SYLLABUS

MASTER OF SCIENCE

CHEMISTRY

JODHPUR NATIONAL UNIVERSITY

JODHPUR

MASTER OF SCIENCE CHEMISTRY

YEAR I

Paper I	**INORGANIC CHEMISTRY**
Paper II	**ORGANIC CHEMISTRY**
Paper III	**PHYSICAL CHEMISTRY**
Paper IV	**GROUPTHEORY, SPECTROSCOPY AND DIFFRACTION METHODS**

YEAR II

Paper V	**SPECTROSCOPY PHOTOCHEMISTRY AND SOLID STATE CHEMISTRY**
Paper VI	**BIO- INORGANIC, BIO- ORGANIC & BIO- PHYSICAL CHEMISTRY**
Paper VII	**ORAGANIC SYNTHESIS**
Paper VIII	**PHOTOINORGANIC CHEMISTRY**
Paper IX	**INDUSTRY BASED ENVIRONMENTAL STUDIES**

Paper I INORGANIC CHEMISTRY

Unit I

Stereochemistry and Bonding in Main Group Compounds: VSEPRT, Walsh diagram (tri- and penta- atomic molecules), dπ –p π bonds, Bent rule and energetics of hybridization, some simple reactions of covalently bonded molecules. B.Metal-Ligand Equilibria in Solution Stepwise and overall formation constants and their interaction, trends in stepwise constant, factors affecting the stability of metal complexes with reference to the nature of metal ion and ligand. Chelate effect and its thermodynamic origin, determination of binary formation constants by pH- metry and spectrophotometry

Unit II

Reaction Mechanism of Transition Metal Complexes: Energy profile of a reaction, reactivity of metal complex, inert and labile complexes, kinetic application of valence bond and crystal field theories, kinetics of octahedral substitution, acid hydrolysis, factors affecting acid hydrolysis, base hydrolysis, conjugate base mechanism, direct and indirect evidences in favour of conjugate mechanism, anation reactions, reactions without metal ligand bond cleavage. Substitution reactions in square planar complexes, the trans effect, mechanism of the substitution reaction. Redox reaction, electron transfer reactions, mechanism of one electron transfer reactions, outer sphere type reactions, cross reactions and Marcus- Hush theory, inner sphere type reactions.

Unit III

Metal-Ligand bondingLimitation of crystal field theory, molecular orbital theory, octahedral, tetrahedral and square planar complexes, π -bonding and molecular orbital theory.

Unit IV

Electronic Spectra and Magnetic Properties of Transition Metal Complexes: Spectroscopic ground states, correlation. Orgel and Tanabe- Sugano diagrams for transition metal complexes (d1-d9 states), calculations of Dα, β and β parameters, charge transfer spectra, spectroscopic method of assignmetnt of absolute configuration in optically active metal chelates and their stereochemical information, anomalous magnetic moments, magnetic exchange coupling and spin crossover.

Unit V

Metal π- Complexes Metal carboynl, structure and bonding, vibrational spectra of metal carbonyls for bonding and structural elucidation, important reactions of metal carbonyls; preparation, bonding structure and important reaction of transition metal nitrosyl, dinitrogen and dioxgen complexes; tertiary phosphine as ligand. Metal Clusters Higher boranes, carboranes, metalloboranes and metallocarboranes. Metal carbonyl and halide clusters, compounds with metal metal multiple bonds.

Books Suggested

1. Advanced Inorganic Chemistry, F.A. Cotton and Wilkinson, John Wiley.
2. Inorganic Chemistry, J.E. Huhey, Harpes & Row.
3. Chemistry of the Elements. N.N. Greenwood and A. Earnshow, Pergamon.
4. Inorganic Electronic Spectroscopy, A.B.P. Lever, Elsevier.
5. Magnetio chemistry, R.1. Carlin, Springer Verlag.

Paper II ORGANIC CHEMISTRY

Unit I

Nature of Bonding in Organic Molecules: Delocalized chemical bonding conjugation, cross conjugation, resonance hyperconjugation, bonding in fullerenes, tautomerism. Aromaticity in benzenoid and non- benzenoid compounds, alternate and non- alternate hydrocarbons. Hűckel's rule, energy level of π- molecular orbitals, annulenes, anti- aromaticity, ψaromaticity, homo- aromaticity, PMO approach. Bonds weaker than covalent- addition compounds, crown ether complexes and cryptands, inclusion compounds, catenanes and rotaxanes.

Unit II

Reaction Mechanism: Structure and Reactivity: Type of mechanisms, types of reactions, thermodynamic and kinetic requirements, kinetic and thermodynamic control, Hammond's postulate,

Curtin- Hammett principle. Potential energy diagrams, transition states and intermediates, methods of determining mechanisms, isotopes effects Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes and nitrenes. Effect of structure on reactivity, resonance and field effects, steric effect, quantitative treatment. The Hammett equation and linear free energy relationship, subsistent and reaction constants, Taft equation.

Unit III

Aromatic Electrophilic Substitution: The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The ortho/para ratio, ipso attack, orientation in other ring systems. Quantitative treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vilsmeir reactiion, Gatterman- Koch reaction. Aromatic Nucleophilic Substitution: The SN Ar SN 1, benzyne and SRN 1 mechanism, Reactivity effect of substrate structure, leaving group and attacking nucleophile. The Von Richte, Sommelet- Hauser, and Smiles rearrangements.

Unit IV

Addition to Carbon- Carbon Multiple Bonds: Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regio- and chemo selectivity, orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Hydroboration, Michael reaction, Sharpless asymmetric epoxidation.

Unit V

Elimination Reactions The E2, E1 and E1cB mechanisms and their spectrum. Orientation of the double bond. Reactitivty- effects of substrate structures, attacking base, the leaving group and the medium.Mechanism and orientation in pyrolytic elimination.

Book Suggested

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March,John Wiley.
2. Advanced Organic Chemistry, F.A. Carey and R.J. Sunderg, Plenum.
3. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
4. Structure and Mechanism in Organic Chemistry, C.K. Ingold, Comell University Press.
5. Organic Chemistry, R.T. Morrison and R.N. Boyd, Prentice- Hall.

Paper III PHYSICAL CHEMISTRY

Unit I

Introduction to Exact Quantum: Mechanical Results the Schrodinger equation and the postulates of quantum mechanics. Discussion of solutions of the Schrodinger equation to some model systesm viz., particle in a box, the harmonic oscillator, the rigid rotor, the hydrogen atom.

Approximate Methods: The variation theorem, linear variation principle. Perturbation theory (First order and nondegenerate). Applications of variation method and perturbation theory to the Helium atom.

Unit II

Classical Thermodynamics: Brief resume of concepts of laws of thermodynamics, free energy, chemical potential and entropies. Partial molar free energy, partial molar volume and partial molar heat content and their significance. Determinations of these quantities. Concept of fugacity and determination of fugacity.
Statistical Thermodynamics: Concept of distribution, thermodynamic probability and most probable distribution. Ensemble averaging, postulates of ensemble averaging. Canonical, grand canonical and microcanonical ensembles, corresponding distribution laws (using Lagrange's method of undetermined multipliers). Partition functions- translation, rotational, vibrational and electronic partition functions, Calculation of thermodynamic properties in terms of partition. Application of partition functions.

Unit III

Chemical Dynamics: Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius equation and the activated complex theory; ionic reactions, kinetic salt effects, steady state kinetics, kinetic and thermodynamic control of reactions, treatment of unimolecular reactions.

Unit IV

Adsorption: Surface tension, capillary action, pressure difference across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, estimation of surface area (BET equation), Surface films on liquids (Electro- kinetic phenomenon), catalytic activity at surfaces.
Macromolecules
Polymer- definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization, mechanism of polymerization. Molecular mass, number and mass average molecular mass, molecular mass determination (Osmometry, viscometry, diffusion and light scattering methods), sedimentation, chain configuration of macromolecules, calculation of average dimension of various chain structures.

Unit V

Electrochemistry of solutions. Debye- Huckel- Onsager treatment and its extension, ion solvent interactions. Debye- Hückel- Jerum mode. Thermodynamics

of electrified interface equations. Derivation of electro capillarity, Lippmann equations (surface excess), methods of determination. Structure of electrified interfaces. Guoy- Chapman, Stern, Grahmam Devanatham- Mottwatts, Tobin, Bockris, Devanathan models, Overpotentials, exchange current density, derivation of Butler Volmer equation, Tafel plot.
Electocatalysis: Influence of various parameters. Hydrogen electrode. Bioelectrochemistry, threshold membrane phenomena, Nernst- Planck equation, hodges- Huxley equation; core conductor models, electrocardiography.

Paper IV GROUPTHEORY, SPECTROSCOPY AND DIFFRACTION METHODS

Unit I

Symmetry and Group Theory in Chemistry: Symmetry elements and symmetry operation, definition of group, subgroup, relation between orders of a finite group all its subgroup. Conjugacy relation and classes. Point symmetry group. SchÖnflies symbols, representations of groups by matrices (representation for the Cn, Cnv, Cnh, Dnh, etc, group to be worked out explicitly). Character of representation. The great orthogonality theorem (without proof) and its importance. Character tables and their use; spectroscopy.

Unit II

Microwave Spectroscopy: Classification of molecules, rigid rotator model, effect of isotopic substitution on the transition frequencies, intensities, non- rigid rotor. Stark effect, nuclear and electron spin interaction and effect of external field applications.
Infrared- Spectroscopy Review of linear harmonic oscillator, vibrational energies of diatomic molecules, zero point energy, force constant and bond strengths; anharmonicity, Morse potential energy diagram, vibration- rotation spectroscopy, P.Q.R. branches. Breakdown of Oppenheimer approximation; vibrations of polyatomic molecules. Selection rules, normal modes of vibration, group frequencies, overtones, hot bands, factors affecting the band positions and intensities, far IR region, metal ligand vibrations, normal co- ordinate analysis.

Unit III

Atomic Spectroscopy: Energies of atomic orbitals, vector representation of momenta and vector coupling, spectra of hydrogen atom and alkali metal atoms. Molecular Spectroscopy Energy levels, molecular orbitals, vibronic transitions, vibrational progressions and geometry of the excited states, Franck- Condon

principle, electronic spectra of polyatomic molecules. Emission spectra; radiative and non- radiative decay, internal conversion, spectra of transition metal complexes, charge- transfer spectra.

Unit IV

Nuclear Magnetic Resonance Spectroscopy: Nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift and its measurements, factors, influencing chemical shift, deshielding, spin- spin interactions, factors influencing coupling constant "j" Classification (AVB, AMX, ABC, A2B2etc.). spin decoupling; basic ideas about instrument, NMR studies of nuclei other than proton-13C, 19F and 31P. FT NMR, advantages of FT NMR, use of NMR in medical diagnostics.

Unit V

X-ray Diffraction: Bragg condition, Miller indices, Laue Method, Bragg method, Debye Scherrer method of X- ray structural analysis of crystals, index reflections, identification of unit cells from systematic absences in diffraction pattern, Structure of simple lattices and X- ray intensities, structure factor and its relation to intensity and electron density, phase problem. Description of the procedure for an X- ray structure analysis, absolute configuration of molecules.
Electron Diffraction: Scattering intensity vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecules. Low energy electron diffraction and structure of surfaces.

Books suggested

1.Modern Spectroscopy, J.M. Hollas, John Wiley.
2.Applied Electron Spectroscopy for chemical analysis ed. H. Windawi and F.L. Ho, Wiley Interscience.
3.NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry, R.V. Parish, Ellis Harwood.
4.Physical Methods in Chemistry, R.S. Drago, Saunders College.
5.Chemical Applications of Group Theory, F.A. Cotton.

Paper V **SPECTROSCOPY PHOTOCHEMISTRY AND SOLID STATE CHEMISTRY**

Unit I

Vibrational Spectroscopy Symmetry and shapes of AB2, AB3, AB4, AB5and AB6, mode of bonding of ambidentate ligands, ethylenediamine and diketonato complexes, application of resonance Raman spectroscopy particularly for the study of active sites of metalloproteins.

Electron Spin Resonance Spectroscopy Hyperfine coupling, spin polarization for atoms and transition metal ions, spin-orbit coupling and significance of g-tensors, application to transition metal complexes (having one unpaired electron) including biological systems and to inorganic free radicals such as PH4, F2- and (BH3)-

Unit II

Ultraviolet and Visible spectroscopy: Various electronic transitions (185- 800 nm) Beer- Lambert law, effect of solvent on electronic transitions, ultraviolet bands for carbonyl compounds, unsaturated carbonyl compounds, dienes, conjugated polyenes, Fieser Woodward rules for conjugated dienes and carbonyl compounds, ultraviolet spectra of aromatic compounds. Steric effect in biphenyls.

Optical Rotatory Dispersion(ORD) and Circular Dichroism (CD) Definition, deduction of absolute configuration, octan rule for ketones.

Unit III

Carbon- 13 NMR Spectroscopy: General considerations, chemical shift (aliphatic olefinic , alkyne, aromatic, heteroaromatic and carboynl carbon), coupling const ants. Two dimension NMR spectroscopy- COSY, NOESY, DEPT, INEPT, APT and INADEQUATE techniques.

Mass Spectrometry Introduction ion production E1, C1 FD and FAB, factors affecting fragmentation, ion analysis, ion abundance Mass spectral fragmentation of organic compounds, common functional groups, molecular ion peak, metastable peak. McLafferty rearrangement. Nitrogen rule. High resolution mass spectrometry. Example of mass spectral fragmentation of organic compounds with respect to their structure determination.

Unit IV

Photochemical Reactions; Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry.

Determination of Reaction Mechanism: Classification, rate constants and life times of reactive energy state determination of rate constants of reactions. Effect of light intensity on the rate of photochemical reactions. Types of photochemical reactions- photo dissociation, gas- phase photolysis.
Miscellaneous Photochemical Reactions: Photo- Fries reactions of anilides, Photo-Fries rearrangement. Barton reaction. Singlet molecular Oxygen reaction. Photochemical formation of smog. Photodegration of polymers. Photochemistry of vision.

Unit V
Solid State Reactions: General principles, experimental procedure, co-precipitation as a precursory to solid state reactions, kinetics of solid state reactions. Crystal Defects and Non- Stoichiometry Perfect and imperfect crystals, intrinsic and extrinsic defects- point defects, line and plane defects, vacancies Schottky defects and Frenkel defects. Thermodynamics of Schottky and Frenkel defect formation, colour centres, non- stoichiometry and defects.

Book Suggested
1.Physical Methods for Chemistry, R.S. Drago, Saunders Compnay.
2.Structural Methods in Inorganic Chemistry, E.A.V. Ebsworth, D.W.H. Rankin and S. Cradock, ELBS.
3.Infrared and Raman Spectral : Inorganic and Coordination Compounds K. Nakamoto, Wiley.
4.Progress in Inorganic Chemistry vol., 8, ed., F.A. Cotton, vol., 15 ed. S.J. Lippard, Wiley.
5.Transition Metal Chemistry ed. R.L. Carlin vol. 3 Dekker.

Paper VI BIO- INORGANIC, BIO- ORGANIC & BIO- PHYSICAL CHEMISTRY

Unit I
Bioenergetics and ATP Cycle. DNA polymerisation, glucose storage, metal complexes in transmission of energy; chlorophylls, photosystem I and photosystem II in cleavage of water.
Nitrogen fixation Biological nitrogen fixation, and its mechanism, nitrogenase, Chemical nitrogen fixation.

Transport and Storage of Dioxygen Heam proteins and oxygen uptake structure and function of haemoglobin, myoglobin, haemocyanin and hemerythrin, model synthetic complexes of iron, cobalt and copper.

Unit II

Introduction: Basic considerations, Proximity effects and molecular adaptation. Enzymes Introduction and historical perspective, chemical and biological catalysis, remarkable properties of enzymes like catalytic power, specificity and regulation. Nomenclature and classification, extraction and purification. Fischer's lock and key and Koshland's induced fit hypothesis, concept and identification of active site by the use of inhibitors, affinity libelling and enzyme modification by site- directed mutagenesis. Enzyme kinetics, Michaelis- Menten and Lineweaver Burk plots, reversible and irreversible inhibition.

Unit III

Kinds of Reactions Catalysed by Enzymes: Nucleophilic displacement on a phosphorus atom, multiple displacement reactions and the coupling of ATP cleavage to endergonic processes. Transfer of sulphate, addition and elimination reactions, enolic intermediates in isomerisation reactions, β- cleavage and condensation, some isomerization and rearrangement reactions. Enzyme catalyzed carboxylation and decarboxylation. Mechanism of enzyme action of Isomerare and Synthetare.

Unit IV

Biotechnological Applications of Enzymes large- scale production and purification of enzymes, techniques and methods of immobilization of enzymes, effect of immobilization on enzyme activity, application of immobilized enzymes, use of enzymes in food and drink industry- brewing and cheese- making, syrups from corn starch, enzymes as targets for drug design. Clinical uses of enzymes, enzyme therapy, enzymes and recombinant DNA Technology.

Unit V

Statistical Mechanics in Biopolymers: Chain configuration of macromolecules, statistical distribution end to end dimensions, calculation of average dimensions for various chain structures.

Polypeptide and protein structures, introduction to protein folding problem. Thermodynamics of Biopolymers Solutions

Thermodynamics of biopolymer solutions, osmotic pressure, membrane equilibrium, muscular contraction and energy generation in mechanochemical system.

Book Suggested

1.Bioorganic Chemistry : A Chemical Approach to Enzyme Action, Hermann Dugas and C. Penny, Springer Verlag.
2.Understanding Enzymes, Trevor Palmer, Prentice Hall.
3.Enzyme Chemistry : Impact and Applications, Ed. Collin J Suckling, Royal Society of Chemistry.
4.Enzyme Mechanisms Ed. M.I. Page and A Williams, Royal Society of Chemistry.
5.Fundamentals of Enzymology, N.C. Price and L. Stevens. Oxford University Press.

Paper VII ORAGANIC SYNTHESIS

Unit I

Organometallic Reagents: Principle, preparations, properties and applications of the following in organic synthesis with mechanistic details. Group I and II metal organic compoundsLi, Mg, Hg, Cd, Zn and Ce Compounds.Transition metals Cu, Pd, Ni, Fe, Co, Rh, Cr, and Ti compounds. Other elements S, Si, B and I compounds.

Unit II

Oxidation: Introduction, Different oxidative processes. Hydrocarbons- alkenes, aromatic rings, saturated C- H groups (activated and unactivated) alcohols, diols, aldehydes, ketones, ketals and carboxylic acids. Amines, hydrazines, and sulphides. Oxidations with ruthenium tetraoxide, iodobenzene diacetate and thallium.(III) Nitrate.

Unit III

Reduction: Introduction, Different reductive processes. Alkanes, alkenes, alkynes, and aromatic rings. Carbonyl compounds- aldehydes, ketones, acids and their derivatives. Epoxides. Nitro, nitroso, azo and oxime groups. Hydrogenolysis.

Unit IV

Rearrangements: General mechanistic considerations- nature of migration, m igratory aptitude, memory effects. A detailed study of the following rearrangements. Pinacol- pinacolone, Wagner- Meerwein, Demjanov, Benzil-

Benzillic acid. Favorskii, Arndt- Eistert synthesis, Neber, Beckmann, Hoffmann, Curtius, Schmidt, Baeyer-Villiger, Shapiro reaction.

Unit V

Metallocenes, Nonbenzenoid Aromatics and Polycyclic Aromatic Compounds General consideration. Synthesis and reactions of some representative compounds. (Tropone, tropolone, azulene, ferrocene, phenanthrene and fluorine)

Paper VIII PHOTOINORGANIC CHEMISTRY

Unit I

Basic of Photochemistry: Absorption, excitation, photochemical laws, quantum yield, electronically excited states- life times- measurements of the times. Flash photolysis, stopped flow techniques Energy dissipation by radiative and non-radiative processes, absorption spectra, Frank- Condon principle, photochemical stages- primary and secondary processes.

Unit II

Properties of Excited States: Structure, dipole moment, acid- base strengths, reactivity. Photochemical kinetics- calculation of rates of radiative processes. Bimolecular deactivation-quenching.

Unit III

Excited States of Metal Complexes: Excited states of metal complexes: Comparison with organic compounds, electronically excited states of metal complexes, charge transfer spectra, charge transfer excitations.

Unit IV

Ligand Field Photochemistry: Photo substitution, photooxidation and photoreduction, lability and selectivity, zero vibrational levels of ground state and excited state, energy content of excited state, zero- zero spectroscopic energy, development of the equations for redox potentials of the excited states.

Unit V

Redox Reactions by Excited Metal Complexes: Energy transfer under conditions of weak interaction and strong interaction- exciplex formation; condition of the excited states to be useful as redox reactants, excited electron transfer, metal complexes as attractive candidates, (2,2- bipyridine and 1,10- phenanthroline complexes), illustration of reducing and oxidising character of Ruthenium+2

(bipyridal complex, comparsion with Fe (bipy)3; role of spin- orbit coupling- life time of these complexes.
Application of redox processes of electronically excited states for catalytic purposes, transformation of low energy reactants into high energy products, chemical energy into light.

PAPER IX INDUSTRY BASED ENVIRONMENTAL STUDIES

UNIT – 1

Environment – Definition – Scope – Structure and function of eco system's procedures, consumers and decomposers – energy flow in the ecosystem – ecological succession – food chain, food web and ecological pyramids - concepts of sustainable development.

UNIT – 2

Natural resources: Renewable – air, water, soil, land and wildlife resources. Non-renewable – mineral, coal, oil and gas. Environmental problems related to the extraction and use of natural resources.

UNIT – 3

Biodiversity – Definition – values – consumption use, productive social, ethical, aesthetic and option values threats to biodiversity – Hotspots of bio diversity – conservation of bio-diversity: In-situ Ex-situ. Bio-wealth – national and global level.

UNIT – 4

Environmental pollution : Definition – causes, effects and mitigation measures – Air pollution, Water pollution, Soil pollution, Noise pollution, Thermal pollution – Nuclear hazards – solid wastes acid rain – climate change and global warming environmental laws and regulations in India – Earth summit.

UNIT – 5

Population and environment – Population explosion – Environment and human health – HIV / AIDS – Women and child welfare – Resettlement and Rehabilitation of people, role of information technology in environmental health – Environmental awareness.