Department of Chemistry
University of Pune

M. Sc. (Chemistry) Syllabus under the credit system at Department of Chemistry, University of Pune, Pune 411007 will be effective from the academic year 2009.
The M. Sc. course in Chemistry for two years will consist of 100 credits. Each semester will run for minimum 15 weeks. We will have 70 credits for theory and 30 for practicals and project work.
The proposed structure of first year is the following:

Semester 1:

DC 100: Mathematics for Chemists (2 credits, 24 lectures)
DC 120: Symmetry, Group Theory and Spectroscopy (5 credits, 60 lectures)
DC 130: Stereochemistry and Mechanism (5 credits, 60 lectures)
DC 140: Chemical Kinetics and Thermodynamics (4 credits, 48 lectures)

Semester 2:

DC 220: Coordination & Bioinorganic Chemistry (5 credits, 60 lectures)
DC 230: Synthetic Organic Chemistry and Spectroscopy **(**5 credits, 60 lectures)
DC 240: Chemical Bonding and Spectroscopy (5 credits, 60 lectures)
DC 241: Nuclear and Radiation Chemistry (2 Credits, 24 lectures)
DC 204 : Optional (2 credits, 24 lectures)
A Main Group Chemistry
B Mechanistic Organic Chemistry
C: Modern Separation Methods
(The student can take any one from the optional part A / B/ C .)

Practicals

DC 127: Experiments and computer applications in Inorganic Chemistry
(5 credits, 9 weeks)
DC 137: Experiments and computer applications in Organic Chemistry
(5 credits, 9 weeks)
DC 147: Experiments and computer applications in Physical Chemistry
(5 credits, 9 weeks)

Note: The numbering of courses is as follows:
Symbol: DC= Courses in Department of Chemistry, University of Pune
Digits: Ist = semester 1, 2, 3, 4
IInd = Disciplines: General-O, Bio-1, Inorg-2, Org-3, Phy-4, Anal-5
IIIrd= Nature of the Course. Core/Compulsory: 0,1,2,3

Optional: 4, 5, 6 Practical: 7, 8, 9

Semester I:

DC 100: Mathematics for Chemists (2 Credits 24L)

1. Functions, differential and integral calculus, limits, derivative, physical significance, basic rules of differentiation, maxima and minima, applications in chemistry, exact and inexact differential, Taylor and McLaurin series, curve sketching, partial differentiation, rules of integration, definite and indefinite integrals. (16L)

2. Differential equations
   Separation of variables, homogeneous, exact, linear equations, equations of second order, series solution method. (4L)

3. Probability
   Permutations, combinations and theory of probability (2L)

4. Vectors, matrices and determinants
   Vectors, dot, cross and triple products, introduction to matrix algebra, addition and multiplication of matrices, inverse, adjoint and transpose of matrices, unit and diagonal matrices, (2L)

Text Books

1. The Chemical Maths Book, E. Steiner, Oxford University Press (1996).

Reference Books

1. Mathematical Preparation for Physical Chemistry, F. Daniels, McGraw Hill (1972).

DC120 : Symmetry, Group Theory and Spectroscopy (5 Credits, 60L)

A. Symmetry, Group Theory

1. Definitions and theorems of group theory, subgroups, classes. 4L

2. Molecular symmetry and symmetry groups - symmetry elements and operations. Symmetry planes , reflections , inversion centre, proper / improper axes and rotations, products of symmetry operations , equivalent symmetry elements and atoms, symmetry elements and optical isomerism , symmetry point groups ,classes of symmetry operations , classification of molecular point groups. 10L

3. Representations of groups.
Great orthogonality theorem, character tables, properties of characters of representations. 6L

4. Group theory and quantum mechanics. Wave function as bases for irreducible representation. 2L

5. Symmetry Adapted Linear Combinations - (SALC) - projection operators and their use to construct SALC. 5L

6. Molecular Orbital Theory.
Transformation properties of atomic orbitals, MO's for Sigma bonding in AB_n molecules, tetrahedral AB_4 case, Hybrid orbitals, MO's for pi bonding in AB_n molecules. 7L

7. Crystallographic Symmetry.
Unit cell, screw axis, glide plane on unit cell, crystal lattice, space lattice, stereographic projections. Bravais lattices, Miller indices in cubic and hexagonal structure. Examples on Atomic packing factor (APF) in cubic and HCP crystal, crystallographic cubic volume density, planar density, linear density and percent transformation of polymorphism in crystal. 6L

B. Spectroscopy

1. NMR: Fundamentals–Coupling, decoupling, first order analysis, second order coupling, relaxation processes. Structure determination of Inorganic systems having ^{11}B,^{19}F,^{31}P nuclei, factors influencing chemical shift and coupling constant, Dynamic Processes and NMR. 10L

2. Mössbauer Spectroscopy: Basic principles, instrumentation, spectral parameter and displays, applications.

(a) Mössbauer parameters– Isomer shifts, quadrupole splitting, Magnetic hyperfine interaction, Doppler effect/shift.

(b) Application of Mössbauer Spectroscopy:

(i) Nature of chemical bonds in Prussian blue and Prussiates,

(ii) covalently bonded compounds,

(iii) oxidation states of metal ion in compounds,

(iv) Structural detetrmination,

(v) magnetically ordered compounds (i.e Ferromagnetic & antiferromagnetic compounds). 10L

Books

1. Chemical applications and group theory F.A.Cotton,3rd edition, John Wiley & Sons Asia Pvt. Ltd. (1999).
2. Group theory and its chemical applications: P.K Bhattacharya, 2nd edn, Himalaya pub. India, (1989).
3. Molecular symmetry and group theory -A. Vincent.
4. Symmetry in Chemistry: H.H.Jaffe' and M.Orchin, Dover Publications Inc, New York, (2002).
5. Symmetry in Inorganic Chemistry: J.P Fackler.
6. Principals of Materials Science and Engineering : William F. Smith (1980) (Chapter 3)
7. Physical Methods in Chemistry, R. S. Drago, Saunders, Harcourt Brace Javanovich College Publishers, (1992).
8. NMR spectroscopy in Inorganic Chemistry, J. A. Iggo, Oxford University Press. (2001).
9. Mössbauer Spectroscopy and Transition Metal Chemistry, P. Gütlich,R. Link, A. Trautwien, Springer-Verlag (1978).
10. Mössbauer Spectroscopy, N.N. Greenwood, T.C. Gibb, Chapman and Hall Ltd. (1971).

DC 130 Stereochemistry and Mechanism

(5 Credits, 60L)

Organic Reaction Mechanism

a) Acidity and basicity, Structure reactivity relationship –Introduction to aromaticity in Benzenoid and non – Benzenoid compounds, Inductive, Mesomeric, and steric effect, hyperconjugation, tautomerism and other effects and their influence on the physical and chemical properties of organic compounds 08L

b) Nucleophilic Substitution Reactions at saturated carbon 12L

The S_N2, S_N1, mixed S_N1 and S_N2 and SET mechanism. The neighboring group mechanism, The Neighboring group participation by π & σ bonds, anchimeric assistance, classical and non classical carbocations, phenonium ions, norbornyl system, carbocation rearrangements in neighboring group participation. The S_Ni, ion pair mechanism, Nucleophilic substitution at an allylic, aliphatic trigonal and vinylic carbon. Reactivity effects of structure, attacking nucleophile, leaving group and reaction mechanism, solvent effect, phase transfer catalyst, ambident nucleophile and regioselectivity.

c) Addition and Elimination reactions 14 L

Mechanistic and Stereochemical aspects of addition reactions of C-C multiple bonds including allenes, Ionic and free radical additions of halogens, halogen halides, hydration and related addition reactions, Electrophilic addition involving metal ions, Regio and Chemoselectivity, Orientation and reactivity, conjugate additions.

Mechanistic and Stereochemical aspects of elimination reactions, E2, E1, E1cb, eliminations not involving C-H bonds, reactivity effect of attacking and leaving groups, competition between substitution and elimination , anti and syn eliminations.

Ref. 1 (Page no. 341 – 396)

d. Aromatic electrophilic and nucleophlic substitution Reactions 11L

Arenium ion mechanism, orientation and reactivity, energy profile diagram, calculation of partial rate factor, the ortho/ para ratio ipso attack, orientation in other ring systems such as Naphthalene, Anthracene, Six and five membered heterocycles, Diazonium coupling Vilsmeier reaction, Gattermann – Koch reaction, and other named reactions of

carbocyclic rings. The ArS_N1, Benzyne and SNR1, Mechanisms, Reactivity effect of substrate structure, leaving group and attacking nucleophile.

Ref. 1 (page no. 539 to 594)

Books –

Texts –

1. F. A. Carey and R. J. Sundberg. (Ed. IV), Part A and part B – Adv. Organic Chemistry, Kluwer Academic pub.
2. J. March, (Ed IV), Adv. Organic Chemistry.
3. R.O.C. Norman, Organic Chemistry.
4. R. T. Morrison and R. N. Boyd, Organic Chemistry

References –

1. J. Clayden, N. Greeves. et. al Organic Chemistry , Oxford Univ. Press, 2001.
2. Gould E.S., Mechanism and Structure in Organic Chemistry.
3. H.O. House, Synthetic Organic Chemistry.

2. Stereochemistry of Organic Compounds 15L

a) Symmetry properties of organic compounds, Chirality of organic compounds, chiral centre, configuration of chiral centre, enantiomerism, diastereomerism, pseudoasymmetric carbon

b) Homotopic and heterotopic ligands and faces, Prochirality of center and faces,

c) Stereochemistry of Natural products as exemplified by the study of stereochemistry of menthol

d) Conformational concepts, conformations of acyclic molecules, cyclohexane and mono, di-substituted cyclohexane, Conformational effect on physical properties of the molecules

Books –

1. F. A. Carey and R. J. Sundberg. (Ed. IV), Part A – Adv. Organic Chemistry, Kluwer Academic pub., 2001.
2. E. L. Eliel, Stereochemistry of carbon compounds.

DC 140: **Chemical Kinetics and Thermodynamics (4 Credits: 48L)**

Chemical Kinetics

1. Recapitulation, First, second, third and n^{th} order reactions, rate equations of fractional order, determining order of reactions, complex reactions, parallel and consecutive reactions, reversible reactions (6L)

2. Techniques and methods for fast reactions, flow techniques, relaxation methods, flash photolysis, kinetic isotopic effect. (3L)

3. Reactions in gas phase, collision theory, steady state approximation, unimolecular reactions, potential energy surfaces, transition state theory, chain reactions (7L)

4. Reactions in solutions, influence of pressure, dielectric constants and ionic strength on rates, linear free energy relationships, enzyme catalysis, Michaelis and Menton enzyme kinetics (8L)

Thermodynamics

1. Recapitulation, laws of thermodynamics and thermodynamics functions, Zeroth, first, second and third laws, attaining low temperatures, Maxwell's equations and their applications, heat capacities, equilibrium and spontaneity, free energy change and equilibrium constant, partial molar quantities, chemical potential (10L)

2. Applications

Heat engines, refrigeration, Joule-Thompson effect, liquefaction of gases, flame temperature, explosion temperature and pressure, phase rule applied to one- and two-component systems, calculation of ΔH, ΔS, ΔG & K and effect of temperature & pressure theorem for various types of chemical reactions such as combustion, oxidation etc. electrochemical cells, electrode potentials and cell E.M.F., determination of ΔG from cell E.M.F., ideal & non-ideal solutions. (10L)

3. Introductory Statistical thermodynamics Translational- rotational- vibrational-electronic partition functions (4L)

Books & References:

1. Principles of Chemical Kinetics, J. C. House, C. Brown (1997).
2. Chemical Kinetics, K. J. Laidler, Mc Graw Hill, 3^{rd} Edition (1987).
3. Physical Chemistry, T. Engel and P. J. Reid, Benjamin-Cummings (2005).
4. Physical Chemistry, P. W. Atkins, 8^{th} Edition, Oxford (2006).

Semester II

DC 220 Coordination & Bioinorganic Chemistry (5Credits,60L)

1. Concept & Scope of ligand Fields. 1L
2. Energy levels of transition metal ions, Free ion terms, spin –orbit coupling. 7L
3. Effect of ligand fields on energy levels of transition metal ions, weak cubic ligand field effect on Russell-Saunders terms, strong field effect, correlation diagrams, Tanabe-Sugano diagrams, Spin-pairing energies. ğ
4. Electronic spectra of complexes, band intensities, band energies, band width & shapes, spectra of 1^{st}, 2^{nd} & 3^{rd} row ion and rare earth ion complexes, spectrochemical & Nephelauxetic series, charge transfer & luminescence spectra, calculations of Dq, B, β parameters. ğ
5. Magnetic properties of complexes, paramagnetism,1^{st} & 2^{nd} ordered Zeeman effect, quenching of orbital angular momentum by Ligand fields, Magnetic properties of A,E,T ground terms in complexes, spin free–spin paired equilibria 6L
6. Overviews of Bioinorganic Chemistry. 2L
7. Principles of coordination Chemistry related to Bioinorganic–Proteins, nucleic acids and other metal binding biomolecules. 6L
8. Choice, uptake and assembly of metal containing units in Biology 6L
9. Control and utilization of metal ion concentration in cells. 6L
10. Metal ion folding and cross –linking of biomolecules. 6L
11. Binding of metal ions and complexes to biomolecular active centers 4L

Books:

1. Ligand field theory & its application: B.N.Figgis & M.A.Hitchman Wiely VCH publ. (2000), Chapters 5,6,8,9,11.
2. Principles of Bioinorganic Chemistry: S.J.Lippard & J.M Berg, University science books, Mill Valley, California (1994), Chapters- 1,2,3,5,6,7,8.
3. Inorganic Chemistry: D. F. Shriver & P. W. Atkins, Oxford (1999).
4. Inorganic Electronic spectroscopy: A.B.P.Lever, 2nd ed^{n} Elsevier Science Publishers, New York, (1984).
5. Biological Chemistry of the Elements: R. J. P. Williams & F. R. DeSalvia, Oxford University Press-(1991).
6. Bioinorganic Chemistry: Inorganic elements in the Chemistry of life: An introduction & guide:W.Kaim,B.Schwederski,VCH,(1991).

DC 230 – Synthetic Organic chemistry and Spectroscopy (5 credits)

1. Synthetic Organic chemistry

Oxidation and Reduction 17L

Oxidation Methods (metal, nonmetal based and organic oxidation methods)

CrO_3 (Jones reagent), PDC, PCC, , $KMnO_4$, MnO_2, $NalO_4$, HIO_4 $Pb(OAc)_4$ OsO_4 , RuO_4, mCPBA, Sharpless epoxidation , H_2O_2-NaOH, ozonolysis, Oxidation involving alkoxysulphonium salts, Swern oxidation, SeO_2, Oppenauer oxidation, palladium catalyzed oxidation, Baeyer-Villiger oxidation, Woodward Prevost reaction, Dess-Martin oxidation, IBX oxidation.

Reduction Methods (hydrogenations, complex metal hydride reductions, dissolving metal reductions, other metal & nonmetal based reductions, organic reagents based reduction methods)

Catalytic hydrogenation, Pd/C, PtO_2, H_2/catalyst, (stereochemistry and mechanism),Wilkinson's catalyst, Boranes and Hydroboration reactions , $NaBH_4$, $NaCNBH_3$, $Na(OAc)_3BH$, LAH, DIBAL, superhydrides, R_3SiH, Bu_3SnH, , MVP, NH_2NH_2, MVP reduction, etc. reductions of conjugated systems, Birch reduction, reductive fission of alcohols, Pinacol coupling, McMurry coupling, Deoxygenation of alcohols and carbonyl compounds such as Shapiro reaction

Books –

Texts –

1. W. Carruther, Modern methods of organic synthesis.
2. F. A. Carey and R. J. Sundberg. (Ed. IV), Part B – Adv. Organic Chemistry, Kluwer Academic pub. 2000.

References –

3. H. O. House, Synthetic Organic Chemistry
4. J. March, (Ed IV), Adv. Organic Chemistry (Ed IV),
5. J. Clayden, N. Greeves. et. al Organic Chemistry , Oxford Univ. Press, 2001.
6. E. S. Gould, Mechanism and Structure in Organic Chemistry, 1964.

2. Reactive intermediates & molecular rearrangements 08L

a) Methods of generation, properties and reactions of carbenes and nitrenes.

b) Rearrangements occurring through carbocations, carbanions, carbenes and nitrenes such as Beckmann, Hofmann, Curtius, Schmidt, Wolf, Lossen, Baeyer – Villiger, Sommelet, Favorskii, Pinacol – Pinacolone, Benzil – Benzillic acid, Claisen and Cope Rearrangements, Fries Migration and others

Books –

Texts

1. F. A. Carey and R. J. Sundberg. (Ed. IV), Part B – Adv. Organic Chemistry, Kluwer Academic pub., 2000.
2. E. S. Gould, Mechanism and Structure in Organic Chemistry, 1964.

References –

3. J. March, (Ed IV), Adv. Organic Chemistry
4. J. Clayden, N. Greeves. et. al Organic Chemistry , Oxford Univ. Press, 2001.

3. Ylids & organo-metallic chemistry 15L

a) Phosphorus and Sulfur based ylids – their methods of generation, properties and reactions

b) Methods of generation, properties and reactions of organo magnesium, lithium, cadmium, zinc, copper, boron (Preliminary reaction).

Books –

Texts

1. F. A. Carey and R. J. Sundberg. (Ed. IV), Part B – Adv. Organic Chemistry, Kluwer Academic pub., 2000.
2. J. Clayden, N. Greeves. et. al Organic Chemistry , Oxford Univ. Press, 2001.

References –

1. J. March, (Ed IV), Adv. Organic Chemistry
2. Gould E.S., Mechanism and Structure in Organic Chemistry, 1964.
3. Carruther W., Modern methods of organic synthesis

4. Spectroscopic methods for structure determination organic Compounds 20L

a. U.V.: Electronic transitions, Chromophores, Auxochromes, Bathochromic and hypsochromic shifts, Solvent effects, Wood ward –Fieser Rules for dienes. enones and aromatic compounds Applications of U.V.

b. I.R.: Vibrational Transitions, Important group frequencies, Factors affecting I.R. group frequency, Applications of I.R. Instrumentation and recording of spectra.

c. NMR. : Elementary ideas of NMR Integration, Chemical shifts. Factors affecting, Chemical shifts, Coupling (First order, analysis), Instrumentation & recording of spectra.

d. Problems in U.V., I.R. and N.M.R

Books –

1. R. M. Silversteine and G. C. Bassler, Spectrometric Identification of Organic Compounds, John Wiley Pub., 1991.
2. Pavia Spectroscopy of Organic Compound
3. J. Bellamy, Infrared spectra of Complex molecules.
4. I. Fleming, Organic Spectroscopy.

DC 240: Chemical Bonding and Molecular Spectroscopy (5 Credits, 60 L)

Chemical Bonding

1. Wave particle duality, uncertainty principle, postulates of quantum mechanics, Schrödinger equation, simple systems- free particle, particle in a box, harmonic oscillator (no detailed derivation), hydrogen-like atoms (no derivation), atomic orbitals. (12L)

2. Variational method, many electron atoms, orbital angular momentum, electron spin, wave functions of many electron atoms, Pauli exclusion principle, spin-orbit interaction, fine structure, vector atom model, spectral terms. (6L)

3. Molecular orbital theory of diatomic molecules, Born-Oppenheimer approximation, H_2 molecule, homo- and hetero-nuclear diatomic molecules, correlation diagrams. (6L)

4. Valence bond theory of simple molecules, quantitative treatment of hydrogen molecule and related systems, hybridization, comparison of VB and MO theories, MO diagrams of simple triatomic molecules. (6L)

5. Pi electron systems, Hückel treatment for conjugated hydrocarbons, Electron densities, Bond orders and free valence indices, Illustrations (6L)

Text Books

1. Quantum Chemistry, I. Levine, 5^{th} Edition, Prentice Hall (1999).

Reference Books

1. Valence, C. A. Coulson, ELBS (1974).
2. Introduction to Quantum Mechanics- with Applications to Quantum Chemistry, L. Pauling and E. B. Wilson, Dover Publishers (1999).
3. Orbitals in Chemistry, V. Gil, Cambridge University Press (2000).

Molecular Spectroscopy

1. Recapitulation, the width and intensity of spectral lines. (2L)

2. Rotational spectra: classification of molecules based on the moment of inertia, non-rigid rotor, diatomic molecules, linear triatomic molecules, symmetric top molecules, stark effect. (3L)

3. Infrared spectra: diatomic molecule, selection rule, anharmonicity, Morse potential, combination overtones, and hot bands in polyatomic molecules. (5L)

4. Vibrational rotational spectra, fine structure in diatomic molecules, break down of the Born-Oppenheimer approximation, effect due to nuclear spin, parallel and perpendicular vibrations. (4L)

5. Raman Spectra: classificaton and quantum theory, polarizability ellipsoid, rotational and vibrational raman spectra, elucidating structure from the combined infrared and raman spectra. (4L)

6. Electronic spectra: Born-Oppenheimer approximation, molecular progression, term symbols, Franck-Condon principle, dissociation energies, oscillator strengths, rotational fine structure, fortrat parabola, predissociation, solvent effects, photoelectron spectroscopy XPS, UVPES). (6L)

Text Books

1) Fundamentals of Molecular Spectroscopy, C. M. Banwell and E. McCash, Tata McGraw Hill, 4th Edition (1994).
2) Molecular Spectroscopy, J. Machale, Prentice Hall, NJ, USA (1999).
3) Vibrating Molecules, P. Gans, Chapman and Hall, UK (1971).

DC 241:

Nuclear and Radiation Chemistry (2 Credits, 24L)

1. Radioactivity: recapitulation: types of radioactive decay, decay kinetics, radiation detection and measurement (G. M. and Scintillation Counter)
   Ref. 1 (7L)

2. Elements of radiation chemistry: Interaction of ionising radiation with matter, units for measuring radiation absorption and radiation energy, radiation dosimetry, radiolysis of water and aqueous solutions.
   Ref. 1 (7L)

3. Applications of radioisotopes - General principles of using radioisotopes, applications of radiotracers in
   I. Physicochemical constants - diffusion coefficient, surface area, solubility, stability constant.
   II. Chemical pathways - kinetic studies, inorganic reactions, organic reaction, biosynthesis, polymerization.
   III. Trace analysis of elements and compounds - neutron activation analysis, isotope dilution analysis. (10L)

Text Books

1. Essentials of Nuclear Chemistry, H. J. Arnikar, 4th Edition Wiley Eastern (1987).
2. Chemical Applications of Radioisotopes, H. J. M. Bowen. Buttler and Tanner (1969).
3. Introduction of Nuclear and Radiochemistry, G Friedlander, T. W. Kennedy, E. S. Macias and J. M. Miller, 3rd Edition, John Wiley (1981).

DC 204 Optional – I (2 credits, 24 lectures)

DC-204: Optional
A. Main Group Chemistry (2 Credits, 24L)

1. Hydrogen & its compounds: 2L
Hydrides →classification, e^- deficient, e^- precise & e^- rich hydrides PH_3,SbH_3,AsH_3, Selenides, Tellurides.

2. Alkali & alkaline earth metals 2L
Solutions in non-aqueous Media.
Application of crown ethers in extraction of alkali & alkaline earth metals .

3. Organometallic compounds of Li, Mg, Be, Ca, Na 3L
Synthesis, properties, uses & structures.

4.Boron group 3L
Boron Hydrides, preparation, structure & bonding with reference to LUMO, HOMO, interconversion of lower & higher boranes, Metalloboranes, Carboranes.

5. Carbon group 5L
Allotropes of Carbon, C_{60} and compounds (fullerenes), Intercalation compounds of Graphite, Carbon nanotubes, synthesis, properties, structure-single walled, multiwalled, applications, classification of organometallic compounds. Organometallic compounds of B, Si, Sn, Pb, Ga, As, Sb, Bi. Structures, Synthesis, Reactions

6. Nitrogen group 3L
Nitrogen activation, Boron nitride, Oxidation states of nitrogen & their interconversion PN & SN compounds NO_x & their redox chemistry

7. Oxygen group 2L
Metal selenides & tellurides ,oxyacids & oxoanions of S & N .
Ring, Cage and Cluster compounds of p-block elements. Silicates, including Zeolites

8. Halogen group 3L
Interhalogens, Pseudohalogen, synthesis, properties & applications, structure, oxyacids & oxoanions of Hallogens Bonding.

9. Noble gases 1L
Synthesis, properties, uses, structure & bonding with respect to VSEPR.

Books:

1. Advanced Inorganic Chemistry: F. A. Cotton, G. Wilkinson,C. A.

Murollo, M. Bochmann, 6th edn. (2003).

2. Inorganic Chemistry: D. F. Shriver and P.W. Atkins, 4th edn. Oxford (2003).

B. Mechanistic Organic Chemistry (2 Credits, 24 L)

Hammett Equation, Ester Hydrolysis, Nonkinetic methods of determining reaction Mechanism**.**

Books-

1. Gould E.S., Mechanism and Structure in Organic Chemistry.
2. J.Hine, Physical Organic Chemistry, (1962)
3. Peter Syke, Reaction Mechanism, (VI edition).

DC 204

C. Modern Separation Methods (2 Credits, 24 L)

1. Gas Chromatography:

Gas chromatography theory and Instrumentation, Column types, Solid/Liquid Stationary phases, Column switching techniques, Basic and specialized detectors, elemental detection, chiral separations, Pyrolysis gas chromatography, High temperature techniques, Applications (Clinical, petrochemical etc.) and problems. 6L

2. High Performance Liquid Chromatography:

HPLC theory and instrumentation, Adsorption chromatography, Liquid-Liquid partition chromatography, Microbore and capillary chromatography, Affinity techniques, Size exclusion, Ion pair separations, Chiral and Isotope separations, Applications and problems.

6L

3. Ion-Chromatography 2L

4. Electrophoresis:

Separation by Adsorption-Affinity techniques, Affinity elution from Ion exchangers and other Adsorbents, Pseudo affinity adsorbents, Polyacrylamide gel electrophoresis, Isoelectric focusing, Isotachophoresis, Two-dimensional gel electrophoresis, Crossing immuno- and affinity techniques, Capillary electrophoresis in rotation-stabilized media, Electrophoresis in stabilized salts, blotting techniques, Applications in Nuclei acids, clinical and capillary zone electrophoresis of carbohydrates.
4L

5. Hyphenated Techniques:

Mass spectrometry principle, Instrumentation, Ionization methods-
EI, CI, FAB, arc & spark, photoionization, thermal ionization, FI & FD, Laser induced, Photoelectric ionization, SIMS, Mass analyzers-Magnetic, Double foucusing, Time of flight, Quadrupolar, Ion cyclotron resonance analyzer. Coupled techniques, GC-FTIR, GC-MS (Use of stable isotopes), HPLC-MS, Tandem mass spectroscopy, MS-MS, Principle, Instrumentation & analysis of micronutrients. 6L

Books:

1. Practical Aspects of Gas Chromatography/Mass Spectrometry.
G.M.Message, John Wiley & Sons, New York, (1984).

2. HPLC: Analytical Chemistry by Open Learning
John Wiley & Sons, New York, (1991).

3. Protein Purification: Principles & Practice.
Springer International, 3rd Edition, New Delhi, Students Edn. (1994).

4. Organic Spectroscopy: Principles & Applications, Jag Mohan, Narosa Publishing House, Chapters 5 &7.

5. Instrumental Methods of Chemical analysis, H. H. Willard, L. L. Merrit, Jr. J. A. Dean & F. A. Settle Jr., 6th Edition, (1986)

Practicals

DC 127: Experiments and computer applications in Inorganic Chemistry. (5 Credits, 9 weeks)

1. Ore Analysis: At least two of the following:
   a) Determination of silica and manganese in pyrolusite .
   b) Determination of copper and iron from chalcopyrite.
   c) Determination of iron from hematite
2. Alloy analysis (At least two of the following)
   a) Determination of tin & lead from solder.
   b) Determination of iron & Chromium from mild steel.
   c) Determination of copper and nickel from cupranickel.
3. Inorganic Synthesis and purity determination (any five)
   a) Cis-trans potassium di-aquo di-oxalato chromate (III)
   b) Chloro penta-ammino cobalt (III) chloride
   c) Nitro penta-ammino cobalt (III) chloride
   d) Nitrito penta-ammino cobalt (III) chloride
   e) Bis,2-4 pentanedionato cobalt (II) and cobalt (III)
   f) Potassium tri-oxalato aluminate
   g) Reineckes salt
4. Chelation in Nickel complexes: Preparation of Ni (II) ethylenediamine complexes and studying their absorption spectra.
5. Instrumental methods of analysis.
   a) Colorimetry.
      I. Simultaneous determination of Cr & Mn.
      II. Determination of K_{eq} of M-L Systems such as ,
      Fe (III)- salicylic acid, Fe(III)-Sulphosalicylic acid
      Fe (III)- β -resorcylicic acid by Jobs's & Mole- ratio method.
      III. Determination of iron by solvent extraction technique in a mixture of Fe^{+3} + Al^{+3} & Fe^{+3} + Ni^{+2} using 8- hydroxyquinoline reagent.
   b) Thermochemistry

I. Lattice energy of binary salt by heat of dissolution, systems such as $CaCl_2$, NaCl, KCl.

II. Determination of heat of neutralization of strong base and strong acid.

c) Conductometry

Verification of Debye Hückle theory of ionic conductance for strong electrolytes KCl,$BaCl_2$.K_2SO_4, $K_3[Fe(CN)_6]$

d) New Experiments : (any one)

i. Data analysis, error analysis, least squares method. Plot of Born Maeyer to determine for 1:1 type molecule to determine internuclear separation. Characterization of metal ligand bonding using IR spectroscopy.

ii. Computer Applications : (1) Electronic structure, vibrational characteristics and charge distributions in first row transition metal complexes.

(2) Visualizing frontier MO's.

iii. Analysis of Electronic spectra of transition metal complexes at least for one system (d^n O_h or T_d) and calculation of Crystal Field parameters, inter electronic repulsion parameter and bonding parameter.

- **References:**

1. Textbook of Quantitative Analysis, A. I. Vogel. 4^{th} edn (1992).
2. Inorganic Electronic spectroscopy: A.B.P.Lever, 2nd ed^n Elsevier Science Publishers, New York, (1984).
3. Inorganic Synthesis (Vol. Series)
4. Practical Manual made By Department of Chemistry, University of Pune.

DC-137 Experiments and computer applications in Organic Chemistry (5 Credits 9 weeks)

1. **Techniques:** Crystallization, fractional crystallization, fractional distillation, sublimation, steam distillation, column chromatography and thin layer chromatography.

2. **Derivatives** of functional groups such as acetyl, 2,4-DNP, anilide, amide and aryloxy acetic acid

3. **Single stage preparations (minimum** 4 preparations)

   Preparation of *p*-nitro acetanilide from acetanilide

   Preparation of *p*-bromo acetanilide from acetanilide

   Diels-Alder reaction of sulpholane and maleic anhydride

   Sandmeyer reaction

   Conversion of *t*-butanol to *t*-butylchloride

4. **Two stage preparations** (minimum 4 preparations)

   Benzoin → Benzil → benzilic acid

   ↓

   quinoxaline

   Acetophenone → oxime → acetanilide

   Phthalic anhydride → *o*-benzoyl benzoic acid → anthraquinone

   Acetophenone → benzalacetophenone → epoxide

   Hydroquinone → uinine → 1,2,4-triacetoxybenzene

5. Three stage preparations (minimum one preparation)

   1. *p*-Nitro toluene → *p*-nitro benzene → ethyl-*p*-nitrobenzoate → *p*-aminobenzene

   2. Pthalic acid → pthalic anhydride → phthalimide → anthranilic acid

6. Computer applications: (1) Conformational energetics of simple organic molecules through molecular mechanics force fields.

   (2) Insights for reaction mechanisms of simple SN^1 and SN^2 reactions.

Reference Books. Vogel's Text book of Practical Organic Chemistry,5th Edition

DC 147: Experiments and computer applications in Physical Chemistry (5 Credits 9 weeks)

Conductometry:
1. Hydrolysis of NH_4Cl or H_3COONa or aniline hydrochloride
2. Solubility of a sparingly soluble salt.
3. Hydrolysis of ethyl acetate by NaOH.
4. Determination of ΔG, ΔH, and ΔS of Silver Benzoate by conductometry.

Potentiometry :
1. Stability constant of a complex ion.
2. Solubility of a sparingly soluble salt.
3. Determination of dissociation constant of acetic acid.
4. Estimation of halide in mixture.
5. pH metry.
6. Hydrolysis of aniline hydrochloride.
7. Determination of the acid and base dissociation constants of an amino acid and hence the isoelectric point of the acid.

Polarography :
1. Determination of half wave potential E ½ and unknown concentration of an ion.
2. Amperometric titration of $Pb(NO_3)_2$ with $K_2Cr_2O_7$.

Colorimetry :
1. Analysis of a binary mixture.
2. Copper EDTA photometric titration.
3. Determination of stability constant of ferrisalicylate complex by colorimetric measurements.

Radioactivity :
1. Estimation of Mn in tea leaves by NAA.
2. Half-life of a radioactive nuclide.
3. Determination of E_{max} of beta radiation and absorption coefficients in Al.
4. Counting errors.

Chemical kinetics :
1. Kinetic decomposition of diacetone alcohol by dilatometry.
2. Determination of an order of a reaction.
3. Bronsted primary salt effect.

Non-Instrumental :
1. Freundlich and Langmuir isotherms for adsorption of acetic acid on active charcoal.
2. Statistical treatment of experimental data.
3. Molecular weight by steam distillation.
4. Glycerol radius by viscosity.
5. Partial Molar volume (Pycnometry) determination of the density of a series of solutions and to calculate the molar volumes of the components.

(Computer applications) :

1. Least square fitting of experimental data.

Each candidate should perform a minimum of 20 experiments with at least two experiments from each technique.

Text Books

(1) Findlay's Practical Physical Chemistry, B. P. Levitt and J.A. Kitchener 9th Edition, Longmans, London (1972).
(2) Experiments in Physical Chemistry by J. M. Newcombe, R. J. Denaro, A. R. Rickett, R.M.W Wilson, Pergamon (1962).
(3) Senior Practical Physical Chemistry, 5th Edition, B. D. Khosla, V. S. Garg and A. Khosla, R. Chand (1987).