SYLLABUS FOR M.Sc. CHEMISTRY
SESSION – 2018-19 & ONWARDS

M.Sc. II SEMESTER
Inorganic Chemistry(MCH201)

Unit I

Metal-Ligand Equilibria in Solution. Stepwise and overall formation constants and their relationship, trends in stepwise constants, factors affecting the stability of metal complexes with reference to the nature of metal ion and ligand, chelate effect and its thermodynamic origin, determination of binary formation constants by Bjerrum method, Job’s and Mole ratio methods.

UNIT II

Reaction Mechanism of Transition Metal Complexes. Base hydrolysis, conjugate base mechanism, direct and indirect evidences in favour of conjugate mechanism. Substitution reactions in square planar complexes: The Trans effect and the trans influence: Polarization and Bonding theories, applications of Trans effect in synthesis, Kurnakove’s test of distinguishing cis and trans isomers using the concept of trans effect, mechanism of substitution reactions in square planar complexes, factors affecting substitution reactions. Acquaintance of Trans effect in octahedral complexes

UNIT III


Electronic Spectra and Magnetic Properties of Transition Metal Complexes. Calculations of Dq, B and parameters for Cr(III), Co(II) and Ni(II) complexes using electronic spectral data. Charge transfer spectra: ligand to metal and metal to ligand.

UNIT IV

Metal-Complexes. Metal nitrosyls: Nitrosylating agents for synthesis of metal nitrosyls, vibrational spectra and x-ray diffraction studies of metal nitrosyls for bonding and structure elucidation, important reactions of transition metal nitrosyl complexes pertaining to potentiality in air pollution control, biomedical applications. Dinitrogen complexes, Vaska’s compound.

UNIT V

Group Theory: Symmetry elements and symmetry operations, symmetry groups or point groups, Schoenflies symbols, point group classifications, matrix representation of symmetry operations, group, necessary conditions for any set of elements to form a group, subgroups, classes in a group.

Books Suggested

UNIT I
Aliphatic Electrophilic Substitution. Bimolecular mechanisms, $S_{E2}$ and $S_{E1}$ mechanisms. The $S_{E1}$ mechanism, electrophilic substitution accompanied by double bond shifts. Effect of substrates, leaving group and solvent polarity on the reactivity.
Aromatic Electrophilic Substitution. The arenium ion mechanism, orientation and reactivity. The ortho/para ratio, ipso attack. Vilsmeier reaction, Fries rearrangement.

UNIT II
Free Radicals. Free radical reactions and their stereochemistry.
Allylic halogenation (NBS), oxidation of aldehydes to carboxylic acids, hydroperoxide formation, replacement of diazonium group. Hunsdiecker reaction.
Electrons spin resonance (ESR) spectroscopy. Electron paramagnetism, derivative curves, g values and hyperfine splitting.

UNIT III
Addition to Carbon-Hetero atom Multiple Bonds. Mechanism of metal hydride reduction of carbonyl compounds, acids, esters and nitriles. Wittig reaction.
Mechanism of condensation reactions involving enolates. Mannich, Benzoin, Perkin, and Stobbe reactions.

UNIT IV
Aromatic Nucleophilic Substitution. The $S_{N}Ar$, $S_{N}1$, benzyne and $S_{RN}1$ mechanisms. Reactivity, effect of substrate structure, leaving group and attacking nucleophile. Bucherer reaction, alkylation, and amination. The Bamberger rearrangement. The von Richter rearrangement.

UNIT V
Infrared and Raman Spectroscopy. Instrumentation and sample handling. Calculation of vibrational frequencies. Characteristic vibrational frequencies of alkanes, alkenes, alkynes, carbonyl compounds, alcohols, ethers, amines, phenols and aromatic compounds. Finger-print region. Effect of hydrogen bonding and solvent effect on vibrational frequencies, overtones, combination bands and Fermi resonance. FT-IR.
Resonance Raman effect. Concept and factors that influence group frequencies.

Books Suggested
UNIT I
Chemical Dynamics (Part III). General features of fast reactions, study of fast reactions by flow method, relaxation method, flash photolysis and the nuclear magnetic resonance method. Dynamics of molecular motions and of barrierless chemical reactions in solution, probing the transition state. Dynamics of unimolecular reactions; Lindemann-Hinshelwood and Rice-Ramsperger-Kassel-Marcus and Slater theories of unimolecular reactions.

UNIT II

UNIT III

UNIT IV

UNIT V

Books Suggested
1. Physical Chemistry, P. W. Atkins, ELBS.
5. Chemical Kinetics, K. J. Laidler, Mcgraw-Hill.
UNIT I
Photoelectron Spectroscopy. Basic principles; photo-electric effect, ionization process, Koopman's theorem. Photoelectron spectra of simple molecules, ESCA, chemical information from ESCA. Auger electron spectroscopy -basic idea.
Photoacoustic Spectroscopy. Basic principles of photoacoustic spectroscopy (PAS), chemical and surface applications.

UNIT II

UNIT III
Electron Diffraction. Scattering intensity vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecules. Low energy electron diffraction and structure of surfaces.
Neutron Diffraction. Scattering of neutrons by solids and liquids, magnetic scattering, measurement techniques. Elucidation of structure of magnetically ordered unit cell.

UNIT IV
Bioenergetics. Standard free energy change in biochemical reactions; exergonic and endergonic reactions. Hydrolysis of ATP. Synthesis of ATP from ADP.
Statistical Mechanics in Biopolymers. Chain configuration of macromolecules, statistical distribution end to end dimensions. Polypeptide chain binding and proteins, introduction to protein folding problem.

UNIT V
Thermodynamics of Biopolymer Solutions. Thermodynamics of biopolymer solutions, osmotic pressure, membrane equilibrium.
Transport of Ions. Biopolymers and their molecular weights. Structure and functions of cell membrane, ion transport through cell membrane, Nerve conduction; Evaluation of size, shape and molecular weight of biopolymers by various experimental techniques.

Books Suggested
This is a theory cum-laboratory course with more emphasis on laboratory work.

UNIT I

UNIT II
Computer Programming in FORTRAN/C/BASIC. (the language features are listed here with reference to FORTRAN. The instructor may choose another language such as BASIC or C the features may be replaced appropriately). Elements of the compute language. Constants and variables. Operations and symbols Expressions. Arithmetic assignment statement. Input and output Format statement. Termination statements. Branching statements as IF or GO TO statement. LOGICAL variables. Double precession variables. Subscripted variables and DIMENSION. DO statement FUNCTION AND SUBROUTINE. COMMON and DATA statement (Student learn the programming logic and these language feature by hands on experience on a personal computer from the beginning of this topic.)

UNIT III
Programming in Chemistry. Developing of small computer codes using any one of the languages FORTRAN/C/BASIC involving simple formulae in Chemistry, such as Van der Waals equation. Chemical kinetics (determination of Rate constant) Radioactive decay (Half Life and Average Life). Determination Normality, Molarity nd Molality of solutions. Evaluation Electronegativity of atom and Lattice Energy from experimental determination of molecular weight and percentage of element organic compounds using data from experimental metal representation of molecules in terms of elementary structural features such as bond lengths, bond angles.

UNIT IV
Use of Computer programmes. Operation of PC. Data Processing. Running of standard Programs and Packages such as MS WORD, MS EXCEL -special emphasis on calculations and chart formations. X-Y plot. Simpson’s Numerical Integration method. Programmes with data preferably from physical chemistry laboratory.

UNIT V
Internet. Application of Internet for Chemistry with search engines, various types of files like PDF, JPG, RTF and Bitmap. Scanning, OMR, Web camera.

Book Suggested
Emphasis should be placed on physical principles, reaction chemistry and the technique involved in experiments. Attention should be placed on stoichiometric calculations and statistical analysis of results. In regular classes, each student should perform all the experiments as selected by the Department from the list in the syllabus. In examination, students should be given different experiments or combination of experiments.

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<tr>
<th>Course: M.Sc. II SEM Paper-I: Inorganic Chemistry</th>
<th>(6 hours; 1 day)</th>
<th>Max. Marks</th>
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<tbody>
<tr>
<td>Two or three Experiments based on the following</td>
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<td>(a) Chromatographic separation</td>
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<td>(b) Synthesis</td>
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<td>(c) Spectral analysis of known compounds</td>
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<td>(a) Synthesis</td>
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<td>(b) Quantitative analysis</td>
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<td>(c) Spectral analysis of known compounds</td>
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<td>Two Experiments based on the following:</td>
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<td>(a) Electrochemistry</td>
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<td>(b) Potentiometry</td>
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<td>(c) Polarimetry</td>
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Chromatography Separation of cations and anions by Column Chromatography, Ion exchange.

**Preparations**

Preparation of selected inorganic compounds and their studies by measurements of decomposition temperature, molar conductance, I.R., electronic spectra, and magnetic susceptibility measurements.

1. \([\text{Co(NH}_3\text{)}_6][\text{Co(NO}_2\text{)}_6]\]
2. \(\text{cis}-[\text{Co(trien)} \text{(NO}_2\text{)}_2]\text{Cl.H}_2\text{O}\)
3. \(\text{Hg}[\text{Co(SCN)}_4]\)
4. \([\text{Co(Py)}_2\text{Cl}_2]\)
5. \([\text{Ni(NH}_3\text{)}_6]\text{Cl}_2\)
6. \([\text{Ni(dmg)}_2]\)
7. \([\text{Cu(NH}_3\text{)}_4]\text{SO}_4 \cdot \text{H}_2\text{O}\)

Interpretation of TG and NMR spectra of some known compounds
Organic Synthesis:-

Oxidation reaction:-
- Synthesis of 9,10-anthraquinone by oxidation of anthracene by chromium trioxide.
- Synthesis of 4-nitrobenzaldehyde by oxidation of 4-nitrotoluene by chromium trioxide.

Cassizzaro reaction:-
- Synthesis of benzyl alcohol from benzaldehyde Claisen-Schmidt reaction.
- Synthesis of dibenzylideneacetone (1,5-diphenylpenta-1,4-dien-3-one) from acetone and benzaldehyde

Sandmeyer reaction:-
- Synthesis of 2-chloroanthranilic acid from anthranilic acid Methylation.
- Synthesis of methyl 2-naphthyl ether (2-methoxynaphthalene, nerolin) by methylation of 2-naphthol by dimethyl sulphate.

Quantitative Analysis
- Determination of the percentage or number of hydroxyl groups in an organic compound by acetylation method
- Determination of aromatic amines or phenols using bromate-bromide mixture Determination of number of double bonds in an organic compound
- Determination of percentage or number of ester groups in an organic compound by saponification
- Interpretation of NMR and mass spectra of some known compounds
A list of experiments under different headings is given below. Typical experiments are to be selected from each type-

**Electrochemistry:**

**A. Conductometry**

(i) Determination of the velocity constant, order of the reaction and energy of activation for saponification of ethyl acetate by sodium hydroxide conductometrically.

(ii) Determination of solubility and solubility product of sparingly soluble salts (e.g., PbSO₄, BaSO₄) conductometrically.

(iii) Determination of the strength of strong and weak acids in a given mixture conductometrically.

(iv) Determination of the activity coefficient of zinc ions in the solution of 0.002 M zinc sulphate using Debye-Hackles’ limiting law.

**B. Potentiometry/pH merry**

(i) Determination of strengths of halides in a mixture potentiometrically.

(ii) Determination of the valency of mercurous ions potentiometrically.

(iii) Determination of the strength of strong and weak acids in a given mixture use potentiometer/pH meter.

(iv) Determination of activity and activity coefficient of electrolytes.

**C. Polarimetry**

(i) Determination of rate constant for hydrolysis/inversion of sugar using a polarimeter.

(ii) Enzyme kinetics -inversion of sucrose

**Books Suggested**

5. Systematic Qualitative Organic Analysis, H. Middleton, Adward Arnold.
9. Findley's Practical Physical Chemistry, B. P. Levitt, Longman
11. Practical Physical Chemistry, A. M. James and F. E. Prichard, Longman