Third Year

Semester V

PAPER M 501 : Quantum Chemistry (Total Marks 75)

Unit 5.1 Quantum Theory Marks 30

Review of experiments leading to the idea of quantization

(a). Black body radiation – Planck's hypothesis

(b). Photoelectric effect – Einstein's explanation

(c). Compton effect

Electron diffraction, de Broglie hypothesis, Heisenberg's uncertainty principle. Postulates of Quantum mechanics.

Wave functions, Operators, Eigen functions and eigen values, the Schrodinger postulates of operator transforms and the wave equation boundary conditions, normalization of the wave functions, expectation values. Interpretation of the wave function orthogonal and orthonormal wave functions.

Model systems – particle in 1D and 3D boxes particle in a ring, harmonic oscillator and rigid rotator (detailed mathematical treatment not necessary) : coordinate systems construction of

Hamiltonian potential function leading to potential energy term Schrodinger equation, outline of solution, energy expression, wave functions, quantum numbers. Special features like degeneracy, energy level diagrams, plot of wave functions and their squares vs displacement from origin, zero point energy, quantum mechanical tunneling, force constant and bond strength (for harmonic oscillator), moment of inertia in 3D, angular momentum, space quantization of angular momentum (for rigid rotator).

Qualitative discussion of all these topics.

Unit 5.2 Atomic Structure Marks 20

The Hamiltonian and Schrodinger equation for hydrogen atom, energy levels and quantum numbers, the radial and the angular part of the wave function, construction of two dimensional plots of probability density and calculation of radial probability functions. The orbitals of hydrogen and hydrogen-like atmos, contour diagrams of electron density. Stern-Gerlach experiment, electron spin and spin quantum number spin orbitals. Electron configuration of many electron atoms, Pauli's exclusion principle illustration by He atom using wave functions.

Spin-orbit interactions, Russel-Saunder's coupling, Term symbols. Effect of magnetic

field on energy levels. Hund's rule.

Unit 5.3 The Nature of Chemical Bond **Marks 15**

Schrodinger equation for a molecule, Born-Oppenheimer approximation. LCAO-MO theory as applied to H_2 and H_2 - drawback of MO theory. MO energy level diagram of homonuclear (O_2, N_2) and heteronuclear (HF, LiF, CO) diatomic molecules. Heitler-London theory wave function and potential energy curve of H_2. Concept of resonance and hybridisation from VB theory. Term symbols of diatomic molecules. Huckel theory for ethene and benzene.

Internal Assessment **(Marks 10)**

PAPER M 502 Physical Chemistry **(Total Marks 75)**

Unit 5.4 Molecular Reaction Dynamics **(Marks 15)**

Collision theory, Activated complex theory; Erying equation - thermodynamic formulation. Theory of unimolecular reactions (Lindemann) dynamic molecular collisions - potential energy surfaces - Molecular beam technique and results of molecular beam studies. Reactions in solution, Bronsted- Bjerrum equation, Kintic salt effect. Introduction to lasers, flash photolysis.

Unit 5.5 Photochemistry **(Marks 15)**

Laws of photochemical equivalence. Quantum yield, chemical actinometry Kinetics of H_2-Br_2 , H_2-Cl_2 reactions, Dissociation of HI, Photostationary equilibrium, Dimerisation of anthracene.

Luminescence phenomenon – fluorescence, phosphorescence, Jablonski diagram, Photosensitised reactions, Quenching of fluorescence. Chemi and bio luminescence.

Photochemistry of air and air pollution.

Unit 5.6 Phase Equilibria **(Marks 20)**

Definition of phase, meaning of components and degrees of freedom. Derivation of phase rule. Phase diagram of one component system (water). Phase diagram of two component system – eutectics, congruent and incongruent melting points, solid solutions.

Interpretation of liquid-vapour, liquid-liquid and liquid-solid phase diagrams. Distillation of partially miscible liquids.

Clausius Clapeyron equation for different phases. Systems of variable composition, partial molar quantities, Gibbs Duhem equation, Thermodynamics of mixing.

Chemical potential, chemical potential of a component in an ideal mixture - fugacity,

activity coefficients. Dependence of chemical potential on temperature and pressure.

Unit 5.7 Surface Chemistry (Marks 15)

Introduction to solid surfaces, adsorption on surfaces – physisorption and chemisorption Adsorption isotherms Langmuir, Freundlich, BET equation. Determination of surface area. Catalytic activity at surface with examples.

Concept of surface excess, Gibbs equation, surface pressure and surface spreading.

Internal Assessment **(Marks 10)**

PAPER M 503 Organic Chemistry (Total Marks 75)

Unit 5.8 Organic Reaction Mechanisms (Marks 35)

A. **Molecular Rearrangements of the types**

Nucleophilic or anionotropic : Whitmore 1,2 Shift, Wagner-Meerwein, Wolff, Hofmann, Lossen, Curtius, Schmidt, Beckman, Favorskii, Benzil- benzilic acid, Baeyer Villiger

Free radical : Wittig

Electrophilic or cationotropic : Pinacol

Special : Fries rearrangement (aromatic electrophilic substitution)

Stevens (ion pairs in solvent cage/ radical pair)

B. **Oxidation - reduction : common oxidizing and reducing agents.**

i) Direct electron transfer: Clemmensen (Nakabayashi mechanism)

ii) Hydride transfer

iii) Hydrogen Atom Transfer: Bouveault-Blanc

iv) Formation of ester intermediate: oxidation by dichromate, permanganate, etc.

v) Displacement mechanism.

vi) Addition- elimination.

Oxidizing agents : Chromium oxide, selenium dioxide, Chromyl chloride, PCC, and Lead tetraacetate.

Catalytic hydrogenation (Pd, Pt, Raney Ni). Reduction by LAH, Sodium Borohydride and metals (Birch). Reduction of nitro group under various condition. Selective reduction- Rosenmund reduction, Lindlars catalyst.

C. **Pericyclic Reactions**

Definition and examples of 2+2 and 2+4 cycloadditions. The conservation of orbital symmetry. Woodward Hoffman rules. Diels Alder reaction. 1,3 Dipolar Cycloaddition. Sigmatopic rearrangements-Cope and Claisen rearrangements. Electrocyclic reactions- HOMO-LUMO approach.

Unit 5.9 Polynuclear Aromatics, Nitro and amino compounds, Organo S and organo P Compounds, Active methylene compounds and Heterocyclic compounds (Marks 30)

Polynuclear aromatic hydrocarbons

Structure, bonding, properties and reactivity of naphthalene and its derivatives. Anthracene, phenanthrene

and anthraquinone-important methods of synthesis.

Nitro and amino compounds

Synthesis, physical properties and reactivity of nitroalkanes, alkyl nitrates, alkyl nitriles, isonitriles and

aromatic nitro compounds. Synthesis, reactions and basicity of aliphatic and aromatic amines.

Diazotization and its mechanism. Distinction between primary, secondary and tertiary amines,

Quarternary ammonium salts, Hofmann exhaustive methylation and Hofmann degradation of amines.

Organo S and organo P compounds

Synthesis and reactions of thiols, thioethers and aliphatic sulphonic acids. Phosphines, Phosphorous esters

and phosphorous ylides- Wittig reaction.

Active methylene compounds

The active methylene groups, synthesis of compounds containing active methylene groups (Ethylacetoacetate, Diethylmalonate and cynaoacetic ester) and their use in organic synthesis.

Heterocyclic compounds

IUPAC nomenclature, Synthesis, structure and bonding, properties (basicity, aromaticity) and reactions of pyrrole, furan, thiophene, pyridine, indole and quinoline

Internal Assessment **(Marks 10)**

PAPER M 504 Inorganic Chemistry **(Total Marks 75)**

Unit 5.10 Bonding in Coordination Compounds **(Marks 25)**

Symmetry elements and Symmetry operation, Point group classification, Symmetry of octahedron, tetrahedron and square planar complexes, Structure and symmetry of inorganic compounds(coordination 2-8), Shape and symmetry of s,p and d orbital.

Crystal field theory, factors affecting 10 Dq value, crystal field stabilization energy, Magnetic properties from crystal field theory, high spin and low spin complexes, structural and thermodynamic affects of orbital splitting, octahedral coordination in Spinels. Adjusted crystal field (or Ligand field) theory, Molecular orbital theory of octahedral complexes (without and with p bonding).

Metal-metal bonding and quadruple bonds.

Unit 5.11 Organometallic Compounds **(Marks 30)**

Synthesis, structure and bonding of complexes with olefins, acetylene, allyl, cyclopentadiene and arenas. IUPAC nomenclature. Effective Atomic number rule, Transition metal to carbon sigma bonds.

Homogeneous catalysis by transition metal complexes (isomerzation, hydrogenation, hydroformylation and Ziegler-Natta Polymerization).

Synthesis and structure of organometallic compounds of Sn and Pb, Organometallic compounds of Zn, Cd and Hg.

Unit 5.12 Bioinorganic Chemistry I **(Marks 10)**

Essential and trace elements and their biological role, Importance of Na K salts and calcium in biology.

Uptake and storage of iron, Introduction to the structure and function of hemoglobin, Synthetic dioxygen carriers, Dioxygen toxicity.

Internal Assessment **(Marks 10)**

PAPER M 505 Practical **(Total Marks 75)**

A. Inorganic Quantitative Analysis **(Marks 40)**

Estimation of inorganic ions by volumetric, complexometric, gravimetric, redox and precipitation methods.

The following one-component systems should be estimated first: Cu, Fe, Ca, Mg, Ni, Cl and SO_4^{2-}. This should be followed by separation and estimation of individual ions in two-component systems of-

a. Cu and Fe

b. Fe and Ca

c. Ca and Mg

d. Cu and Ni and

e. Cl^- and SO_4^{2-}.

(Any one of the above mixtures will be given for estimation in examination.
Determination of marks: Preparation of standard solution and standardization 10 marks. Separation of components 5 marks. Completion of the experiment 10 marks, and Results 25 marks.)

B. Chromatographic separation of cations by paper/TLC (Marks 15)

Colorimetric estimation of Cu^{2+}.

(Any one of these two experiments is to be done in the examination)

C. Sessional **(Marks 10)**

D. Viva **(Marks 10)**

PAPER 506 Practical **(Total Marks 75)**

A. Organic preparation **(Marks 25)**

Any one of the following will have to be done in the examination :

a). Acetylation : Preparation of - acetanilide from aniline and aspirin from salicylic acid.

b). Benzoylation : Preparation of benzanilide from aniline.

c). Nitration : Preparation of - *m*-dinitrobenzene and *p*-nitroacetanilide from acetanilide.

d). Halogenation : Preparation of *p*-bromoacetanilide from acetanilide and 2,4,6-tribromophenol from phenol.

e). Diazo-coupling : Preparation of methyl orange.

f). Oxidation : Preparation of benzyl from benzoin.

g). Reduction : Preparation of *m*-nitroaniline from *m*-dinitrobenzene.

(Distribution of marks : Yield & Quality of the compound 10, Recrystallisation & melting point - 10, completion - 5.)

C. Organic quantitative analysis (Marks 30)

Any one of the following experiments will be asked in the examination :

a). Determination of the equivalent mass of a carboxylic acid by direct titration method.

b). Determination of saponification equivalent of an ester.

c). Determination of amount of glucose by titration with Fehling solution.

d). Estimation of urea by hypobromite method.

(Distribution of Marks : Theory – 4, Preparation of standard solution & standardization – 6, completion - 5, Result – 15.)

D. Sessional (Marks 10)

E. Viva (Marks 10)

Semester VI

PAPER M 601 Spectroscopy (Total Marks 75)

Unit 6.1 Introduction to Spectroscopy (Marks 10)

The nature of electromagnetic radiation. The regions of spectrum. Mechanism of interaction of electromagnetic radiation with matter. Absorption and emission spectroscopy. Basic elements of practical spectroscopy. Representation of spectrum the width of spectral line. Intensity of spectral lines. Selection rules for various transitions. The Beer-Lambert law, molar absorption coefficient and absorbance. Molecular motion

and energy – degree of freedom. Moment of inertia.

Unit 6.2 Rotational, Vibrational and Raman Spectroscopy (Marks 20)

Rotational spectra of diatomic molecules – rigid rotator concept – determination of bond length – effect of isotopic substitution – spectra of non-rigid rotator. Vibrational spectra of diatomic molecules – harmonic and anharmonic oscillator model – Morse potential – calculation of force constants – effect of isotope – vibrations of polyatomic molecules, overtone and combination bands (H_2O, CO_2). Diatomic vibrating rotor – vibration rotation spectrum of CO. Principle of Raman spectroscopy – rotational and vibrational Raman spectra of linear molecules – rule of mutual exclusion.

Structure elucidation by IR spectroscopy – finger print region and group frequencies – effect of hydrogen bonding (alcohol, keto-enol) and coordination to metal.

Unit 6.3 Electronic spectroscopy (Marks 15)

Electronic transitions and selection rule – spectrum of atomic hydrogen – fine structure, spectra of H-like atoms.

Electronic transitions in diatomic molecules – Selection rule – Born Oppenheimer approximation – vibrational coarse structure – Frank Condon principle – electronic transitions in polyatomic molecules.

Structure elucidation by electronic spectroscopy – chromophore, auxochrome – absorption due to ethylenic chromophore – Woodward's rule. Electronic transitions in conjugated polyenes from particle in a box model. Effect of solvents on electronic transition, quantitative estimation by spectrophotometry.

Introduction to photoelectron spectroscopy and its applications in simple diatomic molecules.

Unit 6.4 Spin resonance spectroscopy (Marks 10)

Interaction between spin and magnetic field – Nuclear spin – Nuclear magnetic resonance spectroscopy – ^1H NMR – presentation of the spectrum – chemical shift and its unit chemical shifts for simple organic molecules (alkane, alkene, alkyne, arenas, aldehydes, carboxylic acids and esters). Spin-spin coupling and high resolution ^1H NMR spectra of ethanol, ethyl benzoate, 2-iodopropane, cyanohydrin.

Basic concept of electron spin resonance spectroscopy – presentation of the spectrum – hyperfine structure – esr of H- atom , deuterium atom.

Unit 6.4 Mass spectroscopy (Marks 10)

Mass spectroscopy – principle – idea of mass spectrometer – fragmentation pattern – nitrogen rule – simple applications in structure elucidation (butane, ethane, acetone) McLafferty rearrangement (hexanoic acid, pentanal).

Internal Assessment **(Marks 10)**

PAPER M 602 Physical Chemistry (Total Marks 75)

Unit 6.4 Solid State (Marks 20)

Laws of Crystallography, Miller indices, Symmetry in solids, Bragg's law, Introduction to X-ray crystallography and determination of structure of solids. Packing in solid octahedral hole, tetrahedral hole, radius ratio.

Dislocation in solids – Schottky and Frenkel defects, Dielectric property of solids, Concept of piezo and ferro electricity. Electrical property of solids (conductor, insulator, n type and p type semiconductors. Super conducting materials. Magnetic properties of solids (dia-, para-, ferro- and antiferro magnetism).

Uni 6.5 Macromolecules and Colloids (Marks 20)

Colloids . Definition, sols, lyophobic colloids. Structure, surface and stability of colloids. Sruface-active agents, micelle formation, critical micellar concentration, electrical double layer and Electrokinetic phenomena.

Molecular weight of macromolecules – number average and mass average molecular weight. Determination of molecular weight of macromolecules. Condensation and addition polymerization. Introduction to polymerization kinetics.

Unit 6.6 Statistical Thermodynamics (Marks 20)

Molecular energy levels and Boltzmann distribution, molecular partition function and its significance. Translational, rotational anf vibrational partition functions. Molecular significance of heat and work. Statistical thermodynamics of monatomic and diatomic gases. Applications of statistical thermodynamics for calculation of heat capacity, residual entropy and equilibrium constants.

Unit 6.7 Data Analysis (Marks 5)

Types of errors. Propagation of errors. Accuracy and Precision. Significant figures. Least square analysis. Average standard deviation. Uncertainty in the measurement of physical quantities.

Internal Assessment **(Marks 10)**

PAPER M 603 Organic Chemistry (Total Marks 75)

Unit 6.8 Organic Photochemistry, Polymers and Fibres (Marks 20)

Theory of photochemistry: photophysical processes, electronic excitation, excited states, Jablonski diagram, Franck-Condon Principles. Fluorescence and phosphorescence, FT process, photosensitizers, Einstein's law of photochemical equivalence, quantum yield.

Typical photoreactions: Photoreaction of benzophenone, photolytic reactions of ketones,

Norrish type I & Norrish type II reactions, *cis-trans* isomerisation and dimerisation. cycloaddition of olefins.

Polymers and fibres: Addition and condensation polymers, Preparation of vinyl polymers, synthesis of terylene, nylon, Elastomers-natural rubber synthetic rubber, Urea formaldehyde resins.

Biopolymers: Polysaccharides-structure of cellulose and starch, lignins, Proteins-polypeptides and polynucleotides.

Unit 6.9 Biochemistry (Marks 20)

Structure of cell: lipids and structure of cell membrane; membrane transport

Basic molecules of living systems and their structures-Carbohydrates, proteins, nucleic acids.

Amino acids, peptides and polypeptides: Primary, secondary, tertiary and quarternary structure of proteins. Structure and functions of hemoglobin and and myoglobin.

Enzymes and their function as catalysts: chymotrypsin and lisozyme Metalloenzymes, carboxypeptidase and peptide hydrolysis. Coenzymes and vitamins.

Structure and hydrogen bonding in purines and pyrimidines.

Structure of nucleotides and nucleosides. Structure of RNA and DNA.

Gene and genetic code: biosynthesis of DNA (replication), RNA (transcription) and proteins (translation)

Fundamentals of biological energy production-Glycolysis, Krebs cycle, Photosynthesis, respiration, oxidative phosphorylation and ATP synthesis.

Unit 6.10 Natural Products and Medicinal Chemistry (Marks 25)

Terpenes. Definition, isolation and classification, isoprene rule. Isolation, structure determination, and synthesis of important terpene- citral.

Alkaloids: nicotine only. Definition, classification and functions of hormones.

Definition and classification of carbohydrates. Structure, configuration and reactions of glucose.

Drugs-physiological effect of their structure. Classification Chiral drugs and asymmetric synthesis. Antibiotics and their action. Anticancer and antimalarial drugs. Immunity and AIDS.

Sulpha drugs- their mechanism of action. Preparation of aspirin, quinine, chloroquin, paracetamol, phenacitin, sulphanilamide and other sulpha drugs.

Cisplatin

Internal Assesment **(Marks 10)**

PAPER M 604 Inorganic Chemistry (Total marks 75)

Unit 6.10 Spectra of coordination compounds (Marks 25)

Free ion terms and their splitting in octahedral symmetry. Orgel diagram. Laporte selection rule, vibrionic coupling and colour of complexes. Electronic spectra of $M(H_2O)_6^{n+}$ complex ions.

Principles of colorimetric determination of metals. Thermodynamic stability. Stepwise formation constants, the chelate effect, kinetic lability and inertness. Mechanism of ligand displacement reactions in octahedral and square planar complexes. Determination of composition of ionic compounds by conductometry. Theory of redox and complexometric titrations.

Unit 6.11 Bioinorganic Chemistry II (Marks 15)

Metalloproteins and their role in photosynthesis, respiration, Nitrogen fixation (comparison with Haber's process).

Toxicity due to Metal ions (Fe, Cu, Al, Hg, Pb, Cd, As). The effect of gases and polluted environments (CO_2, CO, NO, SO_2, CN, nitrate, nitrite and phosphate)

Importance of metal salts in diet, diagnosis, chemotherapy and as medicines.

Unit 6.12 Nuclear Chemistry, Lanthanides and Actinides (Marks 25)

Physical properties of the proton and the neutron. Structure of the nucleus. Mass defect and binding energy. Radioactive decay and equilibrium. Nuclear reaction Q value, nuclear cross sections.

Theory of radioactive disintegration. Rates of disintegration, the radiochemical series. Transmutation of elements and artificial radioactivity. Fission and fusion. Nuclear reactors and their use. Methods of measurement of radioactivity.

Isotopes of elements (discovery, atomic weights). Methods of separation of isotopes. Application of isotopes (Tracer technique, neutron activation analysis, radiocarbon dating).

Lanthanides: Electronic configuration, stability of oxidation states, Lanthanide contraction. Coordination compounds. Separation of lanthanides.

Actinides. Discovery, electronic configuration, oxidation states, magnetic properties. Comparison with lanthanides.

Annual Examination (Marks 100)

PAPER VI 605 Practical

(Total Marks

Physical Chemistry Experiments

At least 10 experiments are to be performed from the list of experiments given below

1 To determine the coefficient of viscosity of a given liquid by Ostwald's viscometer

2 To determine the composition of a given mixture by viscosity method

3 To determine the surface tension of a liquid by stalagmometer

4 To determine the composition of a given mixture by surface tension method

5. To determine the mutual solubility curve of phenol and water

6 To determine the molecular mass of a volatile liquid by Victor Meyer's method

7 To determine the specific rotation of an optically active substance by polarimetric method

8 To determine the specific reaction rate of hydrolysis of methyl acetate catalyzed by hydrogen

ions at room temperature

9 To find the rate of decomposition of H_2O_2 catalyzed by Fe^{3+} ions

10 To test the validity of Beer Lambert's law using colorimeter

11 To study the rate of acid catalysed iodination of acetone

12. To obtain Freundlich isotherm for adsorption of oxalic acid on activated charcoal

13. To study the distribution of iodine between CCl_4 and water

14 To prepare arsenous sulphide sol and compare the precipitation power of monovalent and

trivalent

cations

15 To verify Debye, Hückel Onsagar equation for sodium chloride

16 Conductometric titration HCl Vs NaOH, Oxalic acid Vs NaOH, Acetic acid Vs NaOH

17. Potentiometric titration HCl Vs NaOH, Oxalic acid Vs NaOH, Acetic acid Vs NaOH