collision theory etc.

ii. ***Learning outcome***
Students shall learn how to mathematically model chemical reactions and evaluate the necessary rates of chemical reactions. They shall also be able to comprehend enzyme action in human physiology. Students hall be able to visualize complex reaction mechanisms via mathematical modeling and develop an analytical thinking ability.

No. of Required Classes: 45 (Theory) + 30 (Practical)

No. of Contact Classes: 45 (Theory) + 30 (Practical)

No. of Non-Contact Classes:

iii. **Particulars of Course Designer (Name, Institution, email id):**

1) Dr. Dhriti Mahanta, Gauhati University, mdhriti@gauhati.ac.in

2) Dr. Dhruba Jyoti Kalita, Gauhati University, dhrubajyoti.kalita@gauhati.ac.in

## Semester V – Reaction Dynamics (3L-0T-1P)

| Unit | **Content** | **Contact Hrs** |
|---|---|---|
| Unit I: Kinetics I | Order and molecularity of reactions. Rate laws and rate equations for zero, first and second order reactions ($2A \rightarrow P$, $A+B \rightarrow P$): their derivations, graphical representations and examples. Expressing the rate laws in terms of volume and pressure of reactants. Experimental determination of order of reactions (half-life method and initial rate method). Temperature dependence of reaction rate, energy of activation (its connection to Gibbs free energy). Arrhenius equation, energy of activation. Pre-exponential Factor and failure of Arrhenius Equation. | 9 |
| Unit II: Kinetics II | Difference between equilibrium and steady state. Limiting reagents, rate-determining step and steady-state approximation – explanation with suitable examples (eg. dissociation of HBr and acetaldehyde). Opposing reactions, consecutive reactions and parallel reactions (with examples and explanation of kinetic and thermodynamic control of products; all steps first order). Idea on explosive reactions. Enzyme catalysis: Derivation of Michaelis-Menten equation and interpretation of Lineweaver-Burk Plots. Eadie- Hofstee plot. Turn-over number. Oscillating reactions. | 14 |
| Unit III: Reaction Dynamics | Collision theory (detailed treatment). Modeling the Preexponential factor. Sphere of influence and collision cross section, Equivalence between Arrhenius and Collision theory. Failure of Collision theory. Physical interpretation of reaction co-ordinates and potential energy surfaces. Activated complex theory (detailed treatment). Thermodyamic formulation and derivation of Eyring equation. Evaluation of Arrhenius pre-exponential factor from transition state theory. Common examples where transition states have been experimentally identified or predicted.<br>Chemically and Diffusion controlled reactions with examples. Primary and secondary salt effects with examples.<br>Derivation of Bronsted-Bjerrum Equation and its graphical representation. Lindemann and Hinshelwood theory of unimolecular reaction and graphical representation. | 22 |

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| Laboratory experiments | 1. Determine the rate constant of the acid catalyzed hydrolysis of methyl acetate.<br>2. Determine the rate constant of saponification of ethyl acetate.<br>3. Determine the activation energy of the hydrolysis of methyl acetate catalyzed by hydrochloric acid.<br>4. Verify the Freundlich isotherm for the adsorption of oxalic acid on activated charcoal.<br>5. Verify the Langmuir isotherm for the adsorption of acetic acid on activated charcoal.<br>Determine the critical micelle concentration of a surface-active agent by surface tension measurements.<br>6. Study the kinetics of the Iodide-persulphate reaction by Initial rate method.<br>7. Theory and computer aided linear curve-fitting techniques (eg. first order kinetics using least squares) and evaluation of errors and standard deviations. | 30 |

Text Books:

1. Atkins' Physical Chemistry, Atkins, de Paula and Keeler
2. Chemical Kinetics and Reaction Dynamics, Paul L. Houston

Reference books:

1. A Textbook of Physical Chemistry, K. L. Kapoor, Volume V, Macmillan
2. Principles of Physical Chemistry, Puri, Sharma, Pathania, 48th edition, Vishal Publication.
3. Physical Chemistry: P C Rakshit
4. Physical Chemistry: A Molecular Approach by McQuarrie and Simon
5. Chemical Kinetics by Kaith J Laidler, McGraw-Hill

## Semester-V: Light-Matter Interaction (3L-0T-1P)

**Graduate Attributes**

i. ***Course Objective:***
This paper is focused on fundamental theory and application of photochemistry and various spectroscopic techniques such as rotational, vibrational, electronic and Raman spectroscopy. The accompanying laboratory course aims to introduce the students to various computational/experimental tools.

ii. ***Learning outcome:***
Students shall learn about the theory of photochemistry, spectroscopy and their application in chemistry. They shall use the knowledge gained from the quantum theories to identify unknown chemical compounds using modern techniques. The experiments performed in the laboratory course shall enable the learners to analyze/estimate various analytes using different techniques.

No. of Required Classes: 45 (Theory) + 30 (Practical)

No. of Contact Classes: 45 (Theory) + 30 (Practical)

No. of Non-Contact Classes:

iii. ***Particulars of Course Designer*** (Name, Institution, email id):

1) Dr. Himangshu Prabal Goswami, Gauhati University, hpg@gauhati.ac.in

2) Dr. Dhriti Mahanta, Gauhati University, mdhriti@gauhati.ac.in

## Semester V – Light-Matter Interaction (3L-0T-1P)

| **Unit** | **Content** | **Contact Hrs** |
|---|---|---|
| Unit I: Photochemistry: | Laws of photochemistry: Grotthus-Draper law, Stark-Einstein law of photochemical equivalence. Beer-Lambert law (for solids and liquids) and limitations. Quantum yield and its measurement for photochemical processes. Actinometry. Photostationary state. Photosensitized reactions (with examples). Jablonski diagrams: internal conversion, intersystem crossing, fluorescence and phosphorescence. Frank Condon principle. Primary and secondary processes in photochemical reactions. | 10 |
| Unit II: Spectroscopy | Spectroscopy and its importance in chemistry. Wave-particle duality. Link between spectroscopy and quantum chemistry. Electromagnetic radiation and its interaction with matter. Types of spectroscopy. Absorption cross section and Einstein's coefficients. Difference between atomic and molecular spectra. Born- Oppenheimer approximation. Separation of molecular energies into translational, rotational, vibrational and electronic degrees of freedom. Factors affecting intensities and width of spectral lines. Microwave (pure rotational) spectra of diatomic molecules. Selection rules and transition dipole moment. Structural information derived from rotational spectroscopy. IR Spectroscopy: Selection rules, IR spectra of diatomic molecules and organic compounds having functional groups.<br>Structural information derived from vibrational spectra. Vibrations of polyatomic molecules. Group frequencies. Effect of hydrogen bonding (inter and intramolecular) and substitution on vibrational frequencies. Electronic Spectroscopy: electronic excited states and selection rules. Free electron model and its application to electronic spectra of polyenes. Vibronic and spin orbit coupling. Colour and constitution, chromophores, auxochromes, bathochromic and hypsochromic shifts. Woodward-Fieser rules. Qualitative treatment of Raman effect. Elements of rotational Raman spectra Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference. Rule of mutual exclusion. | 35 |

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| Laboratory (minimum of seven to be performed) | 1. Calculation of the rotational constant for simple diatomic systems (eg. $N_2$, $F_2$, $O_2$) via quantum chemistry softwares.<br>2. Calculation of the optimum bond length by hand (theoretical) from the rotational constant via the rigid rotor approximation for a diatomic molecule.<br>3. To perform a series of single point calculations above and below equilibrium bond distance to generate a potential energy surface (PES) followed by a frequency calculation on the optimized geometry. Use of the resulting fundamental frequency to calculate the force constant of the bond.<br>4. Simulating the IR spectra of simple nonlinear molecules (eg. water, ammonia, boron trifluoride etc) using quantum chemistry software and assign the spectra to the corresponding vibrational modes.<br>5. To study the 200-500 nm absorbance spectra of $KMnO_4$ and $K_2Cr_2O_7$ (in dil. $H_2SO_4$) and determine the $\lambda_{max}$ values. Calculate the energies of the two transitions in different units (J molecule$^{-1}$, kJ mol$^{-1}$, cm$^{-1}$, eV).<br>6. Study the pH-dependence of the UV-Vis spectrum (200-500 nm) of $K_2Cr_2O_7$.<br>7. Record the 200-350 nm UV spectra of organic compounds ( eg. acetone, acetaldehyde, 2-propanol, acetic acid) and interprete the spectra. Compare these experimental results with associated theoretical rules.<br>8. Complete spectral analysis of the given (or recorded) vibration-rotation spectrum of HCl (g).<br>9. Verify Lambert-Beer's law and determine the concentration of $CuSO_4$/$KMnO_4$/$K_2Cr_2O_7$ in a solution of unknown concentration<br>10. Determine the concentrations of $KMnO_4$ and $K_2Cr_2O_7$ in a mixture.<br>11. Study the kinetics of iodination of propanone in acidic medium.<br>12. Determine the amount of iron present in a sample using 1,10-phenathroline.<br>13. Determine the dissociation constant of an indicator (phenolphthalein).<br>14. Study the kinetics of interaction of crystal violet/ phenolphthalein with sodium hydroxide. | 30 |

Text Books:

1. Fundamentals of Molecular Spectroscopy, C N Banwell, 4th Edition, McGraw-Hill
2. Atkins Physical Chemistry, P Atkins, J Paula and J Keeler, 11th Edition, Oxford University Press. 2018

Reference Books:

1. Introduction to Spectroscopy, DL Pavia, GL Lampman, GS Kriz and J R Vyvyan, 5th Edition, Cengage India Private Limited, 2015
2. Introduction to Molecular Spectroscopy: GM Barrow, McGraw Hill, 1992.
3. Basic Atomic and Molecular Spectroscopy, Vol 11, J M Hollas, Royal Society of Chemistry, 2002.
4. Symmetry and Spectroscopy: an introduction to vibrational and electronic spectroscopy, DC Harris and M D Bertolucci, 1989, Dover Publications
5. Molecular Spectroscopy, JL McHale, 2nd Edition, CRC Press
6. Atomic and Molecular Spectroscopy: Basic Concepts and Applications. Rita Kakkar, 2nd Edition, S Chand Publishing