West Bengal State University
Barasat, North 24-Parganas

Department of Chemistry

TWO YEAR FOUR SEMESTER M. Sc. COURSE IN CHEMISTRY

COURSE STRUCTURE

Semester	I		II		III		IV		Total Marks
Marks	300		300		300		300		1200
Course Type	Theo	Pract	Theo	Pract	Theo	Pract	Theo	Pract	
General (G)	180	120	180	120	180	120	120	90	1110
Elective (E)							60	30*	90
Total Marks	180	120	180	120	180	120	180	120	1200

Elective Courses (E) in Different Branches of Chemistry: Physical/Inorganic/Organic

* Project work

Semester	I	II	III	IV	Total
Credit Points	24	24	23	25	96

SEMESTER I

Marks 300
Total Credit Points (CP) : 24

Paper	Course ID	Marks		Total Marks
	CHEM	Theo	Pract	
I (Inorganic)	217111	60	40	100 (CP = 8)
II (Organic)	217112	60	40	100 (CP = 8)
III (Physical)	217113	60	40	100 (CP = 8)

		180	120	300 (CP = 24)

SEMESTER II

Marks 300
Total Credit Points (CP) : 24

Paper	Course ID	Marks		Total Marks
	CHEM	Theo	Pract	
IV (Inorganic)	217121	60	40	100 (CP = 8)
V (Organic)	217122	60	40	100 (CP = 8)
VI (Physical)	217123	60	40	100 (CP = 8)
		180	120	300 (CP = 24)

SEMESTER III

Marks 300
Total Credit Points (CP) : 23

Paper	Course ID	Marks		Total Marks
	CHEM	Theo	Pract	
VII (Spectroscopy)	217211	60	-	60 (CP =5)
VIII (Inorganic)	217212	40	40	80 (CP = 6)
IX (Organic)	217213	40	40	80 (CP = 6)
X (Physical)	217214	40	40	80 (CP = 6)
		180	120	300 (CP = 23)

SEMESTER IV

Marks 300
Total Credit Points (CP) : 25

Paper	Course ID	Marks		Total Marks
	CHEM	Theo	Pract	
XI (Inorganic)	217221	40	30	70 (CP = 6)
XII (Organic)	217222	40	30	70 (CP = 6)
XIII (Physical)	217223	40	30	70 (CP = 6)

XIV (Elective)	217224	60	30	90 (CP = 7)
		180	120	300 (CP = 25)

Semester I

Inorganic Chemistry (Paper I)

Unit 1: Symmetry and Bonding 12M

Symmetry in nature, symmetry elements and symmetry operations. Symmetry properties of atomic orbitals. Elements of group theory, multiplication tables, point groups and their stereographic projections.
Born-Oppenheimer approximation, LCAO-MO and VB treatments on H_2^+, H_2 ; application to homo- and hetero- nuclear diatomic molecules/ ions of second period elements, electron density, forces and their role in chemical bonding. Hybridization and valences, MO's of H_2O, NH_3, CH_4; Huckel – pi – electron theory and its applications to ethylene, butadiene and benzene, idea of self consistent field. Concept of resonance.

Unit 2 : Co-ordination Chemistry 1 12M

Crystal filed theory, Splitting of d-orbitals in linear, triangular, tetrahedral, square planar, trigonal bipyrimidal, square pyramidal and octahedral fields of similar and dissimilar ligands. Crystal field stabilization energies in weak field and strong field environment, hole formalism, inversion and equivalence reactions, splitting of d^n terms in octahedral and tetrahedral fields, Octahedral site preference energy, Tetrahedral distortion and Jahn Teller effect. Effect of crystal field stabilization on ionic radii, lattice energy, hydration enthalpy and stabilization of complexes (Irving Williams order). Kinetic aspects of crystal field stabilization. Crystal field activation energy. Labile and inert complexes.

Unit 3 : Metal ligand equilibrium in solution 12M

Stability of mononuclear, polynuclear and mixed ligand complexes in solution. Stepwise and overall formation constants and their relations. Trends in stepwise formation constants, factors affecting the stability of metal complexes with reference to the nature of the metal ions and ligands. Statistical and non statistical factors influencing stability of complexes in solution. Stability and reactivity of mixed ligand complexes with reference to chelate effect and thermodynamic considerations. Macrocyclic effect. Spectrophotometric and pH metric determination of binary formation constants.

Unit 4 : Bio-inorganic chemistry 1 12M

Elements of life, Essential and trace elements in biological systems. Basic reactions in the biological systems and roles of metal ions in biological processes. Bioenergetic principle and role of ATP. Metal ions transport and storage proteins: ferritin, transferin, ceruloplasmin. Transport across biological membrane – Na^+-K^+-ATPase, ionophores. Hydrolytic enzymes:

carbonic anhydrase, carboxy peptidase, urease. Metal dependent diseases: Wilson's disease, Alzheimer disease. Metal complexes as drugs: Pt, Rh, Ru and Au drugs. Toxic effects of metal ions, detoxification by chelation therapy.

Unit 5 : Electrochemical analyses **12M**

Voltammetry, cyclic voltammetry, polarography, anodic stripping voltammetry, amperometry, coulometry, electrogavimetry

Practical: **40M**

Synthesis of some metal complexes: tris(ethylenediamine)nickel(II) thiosulphate, tris(acetylacetonato)manganese(II), hexaminecobalt(III) chloride, mercury tetrathiocyanatocobaltate(II), Reineki salt, bis(biguanido) copper(II) sulphate
Complexometric Estimation of Fe(III) and Al(III) mixture, Cu(II) and Zn(II) mixture
Spectrophotometric Determination of i) Fe(II) in mixture, ii) Mn(II) in mixture

Organic Chemistry (Paper II)

Unit 1 : Structure Activity Relationship **12M**

MO treatment of acyclic and cyclic conjugated systems. Huckel's rule and concept of aromaticity, annulenes, heteroannulenes, fullerenes (C_{60}), alternate and non alternate hydrocarbons, anti aromaticity, pseudoaromaticity, homo-aromaticity. Graphical methods: Frost diagram. Huckel treatment – applications to ethylene, allyl, cyclopropenyl, butadiene, cyclobutadiene systems.

Unit 2 : Stereochemistry **12M**

Acyclic systems upto 4 chiral centers. Compounds with asymmetric carbons in branched chains, symmetry, point groups. Correlation of axial dissymmetry and centrodissymmetry. Nomenclature of compounds involving axial and planar chirality. Winstein-Holness equation. Curtin Hammett principle. Conformational analysis of cyclohexane, cyclohexene, decalins and their derivatives. Effect of conformation on reactivity in acyclic compounds and cyclohexanes.

Unit 3 : Pericyclic Reactions **12M**

Classification and stereochemical modes. Thermal and photopericyclic reactions. Selection rules and stereochemistry of electrocyclic reactions. 2-component cycloadditions. Sigmatropic rearrangement. Carbene addition. Rationalization based on Frontier MO approach, correlation diagrams. Dewer-Zimmermann approach. Mobius and Huckel systems. Sommelet, Hauser, Cope and Claisen rearrangements. Ene reactions, Wittig rearrangement.

Unit 4 : Organic Reaction Mechanisms **12M**

Reactive intermediates – Formation and stability of classical and non classical carbonium ions, carbanions, carbenes, nitrenes, radicals and arynes. Nucleophilic. Electrophilic and radical substitution, addition and elimination reactions. Methods of determining reaction mechanisms. Kinetic isotope effect. Hard and soft acids and bases. Mechanisms of some familiar name reactions.

Unit 5 : Natural Products – Terpenoids **12M**

Isoprene rule. Structure elucidation (by chemical and spectroscopical methods). Synthesis, Biogenesis and Biosynthesis of representative examples of acyclic, monocyclic and bicyclic monoterpenes. Structural types, General introduction to sesqui-, di- and tri- terpenoids.

Practical **40M**

Synthesis of some organic compounds involving some Green methodologies.

Physical Chemistry (Paper III)

Unit 1 : Introductory Quantum Mechanics **12M**

Postulates of quantum mechanics and their analysis; Properties of operators and commutators; Hermitian operators and their properties; Time-independent Schrodinger equation; Concept of stationary states, Free particle, Particle in a ring, Barrier problems and tunneling phenomenon ; Equation of motion; Ehrenfest's theorems, Angular momentum operators, Eigenvalues and eigenfunctions

Unit 2 : Symmetry & Group Theory **12M**

Symmetry elements and operations; Classification of molecules; Group, subgroup etc., class, character; point groups, point group symbols; representations; great orthogonality theorem and its consequences; character table. Symmetry adapted linear combination (SALC) with illustrative examples.

Unit 3 : Kinetics **12M**

Collision theory and activated complex theory. Ionic reactions, kinetic salt effects. Steady state kinetics, kinetic and thermodynamic control of reactions. Unimolecular reactions. Chain reactions. Photochemical and oscillatory reactions. Autocatalysis.

Unit 4 : Electrochemistry 1 **12M**

Debye Huckel theory and its extension. Debye Huckel Onsager theory and its extension. Ion solvent interactions. Electrode surfaces, potential and measurements, thermodynamics of such systems. Lippman equation. Gouy Chapman & Stern models.

Unit 5 : Spectroscopy **12M**

Basic idea of transition. Transition probability and transition integral. Selection rule. Fermi golden rule (no derivation), Einstein A, B coefficient, Basic idea of Molecular Spectroscopy and Spin Resonance spectroscopy.

Practical **40M**

One day based physicochemical experiments.

Semester II

Inorganic Chemistry (Paper IV)

Unit 1: Coordination Chemistry 2 — 12 M

Electronic spectra of transition metal complexes : Microstates, determination of ground and excited state terms of d^n ions; Orgel diagrams (qualitative approach), selection rules for spectral transitions, *d-d* spectra of d^n ions and crystal field parameters, nephelauxetic series. Metal-ligand bonding (pictorial MO approach): sigma and pi-bonding in complexes, CT transitions.
Crystal field splitting of free ion terms in weak and strong crystal fields (Oh and Td), energy level diagrams and symmetries and multiplicities of energy levels in strong crystal fields,
Construction of mo diagrams of polyatomic molecules including coordination complexes (Oh and Td), sandwich complexes: (ferrocene, dibenzenechromium).

Unit 2: Organometallics 1 — 12 M

Stereochemical non-rigidity and fluxional behaviour of organometallic compounds with examples
Metal-alkyl, -allyl, -carbene, -carbonyl, -carbide and cyclopentadienyl complexes. Stucture and bonding in η^2-ethylenic and η^3-allylic compounds with typical examples, structure and bonding of $K[Pt(C_2H_4)Cl_3]$, $[(Ph_3P)_2Pt(Ph\text{-}C{\equiv}C\text{-}Ph)]$.
Different types of organometallic reactions.

Unit 3: Solid state — 12 M

Crystal defects and Non- Stoichiometry: Perfect and imperfect crystals, intrinsic and extrinsic defects- point, line and plane defects, vacancies- Schottky and Frenkel defects. Determination of equilibrium concentrations of Schottky and Frenkel defect formation, non-stoichiometric defects, colour centres in ionic crystals, stoichiometric imbalance in crystals**.**
Bonding in metal crystals: Free electron theory of metals, specific heat, Hall effect and its quantum manifestation, Band theory of metals: band gap, electrical and thermal conductivity of metals, p-n junction semi-conductors (intrinsic and extrinsic), insulators, rectifiers and transistors, super conductors.

Unit 4: Chemistry of Elements 1 (Special Features) — 12 M

d-Block Elements

Electronic configuration, oxidation states; aqueous, redox and coordination chemistry, spectral and magnetic properties of compounds in different oxidation states, horizontal and vertical trends in respect of 3d, 4d, and 5d elements with references to Ti-Zr- Hf , V-Nb-Ta, Cr- Mo- W, Mn-Tc-Re and Pt group metals.
Occurrence and isolation in respect of V, Mo, W, Re, Pt.

Unit 5: Bioinorganic Chemistry 2 **12 M**

Transport and storage of dioxygen: Active site structures and bio functions of O_2-uptake proteins: hemoglobin, myoglobin, hemocyanin and hemerythrin; model synthetic dioxygen complexes.
Electron transfer in biology: Active site structures and functions of cytochromes, cytochrome *c*; iron-sulfur proteins (ferredoxines). Respiratory electron transport chain, cytochrome c oxidase. Photosynthesis and chlorophylls, photosystem-I and photosystem-II and their roles in cleavage of water. Model systems. Biological and abiological nitrogen fixing systems, model study.
Vitamins and coenzymes: Vitamin B_6 and vitamin B_{12} coenzymes, model systems

Practical
Semi-Micro Qualitative Inorganic Analysis: **40M**

Semi-Micro Qualitative Inorganic Analysis of complex inorganic mixtures containing not more than six (6) inorganic radicals from the lists ***(a), (b), (c),*** and ***(d),***of which two (2) radicals must be derived from the rare elements ***(d)***, and the mixture should not contain more than one insoluble material from the lists ***(c),*** and ***(d),*** :

(a) Cation Radicals derived from:
Ag, Hg, Pb, Bi, Cd, Cu, As, Sb, Sn, Fe, Al, Cr, Co, Ni, Mn, Zn, Ba, Sr, Ca, Mg, Na, K and NH_4^+ ion.

(b) Anion Radicals:
F^-, Cl^-, Br^-, I^-, BrO_3^- , IO_3^-, SCN^-, S^{2-}, $S_2O_3^{2-}$,SO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, AsO_3^{3-}, AsO_4^{3-}, BO_3^{3-}, H_3BO_3, SiO^{2-},CrO_4^{2-}, $Cr_2O_7^{2-}$, $[Fe(CN)_6^{4-}]$, $[Fe(CN)_6^{3-}]$.

(c) Insoluble Materials:
$PbSO_4$, $BaSO_4$, $SrSO_4$, $PbCrO_4$, CaF_2, SiO_2 and various silicates, SnO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, AgCl, AgBr, AgI.

(d) Cation radicals, anion radicals and insoluble materials derived from the following rare Elements: V, Mo, W, U, Ti, Zr, Ce, Th and Be.

Organic Chemistry (Paper V)

Unit-1: Synthetic Methodology **12M**

Organoboron: Chemistry of organoboron compounds; Carboranes; Hydroborations; Reduction; Reactions of organoboranes; Unsaturated hydrocarbon synthesis; Allyl borane and boron enolates.

Organophosphorus: Chemistry of organophosphorus compounds; Phophorus ylides; Wittig reaction and its modofications; Chiral phosphines; Phosphine-oxides and its applications.

Organosulphur: Chemistry of organophosulphur compounds, Sulphur stabilization of anions and cations, Sulphonium salts, Sulphonium and sulphoxonium ylides, Chiral sulphoxides

Organosilicon: Chemistry of organosilicon compounds; Synthetic uses of silyl ethers; Silyl enol ethers; TMSCl, TMSI, TMSCN, Alkene synthesis, Alkenyl, Vinyl, Aryl, Allyl and Acyl silanes; Brook rearrangement; Silicon Baeyer-Villiger rearrangement.

Unit-2: Synthetic Strategy **12M**

Retro-synthetic analysis; Disconnection approach; Typical examples to illustrate the disconnection approach; FGI; Umpolung(1,3-dithiane); Convergent synthesis; One-group, Two-group disconnections; Selectivity aspects: Chemo-, Regio-, Stereo -selectivity; Retron; Uses of aliphatic nitro and amines. Protection and deprotection of common functional groups (Hydroxy, Carbonyl, Carboxylic and Amino groups)

Unit-3: Asymmetric Synthesis **12M**

Principles and newer methods of asymmetric synthesis (Including enzymatic and catalytic nexus); Enantio and diastereo selective synthesis; Addition to carbonyl compounds; Reactions of enolates (α-substitution), Alkylation, Asymmetric aldol reaction, Addition to C-C double bond(Electrophile induced cyclization, iodolactonization, hydroboration,conjugate addition, Diels-Alder cycloaddition, cyclopropanation); Reduction of C-C double bond; Carbonyl and Imine groups; Oxidation, Epoxidation, Dihydroxylation, and mono-hydroxylation; Rearrangement: [3,3]-sigmatropic, [2,3]-Wittig,Alkene isomerisation, Hydrolysis and esterification.

Unit-4: Natural Products and Steroids **12M**

Familiarity with methods of structure elucidation (Chemical and spetroscopical methods);
Bio-synthesis; Synthesis and Biological activity of alkaloids (Nicotine, atropin)
General methods of study and structural types; Chemistry of cholesterol, hormones, bile-acids

Unit-5: Bioorganic Chemistry **12M**

Molecular models of biological receptors, Biomimetic chemistry, Design, Synthesis and binding studies of synthetic receptors, Enzyme models, Micelles, Cyclodextrins, Polymers, Remote functionalisation reaction, Catalytic antibodies, Principles of gene synthesis, Proteins, Peptides and Amino acid.

Practical **40M**

Identification of solids from mixture of two solids.

Physical Chemistry (Paper VI)

Unit-1: Quantum Mechanics 2 **10M**

Hydrogen atom, Spherical Harmonics, Rigid Rotator, Ladder operators ; Harmonic Oscillator, Calculation of various quantities (matrix elements, selection rule, etc) using ladder operators and recursion relations of Hermite polynomials, Rayleigh-Schrodinger time-independent perturbation theory for non-degenerate states. Variation theorem and variational methods. Use of these methods illustrated with some examples (particle in a box with a finite barrier, anharmonic oscillator, approximate functions for particle in a box and hydrogen atom)

Unit-2: Statistical Thermodynamics I **10M**

Entropy and Probability; Ensembles-Types; Partition Function and Thermodynamic properties; Maxwell Boltzmann distribution. The molecular partition function and its factorization. Evaluation of translational, rotational and vibrational partition functions for monatomic, diatomic and polyatomic gases ; Calculation of thermodynamic properties of ideal gases in terms of partition function. Calculation of equilibrium constants of gaseous solutions in terms of partition function, perfect gas mixtures.

Unit-3: Macromolecules **10M**

Definition of Polymers; Types of Polymers; Polymerization process – condensation, addition, radical chain, ionic, condensation polymerization, copolymerization; Kinetics of Polymerization, chain transfer, retardation, inhibition; Polymerization in homogeneous and heterogeneous systems; Polymerization conditions; Mechanisms of polymerization; Molecular mass of Polymers, their determination.

Unit-4: Surface Chemistry **10M**

Surface Tension; Adsorption; Electrical Phenomena at Interfaces; Surfactants and Surfactant Assemblies – Micelles, Reverse Micelles and Microemulsions; Modern Techniques for Studying Surfaces.

Unit-5: Bio-physical Chemistry **20M**

Protein structure- primary, secondary, tertiary and quarternary structure; protein denaturation; Titration curves; Forces Involved in Biopolymer Interactions; Ligand binding to Bio-

polymers; Bioenergetics; Ion Transport through Cell Membrane; Nerve Conduction, Muscular Contraction and Energy Generation in Mechanochemical System.

Practical **40M**

One/Two day based physicochemical experiments.

Semester III

Spectroscopy (Paper VII)

Unit-1 : Nuclear magnetic resonance spectroscopy – theory & applications 12M

Basic instrumentation, nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift, and its measurements, factors influencing chemical sift, deshielding, spin-spin interactions, factors influencing coupling constant `J`. Classification of molecules: (ABX, AMX, ABC, A_2B_2, etc. types), spin decoupling. FT-NMR (qualitative idea) and its advantages, Applications of NMR in medical diagnosis.

Unit-2 : Mossbauer spectroscopy **12M**

Principle, experiment, line-width center shift, quadrupole interaction, magnetic interaction, information of spin and oxidation states, structure and bonding, spin transition from spectra of different Mossbauer active nuclei in varieties of environments

Photoelectron spectroscopy
Photo excitation and photoionization, core level photo ionization (XPS, ESCA.) and valence level (UPS) experiments, detection of atoms in molecules, chemical shift, differentiating same element in different environments.

Unit-3 : Emission spectroscopy **12M**

Franck-Condon principle, Mirror-image symmetry and its violation, Radiative and radiationless deactivation, Oscillator strength, Polarization characteristics of emission, Quenchers and life-time variations

Unit-4: Electron spin resonance spectroscopy **12M**

Basic principles, zero field splitting, and Kramer`s degeneracy, factors affecting the `g` value. Isotropic and anisotropic hyperfine coupling constants, spin Hamiltonian, spin densities and McConnell relationship. Basic instrumentation, measurement techniques and simple applications.

Unit-5 : Mass & IR spectroscopy **12M**

Mass spectroscopy

Basic instrumentation, ion production - EI,CI, FD and FAB techniques, Mass spectral fragmentation of typical organic compounds, common functional groups.

IR spectroscopy

Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic and heterocyclic compounds, ethers, phenols and amines, carbonyl compounds (aldehydes, ketones, esters, carboxylic acids, amides, anhydrides, lactones, lactams, and conjugated carbonyl compounds). Effects of solvent, hydrogen bonding on vibrational frequencies, overtones, combination bands and Fermi resonance, FT IR.

Inorganic Chemistry (Paper VIII)

Unit 1: Nuclear Chemistry & Radiochemical Analysis 10 M

Nuclear models: Nuclear forces, liquid drop model, shell model, Fermi gas model; magic numbers, nuclear spin and nuclear isomerism.

Nuclear reactions: Energetics, mechanism and models of nuclear reactions. Nuclear fission and nuclear fusion, fission products and fission yields. Interactions of radiation with matters, chemical effects of nuclear transmutation (elementary idea), Nuclear reactors and particle accelerators.

Radioactive Techniques: Detection and measurement of radiation- GM ionization and proportional counters. Study of chemical reactions by tracer techniques, isotope exchange and kinetic isotope effect. Radiometric analysis: Isotope dilution analysis, age determination, neutron activation analysis (NAA) and their applications. Radiation hazards and safety measures.

Unit 2: Organometallics 2 10 M

Reactions of organometallic complexes: substitution, oxidative addition, reductive elimination, insertion and elimination, electrophilic and nucleophilic reactions of coordinated ligands.

Catalysis by Organometallic compounds: Hydrogenation of olefins, Wilkinson's catalyst, Tolman catalytic loop; synthesis gas, water-gas shift reaction; Hydroformylation (oxo process), Monsanto acetic acid process, Wacker process; synthetic gasoline: Fischer-Tropsch process and Mobile process, polymerization, oligomerization and metathesis reactions of alkens and alkynes, Zieglar- Natta catalysis , photo dehydrogenation catalyst (platinum POP).

Unit 3: Magneto chemistry 1 10 M

Magnetic properties of transition metal compounds: Types of magnetic materials. Magnetic susceptibility and its determination: Gouy, Faraday methods , vibrating sample magnetometer, SQUID and NMR methods. Magnetic anisotropy, diamagnetism in atoms and polyatomic systems, Pascal's constants. Spin and orbital moments, spin-orbit coupling, quenching of orbital moment, spin only formula, temperature dependence of magnetic moment, spin cross over, Lande interval rule, energies of J states. Curie equation, Curie law and Curie-Weiss law.

Unit 4: Advanced Bioinorganic Chemistry 3 **10 M**

Metal ion/complex interactions with purine and pyrimidine bases, nucleosides, nucleotides and nucleic acids, DNA and RNA, metal ions in genetic information transfer.
Redox enzymes: Catalase, peroxidase, super oxide dismutase (SOD), cytochrome P-450, nitric oxide synthases (NOS), ascorbate oxidase, aldehyde oxidase; molybdo enzymes: xanthene oxidase, nitrate reductase, sulfite oxidase including some model study.

Practical

Analysis of Complex Materials **40M**

Quantitative analysis of complex materials, such as, ores and minerals, metals and alloys, industrial materials by conventional and/or instrumental methods as applicable.

Model Samples

Ores, Minerals , Concentrates:

Dolomite ($CaCO_3$, Mg CO_3, Fe_2O_3, SiO_2); Pyrolusite (MnO_2, MnO, Fe_2O_3); Chalcopyrite (CuS, FeS); Bauxite (Al_2O_3, Fe_2O_3, TiO_2, SiO_2); Chromite (Cr_2O_3, Fe_2O_3, MnO, SiO_2); Basic slag (Al_2O_3, Fe_2O_3, P_2O_5, SiO_2).

Metals and Alloys:

Brass (Cu, Zn); Soldier / Type metal (Pb, Sb, Sn); Bronze(Cu, Zn, Sn), Aluminium bronze(Cu, Al, Fe, Mn), Steel (Cr, Mn, Ni, P).

Mixture:
Chromium (III) and Mn(II) in a mixture

At least one ore/ mineral/concentrate and one alloy should be analyzed during the lab. session.

Organic Chemistry (Paper IX)

Unit-1: Photochemistry **10M**

Basic principles, Jablonski diagram, Direct and sensitized reactions, Photochemistry of olefinic compounds; cis-trans isomerisation; Patterno-Buchi reaction; Norish type-I and Norish type-II reaction; Photo-reduction of ketone; Di-pi methane rearrangement; Photochemistry of arynes; Photo-reaction in solid state; Radical initiators; Reactivity pattern of radicals; Substitution and addition reactions involving radicals; Cyclisation of radicals.

Unit-2:Heterocyclic Chemistry **10M**

Systematic nomenclature (Hantzsch-Widman system) for monocyclic, fused and bridged heterocycles; Heterocycles inorganic synthesis-Masked functionalities, Umpolung, Stork amination reation, Rearrangement and ring transformation involving 5-, 6- membered heterocycles with one hetero atom General approach to heterocycle synthesis, cyclisation, cycloaddition route.

Unit-3: Organometallics **10M**

Catalysis by organometallic compounds, Hydrogenation of unsaturated compounds, Wilkinson catalyst, Tolman catalytic loop, Syntheses: gas-water-gas Shift reaction; Hydroformylation, Monsanto acetic acid process, Wacker process, Synthetic gasoline-Fischer-Tropsch process and Mobile process, Polymerisation, Oligomerisation and Metathesis reaction of alkenes and alkynes; Ziegler-Natta catalyst; Photodehydrogenation catalyst (Platinum POP)

Synthesis, Structure, Bonding, Oxidative insertion, Reductive elimination, Ligand migration from metal to carbon, Organometallic reagents in organic synthesis and in homogeneous catalytic reactions (Hydrogenation, Hydroformylation, Isomerisation and Polymerisation), Pi-acid metal complexes, Activation of small molecules by coordination,
Coupling reaction: Heck reaction, Stille, Suzuki, Olefin metathesis, Tebbe's reagent, Pauson-Khand reaction, Functional organometallic compounds, Use of Indium and Zinc.

Unit-4: Supramolecular Chemistry **10M**

From molecular to supramolecular chemistry: Factors leading to strong binding (non-covalent interation), New molecular receptors, Crown ether, Sidero force, Cyclophanes,
Cyclodextrin and their application in specific recognition processes., Supramolecular reactivity and catalysis, Switching devices, self assembling, self replication of supramolecular aggregates and auto-catalysis.

Practical **40M**

Extraction and purification of some natural products.

Synthesis of some useful reagents.

Physical Chemistry (Paper X)

Unit-1 : Quantum Mechanics III **10M**

Ground and excited state of helium atom. Pauli's Exclusion principle. Many-electron atoms. Concept of spin and determinantal wavefunctions, Theories of valence, Born-Oppenheimer approximation. Variational treatment of hydrogen molecule ion. Valence bond and MO (LCAO) treatment of hydrogen molecule. Comparison of the MO and VB treatments and their equivalence limit. *HMO method and its applications:* π-Electron approximation, Hückel Molecular Orbital Theory of conjugated systems, Calculation of properties-Delocalization energy, electron density, bond order, alternant and nonalternant hydrocarbons.

Unit-2 : Statistical Mechanics II **10M**

Phase space and ergodic hypothesis, Gibbs paradox and Sackur-Tetrode equation, system of interacting molecules-imperfect gas, Quantum statistics, BE and FD statistics, Specific heat of electron gas, Bose condensation. Liouville theorem and its consequences, its quantum version. Formulation of Quantum statistics-density matrix.

Unit-3 : Nanomaterials **10M**

Nano-world-definitions and properties, typical synthetic strategies for nanomaterials, characterization and applications

Unit-4 : Electrochemistry II **10M**

Electrode kinetics-Nernst, Butler-Volmer equation, Tafel equation, Overpotential, corrosion, photoelectrochemical splitting of water

Practical **40M**

One/Two day based physicochemical experiments.

Semester IV

Inorganic (Paper XI)

Unit 1: Inorganic Photochemistry **10M**

Excitation modes in transition metal complexes, fate of photo-excited species, fluorescence and phosphorescence applied to Inorganic systems, intramolecular energy transfer, vibrational relaxation, internal conversion and intrasystem crossing. Photochemical process: photo substitution and photoelectron transfer reactions in Co, Cr, and Rh complexes.

Unit 2: Inorganic Rings, Cages and Clusters **10M**

Polymorphism of C, P and S. Structure and bonding in higher boranes and borohydrieds-Lipscomb's topological models, Wade`s rules, carboranes and metallocenecarboranes.

Metal-metal bonding (M.O. Approach), metal-metal single and multiple bonded compounds. Low nuclearity (M_3, M_4) and high nuclearity (M_5-M_{10}) carbonyl clusters: skeletal electron counting, Wade-Mingos-Louher rule, Application of isolobal and isoelectronic relationships, Nb and Ta clusters, Mo and W clusters. Cluster compounds in catalysis.

Unit 3: Chemistry of elements 2 **10M**

f– Block Elements: Lanthanide and Actinide Elements:
Nuclear stability, terrestrial abundance and distribution, relativistic effect, electronic configuration, oxidation states, aqueous-, redox- and complex- chemistry; electronic spectra and magnetic properties. Lanthanide and actinide contractions and their consequences, separation of lanthanides and actinides and their applications (examples).
Compounds of Sc, Y, La and Ac; Ce(III) and Ce(IV) compounds and their reactions,
Lanthanide compounds as high temperature superconductor, nmr shift reagent and MRI reagent.

Unit 4: Inorganic Reaction Mechanism **10M**

Mechanism of electron transfer reactions: General characteristics and classification of redox reactions, self-exchange reactions. Frank-condon principle (non mathematical treatment). Outer sphere and Inner sphere reactions, applications of Marcus expression (simple form), redox catalyzed substitution reactions.
Mechanism of substitution reactions, solvent exchange, aquation, anation, base hydrolysis, acid catalyzed aquation, pseudo-substitution. Four broad classes of mechanism of substitution-D, A, Ia and Id. Mechanism of isomerization reaction-linkage isomerism, cis-

trans isomerism, intramolecular and intermolecular racimization, Ray-Dutta and Bailar twist mechanisms.

Advanced Physicochemical Experiments **30M**

Part A **20M**

Model Experiments

1.Determination of composition of complexes formed in solution by spectrophotometric methods:

(a). Mole-ratio method
(b). Slope- ratio method
(c). Job's method of continuous variation

Model systems:
(i). Fe^{III}-sulfoslicylic acid complex
(ii). Fe^{II}- (1,10- phenanthroline) complex
(iii). Cu^{II}- ethylenediamine complex
(iv). Zn^{II}-alizarin-S complex

2. Determination of stability constants of metal-ligand complexes by pH-metric methods:

Model systems:
(i). Cu^{II}- glycinate complexes
(ii). Cu^{II}-sulfosalicylate

3. Kinetic study on consecutive reactions:

Model system:
Determination of the rates of consecutive aquation of the complex, $H[Co^{III}(DMGH)_2Cl_2]$, by conductance method (where, DMGH = dimethylglyoximate monoanion).

4. Kinetics studies on redox reactions:

Model system:
Determination of the rate constants of reduction of the complex, $[Co(NH_3)_5 (N_3)]Cl_2$, by aqueous Fe^{2+} ions by spectrophotometric method.

5.Kinetics studies on linkage isomerism:

Model system:
Kinetic investigation of transformation of the complex,
$[Co(NH_3)_5 (ONO)]Cl_2$ to $[Co(NH_3)_5 (NO_2)]Cl_2$ by spectrophotometric method.

7. Kinetics studies on substitution reactions:

Model system:
Kinetic investigation of the substitution reaction,
$[Co(NH_3)_5 (SO_3)^+] + NO_2^- \rightarrow$ by spectrophotometric method.

8. Kinetics studies on protolysis reaction:

Model system:
Kinetic investigation on protolysis of the complex, $[Co(NH_3)_5 (CO_3)^+]$ ion by spectropotometric method.

Part B

Spectroscopic Studies on Model Compounds **10M**

Model Inorganic Compounds

(i).Recording of electronic spectra, determination of absorption maxima and molar extinction coefficient values and evaluation of crystal field parameters, magnetic measurements (as applicable) should be carried out by the students. Some model compounds are listed below:

$CuSO_4.5H_2O$, $[Cu(NH_3)_4]SO_4$, $[Cu(en)_2]SO_4$, $(Et_4N)_2[CoX_4]$ (X = Cl^-,Br^-), $[Cu(acac)_2]$; $VOSO_4$, $[VO(acac)_2]$, $(NH_4)_2[VO(C_2O_4)_2].2H_2O$; $CrCl_3.6H_2O$, $K_3[Cr(C_2O_4)_3].3H_2O$, $[Cr(acac)_3]$, $NH_4[Cr(NH_3)_2(NCS)_4]$. xH_2O; $CoCl_2.6H_2O$, $(Et_4N)_2[CoX_4]$ (X = Cl^-,Br^-, I^-), $[Co(NH_3)_6]$ Cl_3, $Co(NH_3)_5$ Cl] Cl_2,$[Co(NH_3)_5$ $H_2O]Cl_3$, $[Co(NH_3)_5$ $(N_3)]$ Cl_2, $Na_3[Co(NO_2)_6]$, $[Co(acac)_3]$ and its nitro derivative, $[Co(en)_2(CO_3)]Cl$
$[Co(NH_3)_4(CO_3)]$ $NO_3.(½)$ H_2O,$[Co(NH_3)_5(SO_3)]_2$ $SO_3.2H_2O$, $[Co(en)_2(N_3)]$ NO_3; $NiSO_4.7H_2O$, $[Ni(NH_3)_6]Cl_2$, [Ni (en)$_3$]X_2. x H_2O (X = Cl^-, SO_4^{2-}, $S_2O_3^{2-}$),$(Et_4N)_2[NiX_4]$, (X = Cl^-, Br^-), $(NH_4)_2$ SO_4 . $MnSO_4$. $6H_2O$, $[Mn(acac)_3]$, $(Et_4N)_2[MnX_4]$, (X = Cl^-, Br^-).

(ii). Analysis of supplied UV-VIS, IR, magnetic moment data and cyclic voltammogram of model compounds.

Organic (Paper XII)

UNIT-1: Stereochemistry **10M**

Advanced course involving conformation and reactivity, cyclic system, monocyclic systems-3 to 10 member rings,6-6,6-5, 6-4, 5-5 bicyclic systems, 6-6-6, 6-5-6, 5-6-6, 5-5-5 tricyclic systems. Chiroptical properties of organic molecules: origin, theory of CD, ORD principles and applications, Haloketone rule, Sector rule, Helicity rule, Exceptions and excitation chirality, Atomic and conformational asymmetry, Chiral analysis by polarimeter, NMR,GC, HPLC and capillary eletrophorasis methods, Baldwin rules- applications.

Unit-2: Green Chemistry **10M**

Green chemistry-overview, twelve principles, Green synthetic methods, Catalytic methods, Organic synthesis in aqueous media, Ionic liquid, Supercritical fluids, Microwave-induced organic reaction, Reactions by sonication, Solvent-free organic reactions.

Unit-3 **10M**

Carbohydrates

Basic structure and type of sugars; Protection and deprotection, Deoxysugars, aminosugars, glycalsugars and their synthetic aspects, Synthetic approach (Combinatorial) towards polysachharides of biological and industrial importance, Carbohydrate as chiral pools in organic synthesis.

Nucleoside and Nucleotide

Chemical synthesis of nucleosides and oligonuleotides, Bio-synthesis of nucleotides and folic acids, Replication, transcription- Protein bio-synthesis, Covalent interaction of nucleic acids with small molecules, Structural features of DNA and RNA.

Unit-4: Medicinal Chemistry **10M**

Pharmacodynamics: Different types of drugs and drug targets, Drug binding forces, Role of enzymes, Drug receptor interactions, Mechanism of drug action, Agonists, Antagonists, Affinity, Efficacy and potency of drug, Dose response curves.

Pharmacokinetics: Drug absorption, Distribution, Metabolism (Phase-I and Phase-II transformations), Excretion, Drug formulation and others.

Drug design and synthesis, Molecular and Quantum mechanics, Drawing chemical structures, equation and diagrams, 3D structures, Molecular modeling and energy minimisation, Molecular properties, Conformational analysis, docking procedures, *De Novo* design, Molecular recognition, Receptor based molecular modeling, QSAR studies, Antineoplastic agent, Cardiovascular drugs, Local anti-infectaive drugs, Antimalarial, antibiotics, anticolenergic and CNS active drugs.

Practical **30M**

Multi-step reactions and purification using column chromatography.

Physical Chemistry (Paper XIII)

Unit 1 : Non-equilibrium thermodynamics **10M**

Meaning and scope of irreversible thermodynamics,Thermodynamic criteria for non-equilibrium states, balance equations for irreversible processes, Phenomenological equations, microscopic reversibility and Onsager reciprocity relations, examples and illustrations. , Entropy production- specific examples of entropy production, Non-equilibrium stationary states, Prigogine's principle of maximum entropy production, Coupled phenomena, Some important applications.

Unit 2 : Theoretical Spectroscopy **10M**

Selection rule for vibrational spectroscopy, anharmonic correction by perturbation, appearance of overtones, selection rule for rotataional spectra, nuclear spin and rotational energy levels, Stark effect, Raman scattering, Selection rule for rotational, vibrational Raman effect. Non linear scattering – hyper Raman, stimulated Raman, Resonanace Raman spectra.

Unit 3 : Laser **10M**

Principles of Laser and Maser action. Population inversion (two/three/four level systems). Basic elements in Laser, Characteristics of Laser Radiation, Single Mode and Tunable Laser, Harmonic generation, Applications.

Unit 4 : Quantum Mechanics IV **10M**

Many electron systems. Closed and open shells. Anti-symmetry principle and antisymmetrization operator. Independent particle model (IPM). Hartree and Hartree Fock methods for closed shells. Koopman's theorem. Limitation of IPM; electron correlation. Restricted and unrestricted Hartree-Fock methods (elementary idea). Multidimensional wave function and Configuration interaction. Brillouin's theorem, Roothan equation
Pictures : Schrodinger, Heisenberg interaction picture and quantum mechanics

Practical **30M**

One/Two day based physicochemical experiments.

ELECTIVE PAPER (Paper XIV)

Inorganic Chemistry

Unit 1: Group Theory **12M**

Effect of lowering of symmetry on the orbitals and energy levels, correlation table, Correlation diagrams, Tanabe-Sugano diagram, Justification of Laporte selection rule, vibronic coupling and vibronic polarization, polarization of electronically allowed transitions. Symmetry adapted linear combinations (SALCs) and the M.O. Description of organic and organometallic molecules.

Unit 2: Crystallography **12M**

Fundamentals of X-ray crystallography, crystal forms, lattice, primitive cell, crystal systems and symmetry, non-primitive lattices, crystal classes, space groups, crystals and their properties, Diffraction of x-ray, lattice planes, indices, Brag's condition, reciprocal lattice, Brag's law in reciprocal, Geometric data collection (simple examples), structure factor, systematic absence, heavy atom method. Fourier synthesis, Patterson function, experimental diffraction methods (Laue method, rotating crystal method).

Unit 3: Magnetochemistry **12M**

First order and second order Zeeman effects, temperature independent magnetism, simplication and application of van Vleck susceptibility equation, quenching of orbital moment, magnetic properties of transition metal complexes in cubic and axially symmetric crystal fields, low spin-high spin crossover, magnetic behaviour of lanthanides and actinides, magnetic exchange interactions, magnetic materials.

Unit 4: Chemistry of elements 3 **12M**

Iso-and heteropolyoxometalates with respect to V, Mo, and W: synthesis, reactions, structures, uses, metal-metal bonded dinuclear d-metal complexes (examples), Bonding in dirhenium complexes.
Mixed valence compounds of Fe, Cu, Pt; Fe-S compounds, cobaloxime related compounds, conformational changes and thermochromism of Ni(II) compounds, Ru(II) and Ru(III) compounds, oxo compounds of Ru and Os, Rh(I) and Ir(I) carbonyl halide and carbonylhydrides. Aqueous chemistry of Be^{II} and Al^{III}, basic beryllium compounds.
Synthesis, properties, reactions, structure and bonding as applicable in respect of: Mo-blue, W-blue, Pt-blue, W-bronze, Ru-red.

Unit 5: Spectroscospic Analysis of Inorganic Compounds **12M**

Application of IR, UV, NMR, ESR, Mossbauer spectroscopy in inorganic chemistry (examples with simple and complex inorganic compounds including organometallic and cluster compounds and bio inorganic system).
Solid state reactions: Kinetics of solid state reactions by TGA, DTA and DSC methods (typical examples)

Organic Chemistry

Unit-1: Reagents in Organic synthesis 15M

One electron and two electron oxidants, Oxidations with Cr (VI): Jones oxidation, Collins oxidation PCC, PDC, PFC; DMSO based oxidations: Swern, Moffat, DMSO-SO_3 complex, DMSO-acetic anhydride, Hypervalent iodine oxidations: Dess-Martine periodinane, IBX, Iodobenzene diacetate; Oxidations with thalium nitrate, Ag_2O, RuO_4, OSO_4, $NaIO_4$.

Reduction with metal-hydrides of B, Al, Sn, Si. Dissolving metal-reduction, Synthetically useful hydrogenolysis reaction, Sm and In based reducing agents and enzymatic reductions.

Unit-2: Advanced Pericyclic Chemistry 15M

General perturbation molecular orbital theory in cycloaddition reaction: Reactivity, Regioselectivity and Periselectivity, Cheletropic reactions, 1,3-dipolar cycloaddition, Cycloadditions involving more than six electrons, Three and four component cycloaddotion, Ene reactions, Group transfer reactions and eliminations, Electrocyclic reactions of charged systems, Sigamatropic rearrangement: [1,5] and [1,7] shifts in neutral systems and [1,4] shift in charged species, [3,3] shifts, Cope rearrangements, Claisen rearrangement, [5,5] shifts, [2,3] shifts in ylides.

Unit-3: NMR Spectroscopy 15M

Application of DEPT,^{1}H-^{1}H COSY, HMBC, HMQC, TOCSY, NOESY in structure elucidation of organic compounds, drug screening, reaction monitoring etc., Solid state NMR (CP-MAS).

Unit-4: Heterocycles 15M

Synthesis and reactions of aziridines, azitidines, oxazoles, thiazoles, imidazoles, isoxazoles, isothiazoles, pyrazoles and higher azoles and corresponding few systems, pyrimidines, pyridazines, pyrazines, purines, pteridines, Role of heterocyclic compounds in biological systems, Nomenclature of bicyclic and tricyclic fused systems, Introduction to the chemistry of azipines, oxepins, thiepins and their aza-analouges, Phosphorus and selenium containing heterocycles, Cyclazines.

Physical Chemistry

Unit 1 : Advanced Quantum Mechanics 15M

Rayleigh-Schrodinger perturbation theory for non-degenerate states with simple applications, Brillouin-Wigner theory, Degenerate perturbation theory, Stark effect, First and second order

lifting of degeneracy, Time-dependent perturbation theory, Fermi's golden rule, Virial theorem and chemical bonding, Hellman-Feynman Theorem.

Unit 2 : Statistical Mechanics III **15M**

Einstein's theory of Brownian motion, Langevin equation, Fokker-Planck equation, Fluctuation-dissipation relation, effect of friction. Applications to rate processes and transport problems. Master equation and its applications.

Unit 3 : Reaction Dynamics **15M**

Basic concepts in classical mechanics of collisions. Intermolecular potential from scattering experiments. Molecular beams, principle of crossed-molecular beams. Molecular encounters and principal parameters, e.g. Impact parameter, Collision cross-section, Reaction cross-section and relation between reaction cross-section and reaction rate (single velocity). Dependence of collisional cross-section on translational energy. Probing the transition state, Dynamics of barrierless chemical kinetics in solution, dynamics of unimolecular reactions.

Unit 4 : Modern Material Chemistry **15M**

Electrically conducting polymers: Discovery of electrically conducting polymers, Factors affecting the conductivity of conducting polymers. Electrochemical polymerization. Doping of conducting polymers. Important structural features. Nature of charge carriers in conducting polymers: solitons, polarons and bipolarons. Mechanism of conduction in polymers.
Electronic structure of polymers: Band theory of polymers. Methods for determining band structure of polymers: An introduction.
Nanomaterials : Hybrid materials as a new tool in material synthesis – advantages and applications. Biomedical applications of nanomaterials – drug delivery.