ST. ALBERT'S COLLEGE (AUTONOMOUS)
ERNAKULAM

CREDIT SEMESTER SYSTEM

SCHEME & SYLLABUS

FOR

POST GRADUATE PROGRAMME IN

CHEMISTRY

2016

FOREWORD

St. Albert's College has become autonomous in this academic year and it is my privilege to introduce the first P.G. Board of Studies in Chemistry. The Board of Studies has decided to adopt the existing syllabus (Branch III- M. Sc Chemistry) along with its prescribed regulations of the Mahatma Gandhi University, Kottayam in its meeting held on 12th May 2016.

I thank the P.G. Board of Studies in Chemistry of the Mahatma Gandhi University, Kottayam for their immense effort in formulating the syllabus. Also, I thank the Chairman Rev. Fr. Antony Arackal and the Principal Dr. M. L. Joseph of our College for their whole hearted support with regard to the adoption of this syllabus

Sri. P. A. Jerald
Chairman, P. G. Board of Studies in Chemistry

2016 ADMISSIONS ONWARDS

BOARD OF STUDIES

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	Code	Course	Hours/ Week	Total Hours	Credit
Semester 1	PCH1CRT01	Organometallics and Nuclear Chemistry	4	72	4
	PCH1CRT02	Structural and Molecular Organic Chemistry	4	72	4
	PCH1CRT03	Quantum Chemistry and Group Theory	4	72	4
	PCH1CRT04	Classical and Statistical Thermodynamics	3	54	3
	PCH1CRP01	Inorganic Chemistry Practical-1	3	54	Evaluation at the end of second semester
	PCH1CRP02	Organic Chemistry Practical-1	3	54	
	PCH1CRP03	Physical Chemistry Practical-1	4	72	
		Total	**25**	**450**	**15**
Semester 2	PCH2CRT01	Coordination Chemistry	4	72	4
	PCH2CRT02	Organic Reaction Mechanisms	4	72	4
	PCH2CRT03	Chemical Bonding and Computational Chemistry	4	72	4
	PCH2CRT04	Molecular Spectroscopy	3	54	3
	PCH2CRP01	Inorganic Chemistry Practical-1	3	54	3
	PCH2CRP02	Organic Chemistry Practical-1	3	54	3
	PCH2CRP03	Physical Chemistry Practical-1	4	72	3
		Total	**25**	**450**	**24**
Semester 3	PCH3CRT01	Structural Inorganic Chemistry	4	72	4
	PCH3CRT02	Organic Syntheses	4	72	4
	PCH3CRT03	Chemical Kinetics, Surface Chemistry and Photochemistry	4	72	4
	PCH3CRT04	Spectroscopic Methods in Chemistry	3	54	3
	PCH3CRP01	Inorganic Chemistry Practical-2	3	54	Evaluation at the end of fourth semester
	PCH3CRP02	Organic Chemistry Practical-2	3	54	
	PCH3CRP03	Physical Chemistry Practical-2	4	72	
		Total	**25**	**450**	**15**
Semester 4	PCH4CRT01	Advanced Inorganic Chemistry	5	90	4
	PCH4CRT02	Advanced Organic Chemistry	5	90	4
	PCH4CRT03	Advanced Physical Chemistry	5	90	4
	PCH4CRP01	Inorganic Chemistry Practical-2	3	54	3
	PCH4CRP02	Organic Chemistry Practical-2	3	54	3
	PCH4CRP03	Physical Chemistry Practical-2	4	72	3
	PCH4CPR01	Project			3
	PCH4CRV01	Viva			2
		Total	**25**	**450**	**26**
Grand Total					**80**

SEMESTER 1

PCH1CRT01 ORGANOMETALLICS AND NUCLEAR CHEMISTRY

Credit: 4 **Contact Lecture Hours: 72**

Unit 1: Organometallic Compounds-Synthesis, Structure and Bonding (18 Hours)

1.1 Organometallic compounds with linear pi donor ligands-olefins, acetylenes, dienes and allyl complexes-synthesis, structure and bonding.

1.2 Complexes with cyclic pi donors-metallocenes and cyclic arene complexes-structure and bonding. Hapto nomenclature. Carbene and carbyne complexes.

1.3 Preparation, properties, structure and bonding of simple mono and binuclear metal carbonyls, metal nitrosyls, metal cyanides and dinitrogen complexes. Polynuclear metal carbonyls with and without bridging. Carbonyl clusters-LNCCS and HNCCS, Isoelectronic and isolobal analogy, Wade-Mingos rules, cluster valence electrons.

Unit 2: Reactions of Organometallic Compounds (9 Hrs)

2.1 Substitution reactions-nucleophilic ligand substitution, nucleophilic and electrophilic attack on coordinated ligands.

2.2 Addition and elimination reactions-1,2 additions to double bonds, carbonylation and decarbonylation, oxidative addition and reductive elimination, insertion (migration) and elimination reactions.

2.3 Rearrangement reactions, redistribution reactions, fluxional isomerism.

Unit 3: Catalysis by Organometallic Compounds (9 Hrs)

3.1 Homogeneous and heterogeneous organometallic catalysis-alkene hydrogenation using Wilkinson catalyst, Tolman catalytic loops.

3.2 Reactions of carbon monoxide and hydrogen-the water gas shift reaction, the Fischer-Tropsch reaction(synthesis of gasoline).

3.3 Hydroformylation of olefins using cobalt or rhodium catalyst.

3.4 Polymerization by organometallic initiators and templates for chain propagation-Ziegler Natta catalysts.

3.5 Carbonylation reactions-Monsanto acetic acid process, carbonylation of butadiene using $Co_2(CO)_8$ catalyst in adipic ester synthesis.

3.6 Olefin methathesis-synthesis gas based reactions, photodehydrogenation catalyst ("Platinum Pop"). Palladium catalysed oxidation of ethylene-the Wacker process.

Unit 4: Organometallic Polymers (9 Hrs)

4.1 Polymers with organometallic moieties as pendant groups, polymers with organometallic moieties in the main chain, condensation polymers based on ferrocene and on rigid rod polyynes, polymers prepared by ring opening polymerization, organometallic dendrimers.

Unit 5: Bioinorganic Compounds (18 Hrs)

5.1 Essential and trace elements in biological systems, structure and functions of biological membranes, mechanism of ion transport across membranes, sodium pump, ionophores, valinomycin and crown ether complexes of $Na^+$and K^+, ATP and ADP. Photosynthesis-chlorophyll a, PS I and PS II. Role of calcium in muscle contraction, blood clotting mechanism and biological calcification.

5.2 Oxygen carriers and oxygen transport proteins-haemoglobins, myoglobins and haemocyanin, haemerythrins and haemevanadins, cooperativity in haemoglobin. Iron storage and transport in biological systems-ferritin and transferrin. Redox metalloenzymes-cytochromes, peroxidases and superoxide dismutase and catalases. Nonredox metalloenzymes-CarboxypeptidaseA-structure and functions. Nitrogen Fixation-nitrogenase, vitamin $B_{12}$and the vitamin B_{12}coenzymes.

5.3 Metals in medicine-therapeutic applications of *cis*-platin, radio-isotopes and MRI agents. Toxic effects of metals(Cd, Hg, Cr and Pb).

Unit 6: Nuclear Chemistry (9 Hrs)

6.1 Fission products and fission yield. Neutron capture cross section and critical size. Nuclear fusion reactions and their applications. Chemical effects of nuclear transformations. Positron annihilation and autoradiography. Principles of counting technique such as G.M. counter, proportional, ionization and scintillation counters. Cloud chamber.

6.2 Synthesis of transuranic elements such as Neptunium, Plutonium, Curium, Berkelium, Einsteinium, Mendelevium, Nobelium, Lawrencium and elements with atomic numbers 104 to 109.

6.3 Analytical applications of radioisotopes-radiometric titrations, kinetics of exchange reactions, measurement of physical constants including diffusion constants, Radioanalysis, Neutron Activation Analysis, Prompt Gama Neutron Activation Analysis and Neutron Absorptiometry.

6.4 Applications of radio isotopes in industry, medicine, autoradiography, radiopharmacology, radiation safety precaution, nuclear waste disposal. Radiation chemistry of water and aqueous solutions.

6.5. Measurement of radiation doses. Relevance of radiation chemistry in biology, organic compounds and radiation polymerization.

References

01. J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry Principles of Structure and Reactivity, 4th Edn., Harper Collins College Publishers,1993.

02. F.A. Cotton, G Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th edition, Wiley-Interscience, 1999.

03. K.F. Purcell, J.C. Kotz, Inorganic Chemistry, Holt-Saunders, 1977.

04. P. Powell, Principles of Organometallic Chemistry, 2nd Edn., Chapman and Hall, 1988.

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07. R.W. Hay, Bio Inorganic Chemistry, Ellis Horwood, 1984.

08. H.J. Arnikar, Essentials of Nuclear Chemistry, Wiley Eastern, 1982.

09. S.N. Goshal, Nuclear Physics, S. Chand and Company, 2006.

PCH1CRT02 STRUCTURAL AND MOLECULAR ORGANIC CHEMISTRY

Credit: 4 **Contact Lecture Hours: 72**

Unit 1: Basic Concepts in Organic Chemistry (18 Hrs)

1.1 Review of basic concepts in organic chemistry: bonding, hybridisation, MO picture, inductive effect, electromeric effect, resonance effect, hyperconjugation, steric effect. Bonding weaker than covalent bonds.

1.2 The formalism of curved arrow mechanisms. Practicing of line diagram drawing.

1.3 Concept of aromaticity: delocalization of electrons – Hückel's rule, criteria for aromaticity, examples of neutral and charged aromatic systems – annulenes. NMR as a tool for aromaticity. Anti-and homo-aromatic systems – Fullerenes, Carbon nanotubes and Graphene.

1.4 Mechanism of electrophilic and nucleophilic aromatic substitution reactions with examples. Arenium ion intermediates. SN1, SNAr, SRN1 and Benzyne mechanisms.

Unit 2: Physical Organic Chemistry and Photochemistry (18 Hrs)

2.1 Energy profiles. Kinetic versus thermodynamic control of product formation,Hammond postulate, kinetic isotope effects with examples, Hammet equation, Taft equation. Linear free energy relationships.

2.2 Catalysis by acids and bases and nucleophiles with examples from acetal, cyanhydrin and ester formation and hydrolysis reactions-AAC2, AAC1, AAL1, BAC2and BAL1 mechanisms. Solvent effect. Bulk and specific solvent effects. Introduction to carbon acids – pKa of weak acids, kinetic and thermodynamic acidity. Hard and soft acids and bases – HSAB principle and its applications.

2.3 Photoreactions of carbonyl compounds: Norrish reactions of ketones. Patterno-Buchi reaction. Barton, Di-π-methane and photo Fries rearrangements. Photochemistry of nitro and azo groups.

Unit 3: Stereochemistry of Organic Compounds (18 Hrs)

3.1 Introduction to molecular symmetry and chirality: examples from common objects to molecules. Axis, plane, center, alternating axis of symmetry.

3.2 Center of chirality: molecules with C, N, S based chiral centers, absolute configuration, enantiomers, racemic modifications, R and S nomenclature using Cahn-Ingold-Prelog rules, molecules with a chiral center and Cn, molecules with more than one center of chirality, definition of diastereoisomers, constitutionally symmetrical and unsymmetrical chiral molecules, erythro, threo nomenclature.

3.3 Axial, planar and helical chirality with examples, stereochemistry and absolute configuration of allenes, biphenyls and binaphthyls, ansa and cyclophanic compounds, spiranes, exo-cyclic alkylidenecycloalkanes.

3.4 Topicity and prostereoisomerism, topicity of ligands and faces as well as their nomenclature. NMR distinction of enantiotopic/diastereotopic ligands.

3.5 Stereoisomerism: definition based on symmetry and energy criteria, configuration and conformational stereoisomers.

3.6 Geometrical isomerism: nomenclature, E-Z notation, methods of determination of geometrical isomers. Interconversion of geometrical isomers.

Unit 4: Conformational Analysis (18 Hrs)

4.1 Conformational descriptors - factors affecting conformational stability of molecules. Conformational analysis of acyclic and cyclic systems: substituted ethanes, cyclohexane and its derivatives, decalins, adamantane, congressane, sucrose and lactose. Fused and bridged bicyclic systems. Conformation and reactivity of elimination (dehalogenation, dehydrohalogenation, semipinacolic deamination and pyrolytic elimination-Saytzeff and Hofmann eliminations), substitution and oxidation of 2^0 alcohols. Chemical consequence of conformational equilibrium - Curtin Hammett principle.

References

01. R. Bruckner, Advanced Organic Chemistry: Reaction Mechanisms, Academic Press, 2002.

02. F.A. Carey, R.A. Sundberg, Advanced Organic Chemistry, Part A: Structure and Mechanisms, 5thEdn., Springer, 2007.

03. J. Clayden, N. Greeves, S. Warren, P. Wothers, Organic Chemistry, Oxford University Press, 2004.

04. T.H. Lowry, K.S. Richardson, Mechanism and Theory in Organic Chemistry, 2nd Edn., Harper & Row, 1981.

05. N.S. Isaacs, Physical Organic Chemistry, ELBS/Longman, 1987.

06. D. Nasipuri, Stereochemistry of Organic Compounds: Principles and Applications, 3rd Edn., New Age Pub., 2010.

07. D.G. Morris, Stereochemistry, RSC, 2001.

08. E.L. Eliel, S.H. Wilen, Stereochemistry of Organic Compounds, John Wiley & Sons, 1994.

09. N.J. Turro, V. Ramamurthy, J.C. Scaiano, Principles of Molecular Photochemistry: An Introduction, University Science books, 2009.

10. N.J. Turro, Modern Molecular Photochemistry, Benjamin Cummings, 1978.

11. K.K.R. Mukherjee, Fundamentals of Photochemistry, New Age Pub., 1978.

PCH1CRT03 QUANTUM CHEMISTRY AND GROUP THEORY

Credit: 4 **Contact Lecture Hours: 72**

Unit 1: Postulates of Quantum Mechanics (9 Hrs)

1.1 State function or wave function postulate: Born interpretation of the wave function, well behaved functions, orthonormality of wave functions.

1.2 Operator postulate: operator algebra, linear and nonlinear operators, Laplacian operator, commuting and noncommuting operators, Hermitian operators and their properties, eigen functions and eigen values of an operator.

1.3 Eigen value postulate: eigen value equation, eigen functions of commuting operators.

1.4 Expectation value postulate.

1.5 Postulate of time-dependent Schrödinger equation, conservative systems and time-independent Schrödinger equation.

Unit 2: Application to Exactly Solvable Model Problems (18 Hrs)

2.1 Translational motion: free particle in one-dimension, particle in a one-dimensional box with infinite potential walls, particle in a one-dimensional box with finite potential walls-tunneling, particle in a three dimensional box-separation of variables, degeneracy.

2.2 Vibrational motion: one-dimensional harmonic oscillator (complete treatment), Hermite equation(solving by method of power series), Hermite polynomials, recursion relation, wave functions and energies-important features, Harmonic oscillator model and molecular vibrations.

2.3 Rotational motion: co-ordinate systems, cartesian, cylindrical polar and spherical polar coordinates and their relationships. The wave equation in spherical polar coordinates-particle on a ring, the phi equation and its solution, wave functions in the real form. Non-planar rigid rotor (or particle on a sphere)-separation of variables, the phi and the theta equations and their solutions, Legendre and associated Legendre equations, Legendre and associated Legendre polynomials. Spherical harmonics (imaginary and real forms)-polar diagrams of spherical harmonics.

2.4 Quantization of angular momentum, quantum mechanical operators corresponding to angular momenta (L_x, L_y, L_z and L^2)-commutation relations between these operators. Spherical harmonics as eigen functions of angular momentum operators L_z and L^2. Ladder operator method for angular momentum. Space quantization.

Unit 3: Quantum Mechanics of Hydrogen-like Atoms (9 Hrs)

3.1 Potential energy of hydrogen-like systems. The wave equation in spherical polar coordinates: separation of variables-R, theta and phi equations and their solutions, wave functions and energies of hydrogen-like atoms. Orbitals-radial functions, radial distribution functions, angular functions and their plots.

3.2 The postulate of spin by Uhlenbeck and Goudsmith, discovery of spin-Stern Gerlach experiment. Spin orbitals-construction of spin orbitals from orbitals and spin functions.

Unit 4: Symmetry and Groups (9 Hrs)

4.1 Symmetry elements, symmetry operations, point groups and their symbols, sub groups, classes, abelian and cyclic groups, group multiplication tables-classes in group and similarity transformation.

4.2 Symmetry in crystals-32 crystallographic point groups (no derivation), Hermann-Mauguin symbols. Screw axis-pitch and fold of screw axis. Glide planes. Space groups-determination of space group symbols of triclinic and monoclinic systems.

Unit 5: Theory of Molecular Symmetry (18 Hrs)

5.1 Matrices: addition and multiplication of matrices, inverse and orthogonal matrices, character of a matrix, block diagonalisation, matrix representation of symmetry operations, representation of groups by matrices, construction of representation using vectors and atomic orbitals as basis, representation generated by cartesian coordinates positioned on the atoms of a molecule (H_2O and SO_2 as examples).

5.2 Reducible and irreducible representations-construction of irreducible representation by standard reduction formula. Statement of Great Orthogonality Theorem (GOT). Properties of irreducible representations. Construction of irreducible representation using GOT-construction of character tables for C2v, C2h, C3vand C4v.Direct product of representations.

5.3 Molecular dissymmetry and optical activity.

Unit 6: Application of Group Theory in Spectroscopy (9 Hrs)

6.1 Applications in vibrational spectra: transition moment integral, vanishing of integrals, symmetry aspects of molecular vibrations, vibrations of polyatomic molecules-selection rules for vibrational absorption. Determination of the symmetry of normal modes of H_2O, Trans N_2F_2 and NH_3 using Cartesian coordinates and internal coordinates. Complementary character of IR and Raman spectra-determination of the number of active IR and Raman lines.

6.2 Application in electronic spectra: selection rules for electronic transition, electronic transitions due to the carbonyl chromophore in formaldehyde.

References

01. I.N. Levine, Quantum Chemistry, 6th Edn., Pearson Education Inc., 2009.
02. P.W. Atkins, R.S. Friedman, Molecular Quantum Mechanics, 4th Edn., Oxford University Press, 2005.
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14. S. Swarnalakshmi, T. Saroja, R.M. Ezhilarasi, A Simple Approach to Group Theory in Chemistry, Universities Press, 2008.
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16. A. Vincent, Molecular Symmetry and Group Theory: A Programmed Introduction to Chemical Applications, 2nd Edn., Wiley, 2000.
17. A.S. Kunju, G. Krishnan, Group Theory and its Applications in Chemistry, PHI Learning, 2010

PCH1CRT04 CLASSICAL AND STATISTICAL THERMODYNAMICS

Credit: 3 **Contact Lecture Hours: 54**

Unit 1: Classical Thermodynamics (27 Hrs)

1.01 Entropy, dependence of entropy on variables of a system (S,T and V; S,T and P). Thermodynamic equations of state. Irreversible processes - Clausius inequality.

1.02 Free energy, Maxwell relations and significance, temperature dependence of free energy - Gibbs Helmholtz equation, applications of Gibbs Helmholtz equation.

1.03 Partial molar quantities, chemical potential and Gibbs-Duhem equations, determination of partial molar volume and enthalpy.

1.04 Fugacity, relation between fugacity and pressure, determination of fugacity of a real gas, variation of fugacity with temperature and pressure. Activity, dependence of activity on temperature and pressure.

1.05 Thermodynamics of mixing, Gibbs-Duhem-Margules equation, Konowaloff's rule, Henry's law, excess thermodynamic functions-free energy, enthalpy, entropy and volume. Determination of excess enthalpy and volume.

1.06 Chemical affinity and thermodynamic functions, effect of temperature and pressure on chemical equilibrium- vant Hoff reaction isochore and isotherm.

1.07 Third law of thermodynamics, Nernst heat theorem, determination of absolute entropies using third law, entropy changes in chemical reactions.

1.08 Three component systems-graphical representation. Solid-liquid equilibria-ternary solutions with common ions, hydrate formation, compound formation. Liquid-liquid equilibria-one pair of partially miscible liquids, two pairs of partially miscible liquids, three pairs of partially miscible liquids.

1.09 Thermodynamics of irreversible processes with simple examples. Uncompensated heat and its physical significance. Entropy production- rate of entropy production, entropy production in chemical reactions, the phenomenological relations. The principle of microscopic reversibility, the Onsager reciprocal relations. Thermal osmosis. Thermoelectric phenomena.

1.10 Bioenergetics: coupled reactions, ATP and its role in bioenergetics, high energy bond, free energy and entropy change in ATP hydrolysis, thermodynamic aspects of metabolism and respiration, glycolysis, biological redox reactions.

Unit 2: Statistical Thermodynamics (27 Hrs)

2.1 Permutation, probability, apriori and thermodynamic probability, Stirlings approximation, macrostates and microstates, Boltzmann distribution law, partition function and its physical significance, phase space, different ensembles, canonical partition function, distinguishable and indistinguishable molecules, partition function and thermodynamic functions, separation of partition function-

translational, rotational, vibrational and electronic partition functions. Thermal de-Broglie wavelength.

2.2 Calculation of thermodynamic functions and equilibrium constants, statistical interpretation of work and heat, Sakur-Tetrode equation, statistical formulation of third law of thermodynamics, thermodynamic probability and entropy, residual entropy, heat capacity of gases - classical and quantum theories, heat capacity of hydrogen.

2.3 Need for quantum statistics, Bose-Einstein statistics: Bose-Einstein distribution, example of particles, Bose-Einstein condensation, difference between first order and higher order phase transitions, liquid helium, supercooled liquids. Fermi-Dirac distribution: examples of particles, application in electron gas, thermionic emission. Comparison of three statistics.

2.4 Heat capacity of solids- the vibrational properties of solids, Einsteins theory and its limitations, Debye theory and its limitations.

References

01. R.P. Rastogi, R.R. Misra, An introduction to Chemical Thermodynamics, Vikas publishing house, 1996.

02. J. Rajaram, J.C. Kuriakose, Thermodynamics, S Chand and Co., 1999.

03. M.C. Gupta, Statistical Thermodynamics, New age international, 2007.

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13. J. Kestin, J.R. Dorfman, A Course in Statistical Thermodynamics, Academic Press, 1971.

SEMESTER 2

PCH2CRT01 COORDINATION CHEMISTRY

Credits: 4 **Contact Lecture Hours: 72**

Unit 1: Structural Aspects and Bonding (18 Hrs)

1.1 Classification of complexes based on coordination numbers and possible geometries. Sigma and pi bonding ligands such as CO, NO, CN^-, R_3P, and Ar_3P. Stability of complexes, thermodynamic aspects of complex formation-Irving William order of stability, chelate effect.

1.2 Splitting of *d* orbitals in octahedral, tetrahedral, square planar, square pyramidal and triagonal bipyramidal fields, LFSE, *Dq* values, Jahn Teller (JT) effect, theoretical failure of crystal field theory, evidence of covalency in the metal-ligand bond, nephelauxetic effect, ligand field theory, molecular orbital theory-M.O energy level diagrams for octahedral and tetrahedral complexes without and with π-bonding, experimental evidences for pi-bonding.

Unit 2: Spectral and Magnetic Properties of Metal Complexes (18 Hrs)

2.1 Electronic Spectra of complexes-Term symbols of d^n system, Racah parameters, splitting of terms in weak and strong octahedral and tetrahedral fields. Correlation diagrams for d^n and d^{10-n} ions in octahedral and tetrahedral fields (qualitative approach), *d-d* transition, selection rules for electronic transition-effect of spin orbit coupling and vibronic coupling.

2.2 Interpretation of electronic spectra of complexes-Orgel diagrams, demerits of Orgel diagrams, Tanabe-Sugano diagrams, calculation of *Dq*, *B* and β (Nephelauxetic ratio) values, spectra of complexes with lower symmetries, charge transfer spectra, luminescence spectra.

2.3 Magnetic properties of complexes-paramagnetic and diamagnetic complexes, molar susceptibility, Gouy method for the determination of magnetic moment of complexes, spin only magnetic moment. Temperature dependence of magnetism-Curie's law, Curie-Weiss law. Temperature Independent Paramagnetism (TIP), Spin state cross over, Antiferromagnetism-inter and intra molecular interaction. Anomalous magnetic moments.

2.4 Elucidating the structure of metal complexes (cobalt and nickel complexes) using electronic spectra, IR spectra and magnetic moments.

Unit 3: Kinetics and Mechanism of Reactions in Metal Complexes (18 Hrs)

3.1 Thermodynamic and kinetic stability, kinetics and mechanism of nucleophilic substitution reactions in square planar complexes, *trans* effect-theory and applications.

3.2 Kinetics and mechanism of octahedral substitution- water exchange, dissociative and associative mechanisms, base hydrolysis, racemization reactions, solvolytic reactions (acidic and basic).

3.3 Electron transfer reactions: outer sphere mechanism-Marcus theory, inner sphere mechanism-Taube mechanism.

Unit 4: Stereochemistry of Coordination Compounds (9 Hrs)

4.1 Geometrical and optical isomerism in octahedral complexes, resolution of optically active complexes, determination of absolute configuration of complexes by ORD and circular dichroism, stereoselectivity and conformation of chelate rings, asymmetric synthesis catalyzed by coordination compounds,

4.2 Linkage isomerism-electronic and steric factors affecting linkage isomerism. Symbiosis-hard and soft ligands, Prussian blue and related structures, Macrocycles-crown ethers.

Unit 5: Coordination Chemistry of Lanthanides and Actinides (9 Hrs)

5.1 General characteristics of lanthanides-Electronic configuration, Term symbols for lanthanide ions, Oxidation state, Lanthanide contraction. Factors that mitigate against the formation of lanthanide complexes. Electronic spectra and magnetic properties of lanthanide complexes. Lanthanide complexes as shift reagents.

5.2 General characteristics of actinides-difference between *4f* and *5f* orbitals, comparative account of coordination chemistry of lanthanides and actinides with special reference to electronic spectra and magnetic properties.

References

01. F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry: A Comprehensive Text, 3rdEdn., Interscience,1972.

02. J.E. Huheey, E.A. Keiter, R.A. Keiter, Inorganic Chemistry Principles of Structure and Reactivity, 4thEdn., Pearson Education India, 2006.

03. K.F. Purcell, J.C. Kotz, Inorganic Chemistry, Holt-Saunders, 1977.

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05. B.E. Douglas, D.H. McDaniel, J.J. Alexander, Concepts and Models of Inorganic Chemistry, 3rd Edn., Wiley-India, 2007.

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11. T. Moeller, International Review of Science: Inorganic Chemistry, Series I, Vol VII, Butterworth, 1972.

PCH2CRT02 ORGANIC REACTION MECHANISM

Credit: 4 **Contact Lecture Hours: 72**

Unit 1: Review of Organic Reaction Mechanisms (9 Hrs)

1.1 Review of organic reaction mechanisms with special reference to nucleophilic and electrophilic substitution at aliphatic carbon (SN_1, SN_2, SN_i, SE_1, SE_2, addition-elimination and elimination-addition sequences), elimination (E_1 and E_2) and addition reactions (regioselectivity: Markovnikov's addition-carbocation mechanism, anti-Markovnikov's addition-radical mechanism). Elimination vs substitution.

1.2 A comprehensive study on the effect of substrate, reagent, leaving group, solvent and neighbouring group on nucleophilic substitution(SN_2 and SN_1) and elimination (E_1 and E_2) reactions.

Unit 2: Chemistry of Carbanions (9 Hrs)

2.1 Formation, structure and stability of carbanions. Reactions of carbanions: C-X bond (X = C, O, N) formations through the intermediary of carbanions. Chemistry of enolates and enamines. Kinetic and Thermodynamic enolates- lithium and boron enolates in aldol and Michael reactions, alkylation and acylation of enolates.

2.2 Nucleophilic additions to carbonyls groups. Named reactions under carbanion chemistry-mechanism of Claisen, Dieckmann, Knoevenagel, Stobbe, Darzen and acyloin condensations, Shapiro reaction and Julia elimination. Favorski rearrangement.

2.3 Ylids: chemistry of phosphorous and sulphur ylids – Wittig and related reactions, Peterson olefination.

Unit 3: Chemistry of Carbocations (9 Hrs)

3.1 Formation, structure and stability of carbocations. Classical and non-classical carbocations.

3.2 C-X bond (X = C, O, N) formations through the intermediary of carbocations. Molecular rearrangements including Wagner-Meerwein, Pinacol-pinacolone, semi-pinacol, Dienone-phenol and Benzilic acid rearrangements, Noyori annulation, Prins reaction.

3.3 C-C bond formation involving carbocations: oxymercuration, halolactonisation.

Unit 4: Carbenes, Carbenoids, Nitrenes and Arynes (9 Hrs)

4.1 Structure of carbenes (singlet and triplet), generation of carbenes, addition and insertion reactions.

4.2 Rearrangement reactions of carbenes such as Wolff rearrangement, generation and reactions of ylids by carbenoid decomposition.

4.3 Structure, generation and reactions of nitrene and related electron deficient nitrene intermediates.

4.4 Hoffmann, Curtius, Lossen, Schmidt and Beckmann rearrangement reactions.

4.5 Arynes: generation, structure, stability and reactions. Orientation effect-amination of haloarenes.

Unit 5: Radical Reactions (9 Hrs)

5.1 Generation of radical intermediates and its (a) addition to alkenes, alkynes (inter and intramolecular) for C-C bond formation - Baldwin's rules (b) fragmentation and rearrangements-Hydroperoxide: formation, rearrangement and reactions. Autooxidation.

5.2 Named reactions involving radical intermediates: Barton deoxygenation and decarboxylation, McMurry coupling.

Unit 6: Chemistry of Carbonyl Compounds (9 Hrs)

6.1 Reactions of carbonyl compounds: oxidation, reduction (Clemmensen and Wolf-Kishner), addition (addition of cyanide, ammonia, alcohol) reactions, Cannizzaro reaction, addition of Grignard reagent. Structure and reactions of α, β- unsaturated carbonyl compounds involving electrophilic and nucleophilic addition-Michael addition, Mannich reaction, Robinson annulation.

Unit 7: Concerted reactions (18 Hrs)

7.1 Classification: electrocyclic, sigmatropic, cycloaddition, chelotropic and ene reactions. Woodward Hoffmann rules-frontier orbital and orbital symmetry correlation approaches-PMO method.

7.2 Highlighting pericyclic reactions in organic synthesis such as Claisen, Cope, Wittig, Mislow-Evans and Sommelet-Hauser rearrangements. Diels-Alder and Ene reactions (with stereochemical aspects), dipolar cycloaddition(introductory).

7.3 Unimolecular pyrolytic elimnination reactions: cheletropic elimination, decomposition of cyclic azo compounds, β-eliminations involving cyclic transition states such as N-oxides, acetates and xanthates.

7.4 Problems based on the above topics.

References

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02. F.A. Carey, R.A. Sundberg, Advanced Organic Chemistry, Part B: Reactions and Synthesis, 5th Edn., Springer, 2007.

03. W. Carruthers, I. Coldham, Modern Methods of Organic Synthesis, Cambridge University Press, 2005.

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08. J. Clayden, N. Greeves, S. Warren, P. Wothers, Organic Chemistry, Oxford University Press, 2004.

PCH2CRT03 CHEMICAL BONDING AND COMPUTATIONAL CHEMISTRY

Credit: 4 **Contact Lecture Hours: 72**

Unit 1: Approximate Methods in Quantum Mechanics (18 Hrs)

1.1 Many-body problem and the need of approximation methods, independent particle model. Variation method, variation theorem with proof, illustration of variation theorem using the trial function x(a-x) for particle in a 1D-box and using the trial function e^{-ar} for the hydrogen atom, variation treatment for the ground state of helium atom.

1.2 Perturbation method, time-independent perturbation method (non-degenerate case only), first order correction to energy and wave function, illustration by application to particle in a 1D-box with slanted bottom, perturbation treatment of the ground state of the helium atom. Qualitative idea of Hellmann-Feynman theorem.

1.3 Hartree Self-Consistent Field method. Spin orbitals for many electron atoms-symmetric and antisymmetric wave functions. Pauli's exclusion principle. Slater determinants. Qualitative treatment of Hartree-Fock Self-Consistent Field (HFSCF) method. Roothan's concept of basis functions, Slater type orbitals (STO) and Gaussian type orbitals (GTO), sketches of STO and GTO.

Unit 2: Chemical Bonding (18 Hrs)

2.1 Schrödinger equation for molecules. Born-Oppenheimer approximation. Valence Bond (VB) theory, VB theory of H_2molecule, singlet and triplet state functions (spin orbitals) of H_2.

2.2 Molecular Orbital (MO) theory, MO theory of H_2^+ion, MO theory of H_2 molecule, MO treatment of homonuclear diatomic molecules Li_2, Be_2, N_2, O_2 and $F_2$and hetero nuclear diatomic molecules LiH, CO, NO and HF. Bond order. Correlation diagrams, non-crossing rule. Spectroscopic term symbols for diatomic molecules. Comparison of MO and VB theories.

2.3 Hybridization, quantum mechanical treatment of sp, sp^2 and sp^3 hybridisation. Semiempirical MO treatment of planar conjugated molecules, Hückel Molecular Orbital (HMO) theory of ethene, allyl systems, butadiene and benzene. Calculation of charge distributions, bond orders and free valency.

Unit 3: Applications of Group Theory in Chemical Bonding (9 Hrs)

3.1 Applications in chemical bonding, construction of hybrid orbitals with BF_3, CH_4, PCl_5 as examples. Transformation properties of atomic orbitals. Symmetry adapted linear combinations (SALC) of C2v, C2h, C3, C3vand D3hpoint groups. MO diagram for water and ammonia.

Unit 4: Computational Chemistry (18 Hrs)

(The units 4 and 5 have been designed to expose the students to the field of computational chemistry, which has emerged as a powerful tool in chemistry capable of supplementing and complementing experimental research. The quantities which can be calculated using computational methods, how to prepare the input to get these results and the different methods that are widely used to arrive at the results are introduced here. Detailed mathematical derivations are not expected. Though computer simulations form an important part of computational chemistry, they are not covered in this syllabus).

4.1 Introduction: computational chemistry as a tool and its scope.

4.2 Potential energy surface: stationary point, transition state or saddle point, local and global minima.

4.3 Molecular mechanics methods: force fields-bond stretching, angle bending, torsional terms, non-bonded interactions, electrostatic interactions. Mathematical expressions. Parameterisation from experiments or quantum chemistry. Important features of commonly used force fields like MM3, MMFF, AMBER and CHARMM.

4.4 Ab initio methods: A review of Hartee-Fock method. Basis set approximation. Slater and Gaussian functions. Classification of basis sets - minimal, double zeta, triple zeta, split valence, polarization and diffuse basis sets, contracted basis sets, Pople style basis sets and their nomenclature, correlation consistent basis sets.

4.5 Hartree-Fock limit. Electron correlation. Qualitative ideas on post Hartree-Fock methods-variational method, basic principles of Configuration Inetraction(CI). Perturbational methods-basic principles of Møller Plesset Perturbation Theory.

4.6 General introduction to semiempirical methods: basic principles and terminology.

4.7 Introduction to Density Functional Theory (DFT) methods: Hohenberg-Kohn theorems. Kohn-Sham orbitals. Exchange correlation functional. Local density approximation. Generalized gradient approximation. Hybrid functionals (only the basic principles and terms need to be introduced).

4.8 Model Chemistry-notation, effect on calculation time (cost).

4.9 Comparison of molecular mechanics, ab initio, semiempirical and DFT methods.

Unit 5: Computational Chemistry Calculations (9 Hrs)

5.1 Molecular geometry input-cartesian coordinates and internal coordinates, Z-matrix. Z-matrix of: single atom, diatomic molecule, non-linear triatomic molecule, linear triatomic molecule, polyatomic molecules like ammonia, methane, ethane and butane. General format of GAMESS / Firefly input file. GAMESS / Firefly key word for: basis set selection, method selection, charge, multiplicity, single point energy calculation, geometry optimization, constrained optimization and frequency calculation.

5.2 Identifying a successful GAMESS/ Firefly calculation-locating local minima and saddle points, characterizing transition states, calculation of ionization energies, Koopmans' theorem, electron affinities and atomic charges.

5.3 Identifying HOMO and LUMO-visualization of molecular orbitals and normal modes of vibrations using suitable graphics packages.

References

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09. F. Jensen, Introduction to computational chemistry, 2ndEdn., John Wiley & Sons, 2007.

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13. A. Hinchliffe, Molecular Modelling for Beginners, 2ndEdn., John Wiley & Sons, 2008.

14. C.J. Cramer, Essentials of Computational Chemistry: Theories and Models, 2nd Edn., John Wiley & Sons, 2004.

15. D.C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems, John Wiley & Sons, 2001.

Softwares

Molecular Mechanics:

1. **Arguslab** availablefrom www.arguslab.com/
2. **Tinker** available from www.dasher.wustl.edu/ffe/

Ab initio, semiempirical and dft:

1. **Firefly / PC GAMESS** available from http://classic.chem.msu.su/gran/gamess/
2. **WINGAMESS** available from http://www.msg.ameslab.gov/gamess/

Graphical User Interface (GUI):

1. **Gabedit** available from http://gabedit.sourceforge.net/
2. **wxMacMolPlt** available from http://www.scl.ameslab.gov/MacMolPlt/
3. **Avogadro** from http://avogadro.openmolecules.net/wiki/Get_Avogadro

PCH2CRT04 MOLECULAR SPECTROSCOPY

Credit: 3 **Contact Lecture Hours: 54**

Unit 1: Foundations of Spectroscopic Techniques (27 Hrs)

1.1 Origin of spectra: origin of different spectra and the regions of the electromagnetic spectrum, intensity of absorption, influencing factors, signal to noise ratio, natural line width, contributing factors, Doppler broadening, Lamb dip spectrum, Born Oppenheimer approximation, energy dissipation from excited states (radiative and non radiative processes), relaxation time.

1.2 Microwave spectroscopy: principal moments of inertia and classification (linear, symmetric tops, spherical tops and asymmetric tops), selection rules, intensity of rotational lines, relative population of energy levels, derivation of J_{max} , effect of isotopic substitution, calculation of intermolecular distance, spectrum of non rigid rotors, rotational spectra of polyatomic molecules, linear and symmetric top molecules, Stark effect and its application, nuclear spin and electron spin interaction, chemical analysis by microwave spectroscopy.

1.3 Infrared spectroscopy: Morse potential energy diagram, fundamentals, overtones and hot bands, determination of force constants, diatomic vibrating rotator, break down of the Born-Oppenheimer approximation, effect of nuclear spin, vibrational spectra of polyatomic molecules, normal modes of vibrations, combination and difference bands, Fermi resonance, finger print region and group vibrations, effect of H-bonding on group frequency, disadvantages of dispersive IR, introduction to FT spectroscopy, FTIR.

1.4 Raman spectroscopy: scattering of light, polarizability and classical theory of Raman spectrum, rotational and vibrational Raman spectrum, complementarities of Raman and IR spectra, mutual exclusion principle, polarized and depolarized Raman lines, resonance Raman scattering and resonance fluorescence.

1.5 Electronic spectroscopy: term symbols of diatomic molecules, electronic spectra of diatomic molecules, selection rules, vibrational coarse structure and rotational fine structure of electronic spectrum, Franck-Condon principle, predissociation, calculation of heat of dissociation, Birge and Sponer method, electronic spectra of polyatomic molecules, spectra of transitions localized in a bond or group, free electron model, different types of lasers-solid state lasers, continuous wave lasers, gas lasers and chemical laser, frequency doubling, applications of lasers, introduction to UV and X-ray photoelectron spectroscopy.

Unit 2: Resonance Spectroscopy (27 Hrs)

2.1 NMR spectroscopy : interaction between nuclear spin and applied magnetic field, nuclear energy levels, population of energy levels, Larmor precession, relaxation methods, chemical shift, representation, examples of AB, AX and AMX types, exchange phenomenon, factors influencing coupling, Karplus relationship.

2.2 FTNMR, second order effects on spectra, spin systems (AB, AB_2), simplification of second order spectra, chemical shift reagents, high field NMR, double irradiation, selective decoupling, double resonance, NOE effect, two dimensional NMR, COSY and HETCOR, ^{13}C NMR, natural abundance, sensitivity, ^{13}C chemical shift and structure correlation, introduction to solid state NMR, magic angle spinning.

2.3 EPR spectroscopy: electron spin in molecules, interaction with magnetic field, g factor, factors affecting g values, determination of g values ($g_{\parallel}$ and $g^{\perp}$), fine structure and hyperfine structure, Kramers' degeneracy, McConnell equation.

2.4 An elementary study of NQR spectroscopy.

2.5 Mossbauer spectroscopy: principle, Doppler effect, recording of spectrum, chemical shift, factors determining chemical shift, application to metal complexes, MB spectra of Fe(II) and Fe(III) cyanides.

References

01. C.N. Banwell, E.M. McCash, Fundamentals of Molecular Spectroscopy, 4thEdn., Tata McGraw Hill, 1994.

02. G. Aruldhas, Molecular Structure and Spectroscopy, Prentice Hall of India, 2001.

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SEMESTERS 1 & 2

PCH1CRP01/PCH2CRP01 INORGANIC CHEMISTRY PRACTICAL-1

Credit: 3 **Contact Lab Hours: 54+54=108**

PART I

Separation and identification of two less familiar metal ions such as Tl, W, Se, Mo, Ce, Th, Ti, Zr, V, U and Li. Anions which need elimination not to be given. Minimum eight mixtures to be given.

PART II

Colorimetric estimation of Fe, Cu, Ni, Mn, Cr, NH_4^+, nitrate and phosphate ions.

PART III

Preparation and characterization complexes using IR, NMR and electronic spectra.

(a) Tris (thiourea)copper(I) complex

(b) Potassium tris (oxalate) aluminate (III).

(c) Hexammine cobalt (III) chloride.

(d) Tetrammine copper (II) sulphate.

(e) Schiff base complexes of various divalent metal ions.

References

01. A.I. Vogel, G. Svehla, Vogel's Qualitative Inorganic Analysis, 7th Edn., Longman,1996.

02. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman, 1966.

03. I.M. Koltoff, E.B. Sandell, Text Book of Quantitative Inorganic analysis, 3rdEdn., McMillian, 1968.

04. V.V. Ramanujam, Inorganic Semimicro Qualitative Analysis, The National Pub.Co., 1974.

PCH1CRP02/PCH2CRP02 ORGANIC CHEMISTRY PRACTICAL-1

Credit: 3 **Contact Lab Hours: 54+54=108**

PART I

General methods of separation and purification of organic compounds such as:

1. Solvent extraction
2. Soxhlet extraction
3. Fractional crystallization
4. TLC and Paper Chromatography
5. Column Chromatography
6. Membrane Dialysis

PART II

1. Separation of Organic binary mixtures by chemical/solvent separation methods
2. Separation of organic mixtures by TLC
3. Separation/ purification of organic mixtures by column chromatography

PART III

Drawing the structures of organic molecules and reaction schemes by ChemDraw, Symyx Draw and Chemsketch. Draw the structures and generate the IR and NMR spectra of the substrates and products in the following reactions:

1. Cycloaddition of diene and dienophile (Diels-Alder reaction)
2. Oxidation of primary alcohol to aldehyde and then to acid
3. Benzoin condensation
4. Esterification of simple carboxylic acids
5. Aldol condensation

References

01. A.I. Vogel, A Textbook of Practical Organic Chemistry, Longman, 1974.

02. A.I. Vogel, Elementary Practical Organic Chemistry, Longman, 1958.

03. F.G. Mann, B.C Saunders, Practical Organic Chemistry, 4th Edn., Pearson Education India, 2009.

04. R. Adams, J.R. Johnson, J.F. Wilcox, Laboratory Experiments in Organic Chemistry, Macmillan, 1979.

PCH1CRP03/PCH2CRP03 PHYSICAL CHEMISTRY PRACTICAL-1

Credit: 3 **Contact Lab Hours: 72+72 =144**

(One question each from both parts A and B will be asked for the examination)

Part A

I. Adsorption

1. Verification of Freundlich and Langmuir adsorption isotherm: charcoal-acetic acid or charcoal-oxalic acid system.
2. Determination of the concentration of the given acid using the isotherms.

II. Phase diagrams

1. Construction of phase diagrams of simple eutectics.
2. Construction of phase diagram of compounds with congruent melting point: diphenyl amine-benzophenone system.
3. Effect of (KCl/succinic acid) on miscibility temperature.
4. Construction of phase diagrams of three component systems with one pair of partially miscible liquids.

III. Distribution law

1. Distribution coefficient of iodine between an organic solvent and water.
2. Distribution coefficient of benzoic acid between benzene and water.
3. Determination of the equilibrium constant of the reaction $KI + I_2 \leftrightarrow KI_3$

IV. Surface tension

1. Determination of the surface tension of a liquid by
   a) Capillary rise method
   b) Drop number method
   c) Drop weight method
2. Determination of parachor values.
3. Determination of the composition of two liquids by surface tension measurements

Part B

Computational chemistry experiments

V. Experiments illustrating the capabilities of modern open source/free computational chemistry packages in computing single point energy, geometry optimization, vibrational frequencies, population analysis, conformational studies, IR and Raman spectra, transition state search, molecular orbitals, dipole moments etc.

Geometry input using Z-matrix for simple systems, obtaining Cartesian coordinates from structure drawing programs like Chemsketch.

References

01. J.B. Yadav, Advanced Practical Physical Chemistry, Goel Publishing House, 2001.

02. G.W. Garland, J.W. Nibler, D.P. Shoemaker, Experiments in Physical Chemistry, 8thEdn., McGraw Hill, 2009.

03. J.H. Jensen, Molecular Modeling Basics, CRC Press, 2010.

04. GAMESS documentation available from: http://www.msg.ameslab.gov/gamess/documentation.html

SEMESTER 3

PCH3CRT01 STRUCTURAL INORGANIC CHEMISTRY

Credits: 4 **Contact Lecture Hours: 72**

Unit 1: Solid State Chemistry (18 Hrs)

1.1 Structure of solids: Imperfections in solids-point defects, line defects and plane defects. Structure of compounds of AX (Zinc blende, Wurtzite), AX_2 (Rutile, fluorite, antifluorite), A_mX_2 (Nickel Arsenide), ABX_3 (Perosvskite, Ilmenite). Spinels. Inverse spinel structures.

1.2 Solid state reactions-diffusion coefficient, mechanisms, vacancy diffusion, thermal decomposition of solid-Type I reactions, Type II reactions.

1.3 Phase transition in solids: classification of phase transitions-first and second order phase transitions, Martensitic transformations, order-disorder transitions and spinodal decomposition. Kinetics of phase transitions, sintering. Growing single crystals-crystal growth from solution, growth from melt and vapor deposition technique.

Unit 2: Electrical, Magnetic and Optical Properties (18 Hrs)

2.1 Kronig-Penney model, Free electron theory, Zone theory and MO theory of solids. Energy bands-conductors and non-conductors, intrinsic and extrinsic semiconductors. Electrons and holes. Mobility of charge carriers. Hall Effect. Pyroelectricity, piezo electricity and ferro electricity. Conductivity of pure metals.

2.2 Magnetic properties of transition metal oxides, garnets, spinels, ilmenites and perovskites, magnetoplumbites.

2.3 Optical properties-photoconductivity, photovoltaic effects, luminescence. Applications of optical properties

2.4 Super conductivity-Type I and Type II superconductors, Frolich diagram, Cooper pairs, theory of low temperature super conductors, junctions using superconductors, BCS theory of superconductivity (derivation not required). Super conducting cuprates - YBaCu oxide system, Meisner effect, conventional superconductors, organic superconductors, fullerenes, carbon nanotubes, high temperature superconductors.

Unit 3: Inorganic Chains and Rings (18 Hrs)

3.1 Chains - catenation, heterocatenation. Silicate minerals. Structure of silicates-common silicates, silicates containing discrete anions, silicates containing infinite chains, silicates containing sheets, framework silicates. Silicones. Zeolites-synthesis, structure and applications. Isopoly acids of vanadium, molybdenum and

tungsten. Heteropoly acids of Mo and W. Condensed phosphates-preparation, structure and applications. Phosphate esters in biological systems. Polythiazil-one dimensional conductors.

3.2 Rings-topological approach to boron hydrides, Styx numbers. Structure and bonding in borazines, ring silicates and silicones, phosphorous-nitrogen compounds, phosphazenes. Heterocyclic inorganic ring systems-structure and bonding in phosphorous-sulphur and sulphur-nitrogen compounds. Homocyclic inorganic ring systems-structure and bonding in sulphur, selenium and phosphorous compounds.

Unit 4: Inorganic Cages and Metal Clusters (9 Hrs)

4.1 Cages: synthesis, structure and bonding of cage like structures of phosphorous. Boron cage compounds-Wade Mingos Lauher rules, MNO rule, boranes, carboranes, metallacarboranes.

4.2 Metal clusters**:** dinuclear compounds of Re, Cu and Cr, metal-metal multiple bonding in $(Re_2X_8)^{2-}$, trinuclear clusters, tetranuclear clusters, hexanuclear clusters. Polyatomic zintl anion and cations. Infinite metal chains.

Unit 5: Chemistry of Materials (9 Hrs)

5.1 Glasses, ceramics, composites, nanomaterials-preparative procedures. Sol-gel synthesis, glassy state-glass formers and glass modifiers, ceramic structures-mechanical properties, clay products, refractories- characterizations, properties and applications.

References

01. L.V. Azaroff, Introduction to Solids, Mc Graw Hill, 1984.

02. A.R. West, Solid State Chemistry and its Applications, Wiley-India, 2007.

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12. C.V. Agarwal, Chemistry of Engineering Materials, 9thEdn., B.S. Pub., 2006.

PCH3CRT02 ORGANIC SYNTHESES

Credit : 4 **Contact Lecture Hours: 72**

Unit 1: Organic Synthesis via Oxidation and Reduction (18 Hrs)

1.1 Survey of organic reagents and reactions in organic chemistry with special reference to oxidation and reduction. Metal based and non-metal based oxidations of (a) alcohols to carbonyls (Chromium, Manganese, aluminium and DMSO based reagents) (b) alkenes to epoxides (peroxides/per acids based)-Sharpless asymmetric epoxidation, Jacobsen epoxidation, Shi epoxidation (c) alkenes to diols (Manganese and Osmium based)-Prevost reaction and Woodward modification (d) alkenes to carbonyls with bond cleavage (Manganese and lead based, ozonolysis) (e) alkenes to alcohols/carbonyls without bond cleavage-hydroboration-oxidation, Wacker oxidation, selenium/chromium based allylic oxidation (f) ketones to ester/lactones- Baeyer-Villiger oxidation.

1.2 (a) Catalytic hydrogenation (Heterogeneous: Palladium/Platinum/Rhodium and Nickel. Homogeneous: Wilkinson). (b) Metal based reductions- Birch reduction, pinacol formation, acyloin formation (c) Hydride transfer reagents from Group III and Group IV in reductions - $LiAlH_4$, DIBAL-H, Red-Al, $NaBH_4$ and $NaCNBH_3$, selectrides, trialkylsilanes and trialkylstannane. Meerwein-Pondorff-Verley reduction. Baker's yeast.

Unit 2: Modern Synthetic Methods and Reagents (18 Hrs)

2.1 Baylis-Hillman reaction, Henry reaction, Nef reaction, Kulinkovich reaction, Ritter reaction, Sakurai reaction, Tishchenko reaction, Ugi reaction, Noyori reaction. Brook rearrangement. Tebbe olefination. Metal mediated C-C and C-X coupling reactions: Heck, Stille, Suzuki, Suzuki-Miyaura, Negishi-Sonogashira, Nozaki-Hiyama, Buchwald-Hartwig, Ullmann and Glaser coupling reactions. Wohl-Ziegler reaction. Reagents such as NBS, DDQ and DCC. Gilmann reagent.

2.2 Introduction to multicomponent reactions-Click reactions.

Unit 3: Construction of Carbocyclic and Heterocyclic Ring Systems (9 Hrs)

3.1 Different approaches towards the synthesis of three, four, five and six-membered rings. Photochemical approaches for the synthesis of four membered rings-oxetanes and cyclobutanes, ketene cycloaddition (inter and intra molecular), Pauson-Khand reaction, Volhardt reaction, Bergman cyclization, Nazarov cyclization, Mitsunobu reaction, cation-olefin cyclization and radical-olefin cyclization.

3.2 Inter-conversion of ring systems (contraction and expansion)-Demjenov reaction, Reformatsky reaction. Construction of macrocyclic rings-ring closing metathesis.

3.3 Formation of heterocyclic rings: 5-membered ring heterocyclic compounds with one or more than one hetero atom like N, S or O – pyrrole, furan, thiophene, imidazole, thiazole and oxazole.

Unit 4: Protecting Group Chemistry (9 Hrs)

4.1 Protection and deprotection of hydroxy, carboxyl, carbonyl, and amino groups. Chemo and regio selective protection and deprotection. Illustration of protection and deprotection in synthesis.

4.2 Protection and deprotection in peptide synthesis: common protecting groups used in peptide synthesis, protecting groups used in solution phase and solid phase peptide synthesis (SPPS).

4.3 Functional equivalence and reactivity Umpolung. Role of trimethyl silyl group in organic synthesis.

Unit 5: Reterosynthetic Analysis (9 Hrs)

5.1 Basic principles and terminology of reterosynthesis: synthesis of aromatic compounds, one group and two group C-X disconnections, one group C-C and two group C-C disconnections.

5.2 Amine and alkene synthesis: important strategies of retrosynthesis, functional group transposition, important functional group interconversions. Enantioselective synthesis of Corey lactone, longifolene and luciferin. Umpolung equivalent – Peterson olefination, enolate formation, Ireland method.

Unit 6: Biosynthesis and Biomimetic Synthesis (9 Hrs)

6.1 Basic principles of the biosynthesis of terpenes, steroids, alkaloids, carbohydrates, proteins and nucleic acids. Biosynthesis of cholesterol, α- terpineol, morphine, glucose and phenyl alanine. Biogenesis of isoprenoids and alkaloids. Biomimetic synthesis of progesterone and spatreine.

References

01. M.B. Smith, Organic Synthesis, 3rd Edn., Wavefunction Inc., 2010.

02. F.A. Carey, R. I. Sundberg, Advanced Organic Chemistry, Part A and B, 5th Edn., Springer, 2007.

03. S. Warren, P. Wyatt, Organic Synthesis: The Disconnection Approach, 2nd Edn., Wiley, 2008.

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09. L. Kuerti, B. Czako, Strategic Applications of Named Reactions in Organic Synthesis, Elsevier Academic Press, 2005.

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PCH3CRT03 CHEMICAL KINETICS, SURFACE CHEMISTRY AND PHOTOCHEMISTRY

Credit: 4 **Contact Lecture Hours: 72**

Unit 1: Chemical kinetics **(27 Hrs)**

1.1 Theories of reaction rates: Collision theory-steric factor, potential energy surfaces. Conventional transition state theory-Eyring equation. Comparison of the two theories. Thermodynamic formulation of the two theories. Thermodynamic formulation of the reaction rates. Significance of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$and $\Delta S^{\ddagger}$. Volume of activation. Effect of pressure and volume on velocity of gas reactions.

1.2 Lindemann-Hinshelwood mechanism, qualitative idea of RRKM theory, chain reactions: free radical and chain reactions, steady state treatment, kinetics of H_2-Cl_2 and H_2-Br_2 reactions, Rice-Herzfeld mechanism, branching chains H_2-O_2, Semonov-Hinshelwood mechanism of explosive reactions, mechanisms of step-growth, ionic and addition polymerization, kinetics of anionic and cationic polymerization.

1.3 Fast reactions: relaxation, flow and shock methods, flash photolysis, NMR and ESR methods of studying fast reactions.

1.4 Reactions in solution: factors determining reaction rates in solutions, effect of dielectric constant and ionic strength, cage effect, Bronsted-Bjerrum equation, primary and secondary kinetic salt effect, influence of solvent on reaction rates, significance of volume of activation, linear free energy relationship, kinetic isotope effect.

1.5 Acid-base catalysis: specific and general catalysis, Skrabal diagram, Bronsted catalysis law, prototropic and protolytic mechanism with examples, acidity function.

1.6 Enzyme catalysis and its mechanism, Michelis-Menten equation, effect of pH and temperature on enzyme catalysis.

1.7 Mechanisms of heterogeneous catalysis: unimolecular and bimolecular surface reactions, mechanisms of catalyzed reactions like ammonia synthesis, Fischer-Tropsch reactions, hydrogenation of ethylene and catalytic cracking of hydrocarbons and related reactions.

Unit 2: Surface Chemistry **(27 Hrs)**

2.1 Different types of surfaces, thermodynamics of surfaces, Gibbs adsorption equation and its verification, surfactants and micelles, general properties of emulsions, foam structure, aerosols, surface films, surface pressure and surface potential and their measurements and interpretation. Application of low energy electron diffraction and photoelectron spectroscopy, ESCA and Auger electron spectroscopy, scanning probe microscopy, ion scattering, SEM and TEM in the study of surfaces.

2.2 Adsorption: The Langmuir theory, kinetic and statistical derivation, multilayer adsorption-BET theory, Use of Langmuir and BET isotherms for surface area determination. Application of Langmuir adsorption isotherm in surface catalysed reactions, the Eley-Rideal mechanism and the Langmuir-Hinshelwood mechanism, flash desorption.

2.3 Colloids: Zeta potential, electrokinetic phenomena, sedimentation potential and streaming potential, Donnan membrane equilibrium.

2.4 Macromolecules: different averages, methods of molecular mass determination-osmotic, viscosity, sedimentation and light scattering methods.

2.5 Surface Enhanced Raman Scattering, surfaces for SERS studies, chemical enhancement mechanism, surface selection rules, spectrum of 2-aminophenol, applications of SERS.

Unit 3: Photochemistry (18 Hrs)

3.1 Quantum yield, chemical actinometry, excimers and exciplexes, photosensitization, chemiluminescence, bioluminescence, thermoluminescence, pulse radiolysis, hydrated electrons, photostationary state, dimerization of anthracene, ozone layer in the atmosphere.

3.2 Principle of utilization of solar energy, solar cells and their working.

3.3 Quenching of fluorescence and its kinetics, Stern-Volmer equation, concentration quenching, fluorescence and structure, delayed fluorescence, E-type and P-type, effect of temperature on emissions, photochemistry of environment, green house effect, two photon absorption spectroscopy, lasers in photochemical kinetics.

References

01. J. Rajaram, J.C. Kuriakose, Kinetics and Mechanisms of Chemical Transformations, Macmillan India, 2000.

02. K.J. Laidler, Chemical kinetics, 3rd Edn., Harper & Row, 1987.

03. C. Kalidas , Chemical Kinetic Methods: Principles of Fast Reaction Techniques and Applications, New Age International, 2005.

04. J.W. Moore, R.G. Pearson, Kinetics and Mechanisms, John Wiley & Sons, 1981.

05. P.W. Atkins, Physical Chemistry, ELBS, 1994.

06. D.A. McQuarrie, J.D. Simon, Physiacl chemistry: A Molecular Approach, University Science Books,1997

07. A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, 6th Edn., John Wiley & sons, 1997.

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09. G. Aruldhas, Molecular structure and Spectroscopy, PHI Learning, 2007.

PCH3CRT04 SPECTROSCOPIC METHODS IN CHEMISTRY

Credit : 3 **Contact Lecture Hours: 54**

Unit 1: Ultraviolet-Visible and Chirooptical Spectroscopy (9 Hrs)

1.1 Energy levels and selection rules, Woodward-Fieser and Fieser-Kuhn rules.

1.2 Influence of substituent, ring size and strain on spectral characteristics. Solvent effect, Stereochemical effect, non-conjugated interactions. Chirooptical properties-ORD, CD, octant rule, axial haloketone rule, Cotton effect.

1.3 Problems based on the above topics.

Unit 2: Infrared Spectroscopy (9 Hrs)

2.1 Fundamental vibrations, characteristic regions of the spectrum (fingerprint and functional group regions), influence of substituent, ring size, hydrogen bonding, vibrational coupling and field effect on frequency, determination of stereochemistry by IR technique.

2.2 IR spectra of C=C bonds (olefins and arenes) and C=O bonds.

2.3 Problems on spectral interpretation with examples.

Unit 3: Nuclear Magnetic Resonance Spectroscopy (18 Hrs)

3.1 Magnetic nuclei with special reference to ^{1}H and ^{13}C nuclei. Chemical shift and shielding/deshielding, factors affecting chemical shift, relaxation processes, chemical and magnetic non-equivalence, local diamagnetic shielding and magnetic anisotropy.^{1}H and^{13}C NMR scales.

3.2 Spin-spin splitting: AX, AX_2, AX_3, A_2X_3, AB, ABC, AMX type coupling, first order and non-first order spectra, Pascal's triangle, coupling constant, mechanism of coupling, Karplus curve, quadrupole broadening and decoupling, diastereomeric protons, virtual coupling, long range coupling-epi, peri and bay effects. NOE. NOE and cross polarization.

3.3 Simplification non-first order spectra to first order spectra: shift reagents, spin decoupling and double resonance, off resonance decoupling. Chemical shifts and homonuclear/heteronuclear couplings. Basis of heteronuclear decoupling.

3.4 2D NMR and COSY, HOMOCOSY and HETEROCOSY

3.5 Polarization transfer. Selective Population Inversion. DEPT, INEPT and RINEPT. Sensitivity enhancement and spectral editing, MRI.

3.6 Problems on spectral interpretation with examples.

Unit 4: Mass Spectrometry **(9 Hrs)**

4.1 Molecular ion: ion production methods (EI). Soft ionization methods: SIMS, FAB, CA, MALDI, PD, Field Desorption Electrospray Ionization. Fragmentation patterns-nitrogen and ring rules. McLafferty rearrangement and its applications. HRMS, MS-MS, LC-MS, GC-MS.

4.2 Problems on spectral interpretation with examples.

Unit 5: Structural Elucidation Using Spectroscopic Techniques **(9 Hrs)**

5.1 Identification of structures of unknown organic compounds based on the data from UV-Vis, IR, ^{1}H NMR and ^{13}C NMR spectroscopy (HRMS data or Molar mass or molecular formula may be given).

5.2 Interpretation of the given UV-Vis, IR and NMR spectra.

References

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02. A.U. Rahman, M.I. Choudhary, Solving Problems with NMR Specroscopy, Academic Press, 1996.

03. L. D. Field, S. Sternhell, J. R. Kalman, Organic Structures from Spectra, 4th Edn., John Wiley & sons, 2007.

04. C.N. Banwell, E.M. McCash, Fundamentals of Molecular Spectroscopy, 4th Edn., Tata McGraw Hill, 1994.

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07. R.M. Silverstein, G.C. Bassler, T.C. Morril, Spectroscopic Identification of Organic Compounds, 5th Edn., Wiley, 1991.

08. D.H. Williams, I. Fleming, Spectroscopic Methods in Organic Chemistry, 6th Edn., McGraw-Hill, 2008.

09. W. Kemp, Organic Spectroscopy, 2nd Edn., Macmillan, 1987.

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11. E.B. Wilson Jr., J.C. Decius, P.C. Cross, Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra, Dover Pub., 1980.

12. Online spectral databases including RIO-DB.

SEMESTER 4

PCH4CRT01 ADVANCED INORGANIC CHEMISTRY

Credit: 4 **Contact Lecture Hours: 90**

Unit 1: Applications of Group Theory (27Hrs)

1.1 Transformation properties of atomic orbitals, hybridization schemes for sigma and pi bonding with examples**,** Symmetry Adapted Linear Combination of Atomic orbitals in tetrahedral, octahedral and sandwich complexes.

1.2 Ligand field theory-splitting of *d* orbitals in different environments using group theoretical considerations, construction of energy level diagrams, correlation diagrams, method of descending symmetry, formation of symmetry adapted group of ligands, M.O. diagrams, splitting terms for orbitals, energy levels, *d-d* transition-selection rules, vanishing integrals. Raman spectra of complexes with oxo anions as ligands, IR and Raman spectra using character tables in tetrahedral, octahedral and square planar complexes.

Unit 2: Inorganic Spectroscopic Methods. (9 Hrs)

2.1 Infrared and Raman Spectroscopy: structural elucidation of coordination compounds containing the following molecules/ions as ligands-NH_3, H_2O, CO, NO, OH^-, SO_4^{2-}**,** CN^-, SCN^-, $NO_2^-$and X^- (X=halogen).

2.2 Electron Paramagnetic Resonance Spectroscopy: EPR of d^1 and d^9 transition metal ions in cubic and tetragonal ligand fields, evaluation of *g* values and metal hyperfine coupling constants.

2.3 Mössbauer Spectroscopy: applications of Mössbauer spectroscopy in the study of Fe(III) complexes.

Unit 3: Inorganic Photochemistry (9 Hrs)

3.1 Excited states, ligand field states, charge-transfer states and Thexi states, phosphorescence and fluorescence. Photochemical reactions-substitution and redox reactions of Cr(III), Ru(II) and Ru(III) complexes. Applications-synthesis and catalysis, chemical actinometry and photochromism. Metal-metal multiple bonds.

3.2 Metal complex sensitizers-electron relay, semiconductor supported metal oxide systems, water photolysis, nitrogen fixation and CO_2 reduction.

Unit 4: Nanomaterials **(18 Hrs)**

4.1 General introduction to nanomaterials and emergence of nanotechnology, Moore's law, synthesis and properties of fullerenes and carbon nanotubes, synthesis of nanoparticles of gold, silver, rhodium, palladium and platinum, techniques of synthesis-electroplating and electrophoretic deposition, conversion through chemical reactions and lithography. Thin films-chemical vapor deposition and atomic layer deposition techniques,

4.2. Diversity in nanosystems: self assembled monolayers on gold-growth process and phase transitions. Gas phase clusters- formation, detection and analysis. Quantum dots- preparation, characterization and applications. Nanoshells-types of systems, characterization and application.

4.3. Evolving interfaces of nanotechnology-nanobiology, nanosensors, nanomedicines.

Unit 5: Analytical Methods **(18 Hrs)**

5.1 The basis and procedure of sampling-crushing and grinding, gross sampling. Sampling of solids, liquids, gas, particulate solids, metals and alloys. Preparation of a laboratory sample. Moisture in samples-essential and non essential water, occluded water. Determination of water in samples-direct and indirect methods.

5.2 Decompositions and dissolution-reagents for decomposition and dissolution like HCl, H_2SO_4, HNO_3, $HClO_4$ and HF. Microwave decompositions, combustion methods. Uses of fluxes like Na_2CO_3, Na_2O_2, KNO_3, $K_2S_2O_7$, NaOH, B_2O_3 and lithium meta borate.

5.3 Elimination of interferences from samples by precipitation, electrolytic precipitation, separation by extraction and ion exchange separation.

5.4 Analytical procedures involved in the environmental monitoring of water quality-BOD, COD, DO, nitrite and nitrate, iron, fluoride, soil moisture, salinity, soil colloids, cation and anion exchange capacity. Air pollution monitoring: sampling and collection of air pollutants-SO_2, NO_2, NH_3, O_3, and SPM.

Unit 6: Acids and Bases and Non-aqueous Solvents **(9 Hrs)**

6.1 Acid base concept in non aqueous media-HSAB concept, solvent effects, linear free energy relationship-mechanism and methods of determination

6.2 Reactions in non-aqueous solvents. Ammonia - solutions of metals in liquid ammonia. Protonic solvents: anhydrous sulfuric acid, hydrogen halides. Aprotic solvents: non-polar solvents, non-ionizable polar solvents, polar solvents undergoing autoionization, liquid halogens, interhalogen compounds, oxy halides, dinitrogen tetroxide, sulphur dioxide

References

01. F.A. Cotton, Chemical Applications of Group Theory, Wiley-Interscince, 1990.
02. V. Ramakrishnan, M.S. Gopinathan, Group Theory in Chemistry, Vishal Pub., 1985.
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12. T. Pradeep, Nano: the Essentials, Tata Mc Graw Hill, 2007.
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19. K.F. Purcell, J.C. Kotz, Inorganic Chemistry, Holt-Saunders, 1977.

PCH4CRT02 ADVANCED ORGANIC CHEMISTRY

Credit : 4 **Contact Lecture Hours: 90**

Unit 1: Molecular Recognition and Supramolecular Chemistry (18 Hrs)

1.1 Concept of molecular recognition, host-guest complex formation, forces involved in molecular recognition.

1.2 Molecular receptors: cyclodextrins, crown ethers, cryptands, spherands, tweezers, carcerands, cyclophanes, calixarenes, carbon nanocapsules.

1.3 Importance of molecular recognition in biological systems like DNA and protein. Controlled release phenomena.

1.4 Applications of supramolecular complexes in perfumery and medicine. Targeted drug delivery.

Unit 2: Green Alternatives to Organic Synthesis (9 Hrs)

2.1 Principles of Green Chemistry: basic concepts, atom economy, twelve principles of Green Chemistry, principles of green organic synthesis.

2.2 Green alternatives to Organic Synthesis: coenzyme catalysed reactions, thiamine catalyzed benzoin condensation. Green alternatives of molecular rearrangements: pinacol-pinacolone and benzidine rearrangements. Electrophilic aromatic substitution reactions. Oxidation-reduction reactions. Clay catalysed synthesis. Condensation reactions. Green photochemical reactions.

2.3 Green Solvents: ionic liquids, supercritical CO_2, fluorous chemistry.

2.4 General principles of microwave and ultrasound assisted organic synthesis.

Unit 3: Principles of Nanochemistry (9 Hrs)

3.1 Basic principles of Nanochemistry: methods of synthesis of Nanomaterials (basic idea only). Characterisation of Nanomaterials: UV-Visible spectroscopy, SEM, TEM, STM, XRD (principles only).

3.2 Applications of nanomaterials in medicine.

Unit 4: Stereoselective Transformations (9 Hrs)

4.1 Assymmetric induction-chiral auxiliaries and chiral pool.

4.2 Enantioselective catalytic hydrogenation developed by Noyori and Knowels.

4.3 Assymetric aldol condensation pioneered by Evans.

4.4 Assymmetric Diels-Alder reactions.

4.5 Assymmetric epoxidation using Jacobsen's catalyst.

Unit 5: Chemistry of Natural Products and Biomolecules (18 Hrs)

5.1 Basic aspects of structure and classification of carbohydrates, terpenoids, alkaloids, steroids, plant pigments, lipids, vitamins, amino acids, proteins and nucleic acids. Nomenclature of prostaglandins.

5.2 Synthesis of camphor, atropine, papaverine, quinine, cyanin, quercetin, β-carotene, testosterone, PGE_2 and $PGF_{2\alpha}$.

5.3 Methods for primary structure determination of peptides, proteins and nucleic acids. Replication of DNA, flow of genetic information, protein biosynthesis, transcription and translation, Genetic code, regulation of gene expression, DNA sequencing. The Human Genome Project. DNA profiling and the Polymerase Chain Reaction (PCR).

Unit 6: Medicinal Chemistry and Drug Designing (9 Hrs)

6.1 Introduction to Drug design: modeling techniques, receptor proteins, drug-receptor interaction, drug action, drug selectivity, drug metabolism.

6.2 Important chemicals used in drug action, anticoagulants and anticoagulant therapy, anti-anginal drugs, antihypertensive agents, antimalarial drugs, aminoquinolines and alkaloids.

6.3 Antibiotics: Important penicillins, chloramphenicol, tetracyclins and cephalosporins. Drugs for cancer, AIDS and diabetes.

Unit7: Advances in Polymer Chemistry (9 Hrs)

7.1 Conducting polymers, polymers for NLO applications, temperature resistant and flame retardant polymers, polymers for medical applications.

7.2 Dendrimers and dendritic polymers: terminology, classification of dendrimers. Methods of synthesis: convergent and divergent approaches. Dendrimers as nanocapsules. Applications of dendrimers. Hyperbranched polymers: definition, synthesis, applications.

Unit 8: Research Methodology of Chemistry (9 Hrs)

8.1 The search of knowledge, purpose of research, scientific methods, role of theory, characteristics of research.

8.2 Types of research: fundamental, applied, historical and experimental research.

8.3 Chemical literature: primary, secondary and tertiary sources of literature. Classical and comprehensive reference. Literature databases: ScienceDirect, SciFinder. Chemical Abstract.

8.4 Scientific writing: research reports, thesis, journal articles, books. Types of publications: articles, communications, reviews.

8.5 Important scientific and Chemistry Journals. Impact factor.

References

01. J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, 1995.

02. F. Vogtle, Supramolecular Chemistry: An Introduction, Wiley, 1993.

03. W. Carruthers, I.Coldham, Modern Methods of Organic Synthesis, Cambridge University Press, 2004.

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11. T. Pradeep, Nano: the Essentials, Tata McGraw Hill, 2007.

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14. H.F. Ebel, C. Bliefert, W.E. Russey, The Art of Scientific Writing, Wiley-VCH, 2004.

PCH4CRT03 ADVANCED PHYSICAL CHEMISTRY

Credit: 4 **Contact Lecture Hours: 90**

Unit 1: Crystallography (18 Hrs)

1.1 Miller indices, point groups (derivation not expected), translational symmetry, glide planes and screw axes, space groups, simple cases like triclinic and monoclinic systems, interplanar spacing and method of determining lattice types, reciprocal lattices, methods of characterizing crystal structure, rotating crystal method, powder X-ray diffraction method, determination of structure of sodium chloride by powder method, comparison of the structures of NaCl and KCl, brief outline of single crystal X-ray diffraction and crystal growth techniques.

1.2 Structure factor: atomic scattering factor, coordinate expression for structure factor, structure by Fourier synthesis.

1.3 Liquid crystals: mesomorphic state, types, examples and application of liquid crystals. Theories of liquid crystals. Photoconductivity of liquid crystals.

Unit 2: Gaseous State (9 Hrs)

2.1 Derivation of Maxwell's law of distribution of velocities, graphical representation, experimental verification of the law, most probable velocity, derivation of average, RMS and most probable velocities, collision diameter, collision frequency in a single gas and in a mixture of two gases, mean free path, frequency of collision, effusion, the rate of effusion, time dependence of pressure of an effusing gas, the law of corresponding states, transport properties of gases.

Unit 3: Fluorescence Spectroscopy (9 Hrs)

3.1 Instrumentation: light source, monochromator, optical filters, photomultiplier tube, polarizers. Fluorescence sensing, mechanism of sensing, sensing techniques based on collisional quenching, energy transfer and electron transfer, examples of pH sensors. Novel fluorephores: long life time metal-ligand complexes.

Unit 4: Electrochemistry and Electromotive Force (27 Hrs)

4.1 Conductance measurements, technique at high frequency and high voltage, results of conductance measurements, ionic mobilities, influence of pressure and temperature on conductance of ions, Walden equations, abnormal ionic conductance.

4.2 Theories of ions in solution, Drude and Nernst's electrostriction model and Born's model, Debye-Huckel theory, Derivation of Debye-Huckel-Onsager equation, validity of DHO equation for aqueous and non aqueous solutions, Debye-Falkenhagen effect, conductance with high potential gradients, activity and

activity coefficients in electrolytic solutions, ionic strength, Debye-Huckel limiting law and its various forms, qualitative and quantitative tests of Debye-Huckel limiting equation, deviations from the DHLL. Osmotic coefficient, ion association, fraction of association, dissociation constant, triple ion and conductance minima, equilibria in electrolytes, association constant, solubility product principle, solubility in presence of common ion, instability constant, activity coefficient and solubility measurement, determination of activity coefficient from equilibrium constant measurement.

4.3 Electrochemical cells, concentration cells and activity coefficient determination, liquid junction potential, evaluation of thermodynamic properties, the electrode double layer, electrode-electrolyte interface, different models of double layer, theory of multilayer capacity, electrocapillary, Lippmann equation, membrane potential.

4.4 Fuel cells, classification based on working temperature, chemistry of fuel cells, H_2-O_2 fuel cells.

4.5 Polarization - electrolytic polarization, dissolution and decomposition potential, concentration polarization, overvoltage, hydrogen and oxygen overvoltage, theories of overvoltage, Tafel equation and its significance, Butler-Volmer equation for simple electron transfer reactions, transfer coefficient, exchange current density, rate constants.

Unit 5: Diffraction Methods and Atomic Spectroscopic Techniques (9 Hrs)

5.1 Electron diffraction of gases. Wierl's equation. Neutron diffraction method. Comparison of X-ray, electron and neutron diffraction methods.

5.2 Atomic absorption spectroscopy (AAS), principle of AAS, absorption of radiant energy by atoms, classification of atomic spectroscopic methods, measurement of atomic absorption, instrumentation.

5.3 Atomic emission spectroscopy (AES), advantages and disadvantages of AES, origin of spectra, principle and instrumentation.

5.4 Flame emission spectroscopy (FES), flames and flame temperature, spectra of metals in flame, instrumentation.

Unit 6: Electroanalytical Techniques (18 Hrs)

6.1 Voltametry and polarography: Voltametry-cyclic voltametry, ion selective electrodes, anodic stripping voltametry. Polarography-decomposition potential, residual current, migration current, supporting electrolyte, diffusion current, polarogram, half wave potential, limiting current density, polarograph, explanation of polarographic waves.

6.2 The dropping mercury electrode, advantages and limitations of DME, applications of polarography, quantitative analysis- pilot ion procedure, standard

addition methods, qualitative analysis-determination of half wave potential of an ion, advantages of polarography.

6.3 Amperometric titrations: general principles of amperometry, application of amperometry in the qualitative analysis of anions and cations in solution, instrumentation, titration procedure, merits and demerits of amperometric titrations.

6.4 Coulometry: coulometer-Hydrogen Oxygen coulometers, silver coulometer, coulometric analysis with constant current, coulometric tritrations, application of coulometric titrations-neutralization titrations, complex formation titrations, redox titrations. Advantages of coulometry.

References

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03. R.J. Silbey, R.A. Alberty, M.G. Bawendi, Physical Chemistry, 4thEdn., Wiley, 2005.

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SEMESTERS 3 & 4

PCH3CRP01/PCH4CRP01 INORGANIC CHEMISTRY PRACTICAL-2

Credit: 3 **Contact Lab Hours: 54+54 =108**

PART I

Estimation of simple binary mixtures (like Cu-Ni, Cu-Zn, Fe-Cr, Fe-Cu, Fe-Ni, Pb-Ca) of metallic ions in solution by volumetric and gravimetric methods.

PART II

Analysis of one of the alloys of brass, bronze and solder. Analysis of one of the ores from hematite, chromite, dolomite, monazite, illmenite.

References

01. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman, 1966.
02. I.M. Koltoff, E.B. Sandell, Text Book of Quantitative Inorganic Analysis, 3rd Edn., Mc Millian, 1968.
03. G. Pass, H. Sutcliffe, Practical Inorganic Chemistry, Chapman & Hall, 1974.
04. N.H. Furman, Standard Methods of Chemical Analysis: Volume 1, Van Nostrand, 1966.
05. F.J. Welcher, Standard Methods of Chemical Analysis: Vol. 2, R.E. Kreiger Pub., 2006

PCH3CRP02/PCH4CRP02 ORGANIC CHEMISTRY PRACTICAL-2

Credit: 3 **Contact Lab Hours: 54+54=108**

PART I

Preparation Involving Two step Synthetic Sequences by Chemical Methods

PART II

Enzyme/coenzyme catalyzed reactions

PART III

Preparation Involving Multistep Synthetic Sequences by the Green Alternatives of Chemical Methods

PART IV

Microwave assisted Organic Synthesis

PART V

Prediction of FTIR, UV-Visible, $_{1}H$ and $_{13}C$ NMR spectra of the substrates and products at each stage of the products synthesized by the above methods.

References

01. A.I. Vogel, A Textbook of Practical Organic Chemistry, Longman,1974.
02. A.I. Vogel, Elementary Practical Organic Chemistry, Longman, 1958.
03. F.G. Mann and B.C Saunders, Practical Organic Chemistry, 4th Edn., Pearson Education India, 2009.
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PCH3CRP03/PCH4CRP03 PHYSICAL CHEMISTRY PRACTICAL-2

Credit: 3 **Contact Lab Hours: 72+72=144**

I Chemical Kinetics

1. Determination of the rate constant of the hydrolysis of ester by sodium hydroxide.
2. Determination of Arrhenius parameters.
3. Kinetics of reaction between $K_2S_2O_8$ and KI
4. Influence of ionic strength on the rate constant of the reaction between $K_2S_2O_8$ and KI
5. Iodination of acetone in acid medium.

II Polarimetry

1. Kinetics of the inversion of sucrose in presence of HCl.
2. Determination of the concentration of a sugar solution.
3. Determination of the concentration of HCl.
4. Determination of the relative strength of acids.

III Refractometry

1. Identification of pure organic liquids and oils.
2. Determination of molar refractions of pure liquids.
3. Determination of concentration of solutions (KCl-water, glycerol-water).
4. Determination of molar refraction of solids.
5. Study of complex formation between potassium iodide and mercuric iodide system.

IV Viscosity

1. Determination of viscosity of pure liquids.
2. Verification of Kendall's equation.
3. Determination of the composition of binary liquid mixtures (alcohol-water, benzene-nitrobenzene).
4. Determination of the molecular weight of a polymer (polystyrene in toluene).

V Conductivity measurements

1. Verification of Onsager equation.
2. Determination of the degree of ionization of weak electrolytes.

3. Determination of pKa values of organic acids.
4. Determination of solubility of sparingly soluble salts.
5. Titration of a mixture of acids against a strong base.
6. Titration of a dibasic acid against a strong base.

VI Potentiometry

1. Determination of single electrode potentials (Cu and Zn).
2. Application of Henderson equation.
3. Titration of a mixture of acids against a strong base.
4. Determination of end point of a titration using Gran Plot.
5. Determination of the concentration of a mixture of Cl^- and I^- ions.

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