

Shivaji University, Kolhapur
School of Nanoscience and Technology

Entrance examination syllabus for M.Sc. in Nanoscience and Technology
(Weightage Physics - 30%, Chemistry - 30% and Nanoscience and Technology - 40%)

Physics

Thermal Physics and Statistical Mechanics

Basic Concepts and Laws of Thermodynamics:

Basic Concepts in Laws of Thermodynamics, Zeroth Law of thermodynamics and temperature, first law of thermodynamics and internal energy, Applications of First Law, reversible and irreversible processes, second law of thermodynamics, Entropy, Carnot heat engine, construction, working and derivation of efficiency. Carnot's theorem, Entropy changes in reversible & irreversible processes, Entropy temperature diagrams, Third law of thermodynamics, Unattainability of absolute zero.

Thermodynamic Potentials:

Enthalpy, Gibbs, Helmholtz and Internal Energy functions, Maxwell's relations & applications - Joule-Thompson Effect, Clausius-Clapeyron Equation, Expression for $(C_P - C_V)$, C_P/C_V , TdS equations.

Transport Phenomena:

Concept of mean free path, expression for mean free path, Transport Phenomena: Viscosity, Conduction and Diffusion, Law of equipartition of energy and its applications to specific heat of gases; mono-atomic and diatomic gases.

Theory of Radiation:

Blackbody radiation, Spectral distribution, Concept of Energy Density, Derivation of Planck's law, Deduction of Wien's distribution law, Rayleigh Jeans Law, Stefan Boltzmann Law and Wien's displacement law from Planck's law.

Statistical Mechanics:

Phase space, Macrostate and Microstate, Entropy and Thermodynamic probability, Maxwell Boltzmann law - distribution of velocity - Quantum statistics - Fermi-Dirac distribution law - electron gas - Bose-Einstein distribution law - photon gas - comparison of three statistics.

Waves and Optics

Superposition of Harmonic Oscillations:

Linearity and superposition principle, Superposition of two collinear harmonic oscillations for oscillations having equal frequencies: Analytical method, oscillations having different frequencies, Superposition of two perpendicular harmonic oscillations: for oscillations having equal frequencies. Oscillations having different frequencies (Lissajous figures), Uses of Lissajous figures.

Coupled Oscillations:

Frequencies of coupled oscillatory systems, normal modes and normal co-ordinates, energy of coupled oscillations, energy transfer in coupled oscillatory system.

Wave Motion and Ultrasonic Waves:

Wave Motion: Transverse waves on a string, travelling and standing waves on a string, Normal modes of a string, Group velocity and Phase velocity, Plane waves, Spherical waves. Ultrasonic waves: Piezo-electric effect, Production of ultrasonic waves by Piezoelectric oscillator, Detection of ultrasonic waves, Properties of ultrasonic waves, Applications of ultrasonic wave.

Sound and Acoustics of Buildings:

Sound: Transducers and their characteristics, Pressure microphone, Moving coil loudspeaker, Intensity and loudness of sound, Decibels, Intensity levels, Acoustics of buildings: Reverberation and time of reverberation, Absorption coefficient, Sabine's formula for reverberation time, Acoustic aspects of halls and auditoria

Cardinal Points:

Cardinal points of an optical system (definitions only), graphical construction of image using cardinal points, Newton's formula, relation between f and f' for any optical system, relation between lateral, axial and angular magnifications.

Interference:

Principle of Superposition, Coherence and condition for interference, Division of amplitude and division of wave front, Lloyds single mirror, Interference in thin parallel films, Wedge shaped films, Newton's rings and its application for determination of wavelength and refractive index of light.

Diffraction:

Fraunhofer diffraction, Fresnel's diffraction, Elementary theory of plane diffraction grating, Determination of wavelength of light using diffraction grating, Theory of Fresnel's half period zones, Zone plate, Fresnel's diffraction at straight edge.

Resolving Power of Optical Instruments:

Resolution, resolving power (RP) of optical instruments, Rayleigh's criterion for the limit of resolution, Modified Rayleigh's criterion, comparison between magnification and resolution, RP of plane diffraction grating, RP of a prism.

Polarization of Light:

Idea of polarization, polarization by double refraction, Huygens explanation of double refraction through uniaxial crystal, Nicol prism (construction, working), production of circularly and elliptically polarized light, optical rotation - laws of rotation of plane of polarization, polarimeter.

Classical Mechanics, Classical Electrodynamics and Quantum Mechanics

Lagrangian Formulation:

Constraints, Degrees of freedom, generalized coordinates, Principle of virtual work, D'Alembert's principle, Lagrange's equation from D'Alembert's principle, Applications of Lagrange's equation to a particle in space, Atwood's machine and a bead sliding on uniformly rotating wire under force free condition.

Techniques of Calculus of Variation:

Hamilton's principle, Deduction of Hamilton's principle from D'Alembert's principle, Deduction of Lagrange's equation from Hamilton's principle, Applications-shortest distance between two points in a plane, Brachistochrone problem.

Charged Particles Dynamics:

Poisson's and Laplace's equations and their physical significance, Laplace's equation in one dimension and its solutions, Motion of charged particle - in uniform electric field E, magnetic field B, Crossed uniform electric field E and magnetic field B.

Matter Waves

Wave particle duality, De-Broglie hypothesis of matter waves, Derivation of wavelength of matter wave, Concept of wave packet, Relation between group velocity - phase velocity and group velocity-particle velocity, Davisson and Germer experiment, Uncertainty principle (statements only): position-momentum and energy- time, Application of uncertainty principle- non existence of free electrons in the nucleus.

Schrodinger's Wave Equation:

Wave function and its physical interpretation, Condition of physically acceptable wave function, Normalized and orthogonal wave function, Schrödinger time dependent and time independent (steady state) wave equations in 1D and 3D, Probability current density (continuity equation), Eigen values and Eigen functions, Expectation values of dynamic variables.

Operators in Quantum Mechanics:

Definition of an operator, Position operator (x), Linear momentum operator (p), Commutation relation in quantum mechanics, Commutation relation between x and p, Kinetic energy operator (T), Hamiltonian operator (H), Parity operator (π), Angular momentum operator (L) – components of angular momentum operator in Cartesian coordinate system, Ladder operators, Eigen values of L_z and L^2 (use equations for L^2 and L_z in spherical polar coordinates).

Applications of Schrodinger Equation:

Particle in a rigid box (infinite potential well) in one dimension and three dimension, Step potential- reflection and transmission coefficients, Potential barrier- tunneling effect (qualitative treatment), One dimensional simple harmonic oscillator (operator method)- energy levels, zero point energy, Schrodinger equation for Hydrogen atom in spherical polar coordinates, Separation of radial and angular parts, Solution of radial part of Schrodinger's equation - Energy Eigen values.

Solid State Physics and Nuclear and Particle Physics

Crystal Structure: Solids, amorphous, polycrystalline and crystalline materials; lattice, basis, unit cell- primitive, non-primitive unit cell, symmetry operations, symmetry elements of cube, Bravais lattice in two and three dimensions, Miller indices, Miller indices and inter-planer spacing, Simple crystal structures: SC, BCC, FCC and HCP (Co-ordination number, atomic radius, atoms per unit cell and packing fraction) 2. X-Ray Diffraction

Reciprocal lattice and its properties, Brillouin zone, Diffraction of X-rays by crystals, Ewald construction, Bragg's law in reciprocal lattice, Experimental methods in X-ray diffraction (Laue method, rotating crystal method, powder photograph method), Analysis of cubic crystal by powder method.

Magnetic Properties of Matter: Classical Langevin theory of diamagnetic and paramagnetic materials, Quantum mechanical treatment of paramagnetism, Curie's law, Weiss theory of ferromagnetism and ferromagnetic domains, Explanation of B-H curve, Hysteresis and energy loss.

Superconductivity: Idea of superconductivity, Critical temperature, Critical magnetic field, Meissner effect, Type-I and Type-II superconductors, London equation and penetration depth, Isotope effect, Application (magnetic levitation)

Elementary Band Theory of Solids Concept of density of states, Bloch theorem (statement only), Kroning– Penny model, Origin of energy gap, Velocity of electrons according to 8 band theory, Effective mass of an electron, Distinction between metals, semiconductors and insulators, Hall Effect - Hall voltage and Hall Coefficient.

General Properties of Nuclei and Nuclear Model: Constituents of nucleus and their intrinsic properties, Quantitative facts about size, mass, charge density (matter energy), binding energy, average binding energy and its variation with mass number, Liquid drop model approach, Semi empirical mass formula, Magic numbers. Particle Accelerators: Need of accelerators, Cyclotron-construction, working, theory and its limitations, Principle of phase stable orbit, Synchrocyclotron - construction and working, Synchrotrons- electron synchrotron and proton synchrotron, Betatron - principle, construction and working condition, expression of energy gain.

Chemistry

Conductance, Corrosion, Electroplating, Electrochemistry, Thermodynamics, States of Matter, Chemical Kinetics, Gravimetric Analysis, Chromatographic Techniques, Water Analysis, Surface Chemistry, Petroleum Industries, Biofuels

Conductance, Corrosion, Electroplating and Electrochemistry:

Conductance: Introduction, Migration of ions. Hittorf's rule, Transference number, determination of transport number using Hittorf's method and moving boundary method, factors affecting transport number: nature of electrolyte, concentration, temperature, complex formation and degree of hydration. Conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Kohlrausch's law of independent migration of ions and its applications such as relations between ionic conductance, ionic mobility and transport number, determination of equivalent conductance at infinite dilution of weak electrolytes, determination of degree of ionization of weak electrolyte, solubility and solubility products of sparingly soluble salts.

Conductometric titrations. Introduction to conductivity measurement of nanomaterials in solution, Zeta Potential

Corrosion and electroplating:

Introduction of corrosion, Electrochemical theory of corrosion, Factors affecting on corrosion: Position of metals in the electrochemical series on the basis of standard reduction potential. Purity of metal iii. Effect of moisture. Effect of oxygen (differential aeration principle). Hydrogen overvoltage, Methods of protections of metals from corrosion alloy formation, making metal cathodic, controlling external condition. Coating-galvanising, Tinning, electroplating, metal cladding, organic coating.

Electroplating:

Electrolysis, Faraday's laws, Cathode current Efficiency, Basic principles of electroplating, cleaning of articles, Electroplating of chromium by anodizing.

Electrochemistry:

Concept of EMF of a cell. Measurement of EMF of a cell. Nernst equation and its importance. Types of electrodes. Standard electrode potential.

Nanophase electrochemistry (definition and application only)

Thermodynamics, States of Matter and Chemical Kinetics: Thermodynamics:

Introduction, Concept of Entropy: Definition, mathematical expression, unit. Physical significance of Entropy. Entropy changes for reversible and irreversible processes in isolated systems. Entropy changes for an ideal gas as a function of V & T and as function of P & T. Entropy change in mixing of gases. Entropy change in phase transformations. Third law of thermodynamics, standard entropy, application of third law of thermodynamics in determination of absolute entropy, Entropy changes in chemical reactions. Numerical problems. Concept of Nano thermodynamics.

States of Matter:

Introduction, States of matter and their properties.

Gaseous state: Postulates of Kinetic Theory of Gases and derivation of the kinetic gas equation. Ideal and Non-ideal gases, Deviation of real gases from ideal behavior, compressibility factor, causes of deviation. van der Waals equation of state for real gases. Explanation of real gas behavior by van der Waal's equation, Boyle temperature. Critical Phenomena: PV-isotherms of real gases (Andrew's isotherms), Continuity of state, Critical constants and their calculation from Vander Waals equation. Liquid state: Liquid crystals: Difference between liquid crystal, solid and liquid. Classification, structure of nematic, smectic and cholestric liquid crystal. Thermography and seven segment cell.

Numerical Problems. Plasma.

Chemical Kinetics:

The concept of reaction rates. Order and molecularity of a reaction. Rate equations for zero, first, second order reactions (both for equal and unequal concentrations of reactants, derivation not required). Determination of order of reaction by integration method, graphical method and half-life. Derivation of third order rate constant considering reaction with equal initial concentration. Characteristics and examples of third order reaction. Concept of activation energy. Effect of temperature, pressure, catalyst and other factors on reaction rates.

Theories of Reaction Rates: Collision theory and Activated Complex theory of bimolecular reactions. Comparison of the two theories (qualitative treatment only).

Catalysis (definition, classification, including enzyme catalysis with examples). Concept of nanocatalysis (definition and application only)

Gravimetric Analysis, Chromatographic Techniques and Water Analysis

Gravimetric Analysis:

Introduction, Gravimetric analysis by precipitation: nucleation, crystal growth, digestion/ageing, filtration, drying, ignition, weighing, optimum condition for good precipitation, Physical nature of precipitate, Purity of precipitate: co-precipitation, post-precipitation Organic precipitates and their applications.

Chromatographic Techniques:

Introduction, classification. Column chromatography: Introduction, types, Principle of adsorption column chromatography, solvent system, stationary phases, Methodology-Column packing, applications of sample, development, detection methods, recovery of components, Applications. Ion exchange chromatography: Introduction, Principle, Types and properties of ion exchangers, Methodology Column packing, application of sample, elution, detection/analysis, Applications.

Water Analysis:

Physical analysis of water: pH, Conductance, Color, Odor, Turbidity and taste, Chemical Analysis Total dissolved solids, Hardness and its determination, Salinity, Alkalinity, Acidity Sulphates, Nitrates, Dissolved oxygen, Chemical oxygen demand, Biological oxygen demand.

Surface Chemistry, Petroleum Industries, Biofuels

Surface Chemistry:

Introduction, Adsorption as a surface phenomenon, Definition of adsorption, adsorbent, adsorbate. Characteristics of adsorption. Factors affecting adsorption, Types of adsorption, Distinction between physical and chemical adsorption. Adsorption isotherms: Freundlich adsorption isotherm, Langmuir adsorption isotherm. BET equation. Applications of adsorption. Concept of surface area, pore size, pore volume of nanomaterials.

Petroleum Industries and Biofuels:

Petroleum industry Introduction, occurrence, composition of petroleum, resources, processing of petroleum, calorific value of fuel, cracking, octane rating (octane number), cetane number, flash point, petroleum refineries, applications of petrochemicals, synthetic petroleum, lubricating oils & additives.

Biofuels: Biodiesel, Bio-ethanol.

Concepts of sustainable development, circular economy, waste valorization, carbon credit,

Coordination Chemistry, Semi-Micro Qualitative Analysis, Transition Elements, Chelation, Carboxylic acids, Carbonyl Compounds, Amines, Diazonium Salts, Carbohydrates, Stereochemistry

Coordination Chemistry, Inorganic Semi-Micro Qualitative Analysis

Coordination Chemistry:

Introduction-Definition and formation of co-ordinate covalent bond in BF_3-NH_3 , $[\text{NH}_4]^+$ and H_2O . Terminology- Description of the terms- ligand, co-ordination number, coordination sphere. Effective atomic number rule. Distinguish between double salt and complex salt. Werner's theory. Postulates. The theory as applied to cobalt amines viz. $\text{CoCl}_3.6\text{NH}_3$, $\text{CoCl}_3.5\text{NH}_3$, $\text{CoCl}_3.4\text{NH}_3$, $\text{CoCl}_3.3\text{NH}_3$, IUPAC nomenclature of coordination compounds. Isomerism in complexes with C.N. 4 and 6. Geometrical Isomerism, Optical Isomerism. Structural Isomerism Ionization Isomerism, Hydrate Isomerism, Coordination Isomerism, Linkage Isomerism and Co-ordination position Isomerism Valence bond theory of transition metal complexes with respect to, C.N. = 4, complexes of Cu and Ni, C.N. = 6 complexes of Fe and Co Valence Bond Theory (VBT): Inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu (coordination numbers 4 and 6). Structural and stereoisomerism in complexes with coordination numbers 4 and 6. Drawbacks of VBT. IUPAC system of nomenclature.

Inorganic Semi-Micro Qualitative Analysis:

Theoretical principles involved in qualitative analysis.

Applications of solubility product and common ion effect in separation of cations into groups.

Applications of complex formation in

- Separation of II group into IIA and IIB sub-groups.
- Separation of Copper from Cadmium.
- Separation of Cobalt from Nickel.
- Separation of Cl^- , Br^- , I^- .
- Detection of NO_2^- , NO_3^- (Brown ring test).

Application of oxidation and reduction in a) Separation of Cl^- , Br^- , I^- in mixture

b) Separation of NO_2^- and NO_3^- in mixture.

Chemistry of Elements of 3d, 4f Series Elements, Chelation

3d Series Elements:

Position of elements in periodic table

Characteristics of d-block elements with special reference to i) Electronic structure ii) Oxidation states, stability of oxidation states of Fe with respect to Latimer diagram iii) Magnetic character iv) Colored ions v) Complex formation.

4f Series Elements:

Position of lanthanides in periodic table, Occurrence Characteristics of 4f elements with special reference to 1. Electronic configuration 2. Oxidation states 3. Magnetic properties 4. Lanthanide contraction Separation of lanthanides by ion exchange method.

Chelation: A brief introduction with respect to ligands, chelating agent, chelation and metal chelates. Structural requirements of chelate formation. Difference between metal chelate and metal complex. Classification of chelating agents (with specific illustration of bidentate chelating agents). Application of chelation with respect to chelating agents - EDTA and DMG.

Carboxylic acids and derivatives, Carbonyl Compounds, Amines, Diazonium Salts

Carboxylic acids and derivatives:

Carboxylic acids (aliphatic and aromatic) Preparation: Acidic and Alkaline hydrolysis of esters. Monocarboxylic acid: Introduction, Methods of Formation from Alcohols, Aldehydes, Ketones, Nitriles and Alkyl benzenes.

Halo acids: a) Synthesis of halo acids-Mono, Di, Tri- chloro acetic acid by HVZ reaction b) Reactions - Substitution reaction of Monochloro acetic acid by Nucleophile OH^- , I^- , CN^- and NH_3 , Hydroxy acids: Citric acid, Methods of formation of Citric acid from glycerol. Chemical Reactions: Reaction of citric acid: acetylation by acetic anhydride, reduction by HI , action of heat.

Di carboxylic acids: Introduction, Method of formation of succinic acid from ethylene dibromide, maleic acid, Chemical Reactions: Action of heat, Action of NaHCO_3 , $\text{C}_2\text{H}_5\text{OH}$ in presence of

Acid. Method of formation Phthalic acid from o-xylene and Naphthalene, Chemical Reactions of Phthalic acid : Action of heat, reaction with sodalime, ammonia. Carboxylic acid derivatives: Introduction, Acid halide derivative: Acetyl chloride: Synthesis from acid, by action with PCl_3 and SOCl_2 . Reaction with water, alcohol (Mechanism of esterification is expected) and ammonia. Acid anhydride derivative: Synthesis of acetic anhydride by dehydration of acetic acid. Reactions with water, alcohol and ammonia. Hell – Vohlard - Zelinsky Reaction. Carboxylic acid derivatives (aliphatic): (Upto 5 carbons). Comparative study of nucleophilicity of acyl derivatives. Use of carboxylic acids and derivatives for nanoparticle synthesis and stabilization like citric acid, oxalic acid. (examples with schemes only).

Carbonyl Compounds:

Introduction, Nomenclature of aliphatic and aromatic aldehydes and ketones. Structure and reactivity of Carbonyl group. Reactions of Carbonyl Compounds- Mechanism and applications of ----

i) Aldol condensation, ii) Claisen and Benzoin Condensation, iii) Perkins reaction, iv) Cannizaros reaction, v) Knoevenagel condensation and vi) Reformatsky reaction. vii) Perkin condensation.

Amines, Diazonium Salts:

Amines: i) Introduction, Classification and Nomenclature ii) Methods of preparation: a) From alkyl halide by amonolysis

b) By reduction of nitriles or cyanides c) From unsubstituted amides (Hoffmann degradation), d) By Gabriel synthesis (From Phthalamide). iii) Reactions: Carbylamine reaction, SchottenBaumann reaction, Electrophilic substitution (Aniline) - Nitration, Bromination, Sulphonation. Diazonium salt: i) Introduction. ii) Preparation of Benzene diazonium chloride. iii) Reactions of Benzene diazonium chloride. a) Replacement reaction -Sandmeyer's reaction. b)

Coupling reactions: Synthesis of Congo red. Concept of catalytic reduction reaction of p-nitrophenol to p-amino phenol towards circular economy.

Carbohydrates, Stereochemistry

Carbohydrates:

Introduction Classification of carbohydrates, reducing and nonreducing sugars. Physical properties of glucose and fructose. Killiani's synthesis of Glucose from D- Arabinose. Determination of structure of D-Glucose. a) Open chain structure of D- Glucose. b) Configuration of D- Glucose from D- Arabinose. c) Ring structure of D- Glucose. d) Size of ring in D- Glucose by methylation Method. e) Haworth projection for D- Glucose. Cyclic structure of Fructose. Structures of Disachharides: a) Linkage between Monosachharides. b) Open chain and Haworth cyclic structures of Sucrose, Lactose and Maltose. Structures of Polysachharides: a) Starch b) Cellulose

Concept of glucose as reducing agent for nanoparticle synthesis, nanocellulose and their sources.

Stereochemistry:

Basic Concept of stereochemistry, Introduction to D/L, d/l, R/S, E/Z nomenclature, Stereochemistry of Carbohydrate (few examples) and Symmetry elements and operations (concepts only)

Inorganic and Organic Chemistry:

Theories of Acids, Bases, Chemistry of f-Block Elements, Metal Bondings in Transition Metal Complex and Co-ordination Chemistry, Organic Reagents, and Reactions

Acids, Bases and Non-aqueous Solvents and Chemistry of f- Block Elements:

Introduction to theories of Acids and Bases-Arrhenius concept, Bronsted-Lowry concept, Lewis Concept, Lux-Flood Concept (definition and examples), Hard and Soft Acids and Bases. (HSAB Concept), Classification of acids and bases as hard, soft and borderline. Pearson's HSAB concept. Acid-Base strength and hardness-softness. Applications and limitations of HSAB principle. Chemistry of Non aqueous Solvents. Introduction, definition and characteristics of solvents. Classification of solvents. Physical properties and Acid-Base reactions in Liquid Ammonia (NH₃) and Liquid Sulphur Dioxide (SO₂).

Lanthanides: Introduction and Occurrence. Electronic Configuration. Oxidation State. Lanthanide contraction. Separation of Lanthanides by Ion exchange method.

Actinides: Position in periodic table. Electronic configuration. General methods of preparation of transuranic elements. Neutron capture – followed by β decay. Accelerated projectile bombardment. Heavy ion bombardment. IUPAC nomenclature of the super heavy elements with atomic number (Z) greater than 100.

Metal Ligand bonding in Transition Metal Complexes and Co-ordination Chemistry

Crystal field theory (CFT): Introduction: Shapes of d-orbitals, Basic assumptions of CFT. Crystal field splitting of d-orbitals of metal ion in octahedral, tetrahedral, square planar complexes and John-Teller distortion. Factors affecting the Crystal field splitting. High spin and low spin octahedral complexes w.r.t. Co (II). Crystal Field stabilization energy (CFSE), Calculation with respect to octahedral complexes only. Limitations of CFT.

Molecular orbital theory (MOT): Introduction, MOT of octahedral complexes with sigma bonding. Merits and demerits of MOT.

Coordination Chemistry: Inorganic Reaction mechanism Introduction, Classification of Mechanism: Association, dissociation, interchange and the rate determining steps. S_N^1 and S_N^2 reactions for inert and labile complexes. Mechanism of substitution in cobalt (III) octahedral complexes. Trans effect and its theories. Applications of trans effect in synthesis of Pt (II) complexes.

Reagents and Reactions in Organic Synthesis and Retrosynthesis Reagents: Preparation and Applications of following reagents. Lithium aluminium hydride $LiAlH_4$. Raney Nickel. Osmium tetroxide. Selenium dioxide (SeO_2). Dicyclohexyl Carbodiimide (DCC). Diazomethane.

Reactions : Statement, General Reaction, Mechanism and Synthetic applications: Diels -Alder reaction. Meerwein -Pondorff-Verley reduction. Hofmann rearrangement. Wittig reaction. Wagner-Meerwein rearrangement. Baeyer Villiger oxidation. Problem based on above reactions.

Retrosynthesis: Introduction. Recapitulation of basics of reaction mechanism and reagents. Terms used- Target molecule (TM), Disconnection, Synthons, Synthetic equivalence, Functional group interconversion (FGI), one group disconnection (w. r. t. suitable examples). Retrosynthetic analysis and synthesis of target molecules: Cinnamaldehyde, Cyclohexene, para methoxy acetophenone, Methyl-3-phenyl propionate, α,α -dimethyl benzyl alcohol, Paracetamol.

Electrophilic addition to $>C=C<$ and $-C\equiv C-$ bonds and Natural products

Addition to Carbon-Carbon double ($>C=C<$): Introduction. Examples of addition reactions. Mechanism of electrophilic addition to $>C=C<$ bond, $C=C<$ bond, orientation & reactivity, Hydrohalogenation. Anti-Markovnik off's addition (peroxide effect). Rearrangements (support for formation of carbocation). Addition of halogens. Addition of water. Addition of hypohalous acids ($HO-X$). Hydroxylation (formation of 1,2-diols). Hydroboration-oxidation (formation of alcohol). Hydrogenation (formation of alkane). Ozonolysis (formation of aldehydes & ketones).

Addition to Carbon-Carbon triple ($-C\equiv C-$) bond: Introduction. Examples of addition reactions. Mechanism of electrophilic addition to $-C\equiv C-$ bond. Addition of halogens. Addition of halogen acids. Addition of hydrogen. Addition of water. Formation of metal acetylides. Named Reactions [4] Diels -Alder reaction. Meerwein -Pondorff-Verley reduction. Hofmann rearrangement. Wittig reaction. Wagner- Meerwein rearrangement. Baeyer Villiger oxidation.

Physical Chemistry

(Elements of Quantum Mechanics, Chemical Kinetics, Thermodynamics, Chemistry of Solutions, Solid State Chemistry, Electrochemistry, Spectroscopy and Photochemistry)

Elementary quantum mechanics, Thermodynamics and Chemical Kinetics

Elementary quantum mechanics: Introduction, Drawbacks of classical mechanics, Black body radiation, Photoelectric effect, Compton effect, Dual nature of matter and energy: De Broglie hypothesis. The Heisenberg's uncertainty principle. Concept of energy operators (Hamiltonian). Derivation of Schrodinger wave equation, well behaved function. Physical interpretation of the ψ and ψ^2 . Particle in a one dimensional box. Numerical problems.

Thermodynamics: Introduction. Free energy: Gibbs function (G) and Helmholtz function (A), Criteria for thermodynamic equilibrium and spontaneity. Relation between ΔG and ΔH : Gibbs-Helmholtz equation. Phase equilibria: Clapeyron - Clausius equation and its applications. Thermodynamics derivation of law of mass action, Van't - Hoff isotherm and isochore. Fugacity

and activity concepts. Partial molar quantities, Partial molar volume, Concept of chemical potential, Gibbs-Duhem equation. Numerical problems.

Chemical Kinetics and Catalysis: Introduction. Simultaneous reactions such as: Opposing reaction: (Derivation of rate equation for first order opposed by first order expected). Side reaction. Consecutive reactions. Chain reaction. Explosive reaction (Derivation of rate equation and Numerical problems are not expected).

Catalysis: Introduction. Classification of catalytic reaction- Homogenous and Heterogeneous. Types of Catalysis. Characteristics of catalytic reactions. Mechanism of catalysis. Intermediate compound formation theory. Adsorption theory. Industrial applications of catalysis.

Solid State Chemistry, Solutions, Phase Equilibria and Distribution Law:

The Solid State: Introduction: Space lattice, lattice sites, lattice planes, unit cell. Laws of crystallography: Law of constancy of interfacial angles, Law of rational indices, Law of crystal symmetry. Weiss indices and Miller indices. Cubic lattice and types of cubic lattice, planes or faces of a simple cubic system, spacing of lattice planes. Diffraction of X-rays, Derivation of Bragg's equation. Determination of crystal structure by Bragg's method. Determination of crystal structure of NaCl and KCl on the basis of Bragg's equation. Numerical problems. Solutions Introduction. Ideal solutions, Raoult's law, Vapour pressure of ideal and non ideal solutions of miscible liquids. Composition of liquid and vapour, vapour pressure and boiling point diagrams of miscible liquids. Distillation of miscible liquid pairs. Type I : Systems with intermediate total vapour pressure (i.e. System in which b.p. increases regularly – Zeotropic). Type II : Systems with a maximum in the total vapour pressure (i.e. System with a b.p. minimum – Azeotropic). Type III : Systems with a minimum in the total vapour pressure (i.e. System with a b.p. Maximum – Azeotropic). Solubility of partially miscible liquids. Maximum solution temperature type: Phenol – water system. Minimum solution temperature type: Triethyl amine – water system. Maximum and minimum solution temperature type: Nicotine – water system. Distillation of partially miscible liquid pairs. Vapour pressure and distillation of immiscible liquids, steam distillation.

Phase Equilibria: Introduction. Gibbs phase rule : Phase rule equation and explanation of terms involved in the equation. Phase diagram, true and metastable equilibria. One component systems: Water system. Sulphur system with explanation for polymorphism. Two component systems: Eutectic system: (Ag – Pb system); Desilverisation of lead. Freezing mixture: (KI – H₂O system). Formation of compound with congruent melting point (FeCl₃ – H₂O). Three component solidliquid system: Development of triangular phase diagram: (Acetic acid – Chloroform – water system). **Distribution law:** Introduction, solute, solvent and solution, miscible and immiscible liquids. Nernst distribution law and its limitations. Modification of distribution law with respect to change in molecular state of solute (association and dissociation of solute in one of the solvent). Applications of the distribution law: Process of extraction (derivation expected). Determination of solubility of solute in particular solvent. distribution indicators. determination of molecular weight of solute in different solvents. Numerical problems.

Electromotive force: Convention: Reduction potentials to be used) Introduction. Thermodynamics of electrode potentials, Nernst equation for electrode and cell potentials in terms of activities. E.M.F. series. Types of electrodes: Description in terms of construction, representation, half cell reaction and emf equation for: Metal – metal ion electrode. Amalgam electrode. Metal – insoluble salt electrode. Gas – electrode. Oxidation – Reduction electrode. Reversible and Irreversible cells. Chemical cells without transference. Concentration cells with and without transference. Liquid – Liquid junction potential: Origin, elimination and

determination. Equilibrium constant from cell emf, Determination of the thermodynamic parameters such as ΔG , ΔH and ΔS . Applications of emf measurements: Determination of pH of solution using Hydrogen electrode. Solubility and solubility product of sparingly soluble salts (based on concentration cells). Numerical problems.

Spectroscopy and Photochemistry

Spectroscopy: Introduction. Electromagnetic radiation. Interaction of radiation with matter, Electromagnetic spectrum, Energy level diagram. Electronic Spectra (UV-Vis), Modes of electronic transitions. Rotational spectra of diatomic molecules: Rigid rotor model, moment of inertia, energy levels of rigid rotor, selection rules, Intensity of spectral lines, determination of bond length, isotope effect, Microwave oven. Vibrational spectra of diatomic molecules: Simple Harmonic oscillator model, Vibrational energies of diatomic molecules, Determination of force constant, Hook's Law for Calculation of vibrational frequency, overtones. Raman spectra: Concept of polarizability, pure rotational and pure Vibrational Raman spectra of diatomic molecules, selection rules. Comparative study of IR and Raman spectra, rule of mutual exclusion- CO₂ molecule. Magnetic Resonance (NMR and ESR). Magnetic and nonmagnetic nuclei, Chemical shift: definition, measurement, calculation, Factors affecting Chemical shift, Shielding & deshielding. Numerical problems.

Photochemistry: Introduction, Difference between thermal and photochemical processes. Laws of photochemistry: i) Grotthus - Draper law ii) Lambert law iii) Lambert – Beer's law (with derivation) iv) Stark-Einstein law. Quantum yield, Reasons for high and low quantum yield. Factors affecting Quantum yield. Photosensitized reactions – Dissociation of H₂, Photosynthesis. Photodimerisation of anthracene. Jablonski diagram depicting various processes occurring in the excited state: Qualitative description of fluorescence and phosphorescence. Chemiluminescence, Electroluminescence and Bioluminescence. Numerical problems.

Nanoscience and Technology

Phy & Chem. at Nanoscale: Physics and Chemistry at Nanoscale

Introduction to Nanoscience: Introduction to Nanoscale, Nanomaterials, Nanoscience and Nanotechnology. Nanoscience effects: Quantum size effects, Quantum confinement effect, Bohrexciton radius, surface area to volume ratio etc. The development of nanoscale science: scaling up approach, scaling down approach, Generations of nanotechnology/ Nanotechnology Timeline: Pre-18th Century, 19th Century, 20th Century, 21st Century. Classification of nanomaterials: 0D, 1D, 2D and 3D and types of nanomaterials (QDs, QW, CNT's, Bucky Balls, etc.) Nanocomposites: Types of nanocomposites and applications. Nano and Nature: Lycurgus Cup, stained glass windows, Damascus saber blades, Nanoscopic colours (Butterfly wings), Bioluminescence (fireflies), Tribology, Nano tribology (Gecko's Sticky Feet, Nasturtium Leaf/Lotus effect etc.) in nature. Brief applications of nanomaterials / Consumer products: Television, Energy, Automobile, Textile, Space, Defense and Engineering etc.

Making of nanostructures: Top down: Overview of top down nanofabrication processes. Mechanical methods: Mechanical grinding (ball milling), Lithographic methods: Types of lithography techniques i.e. photolithography, electron beam lithography, X-ray lithography, Nanoimprint lithography. Thin film technologies: Thermal methods: Thermal evaporation, e-

beam evaporation. Plasma methods: DC and RF Magnetron Sputtering, High-energy methods: Pulsed Laser Deposition etc. Advantages and disadvantages of Top down approaches.

Making of nanostructures: Bottom up: Overview of bottom up nanofabrication processes. Growth mechanism: nucleation and growth of nanomaterials: Ostwald Ripening, sintering. Vapor – phase synthesis: Chemical vapor deposition (CVD): Types of CVD process, Atomic Layer Deposition, Molecular beam epitaxy (MBE), Inert gas condensation, Spray Pyrolysis, Flame pyrolysis. Liquid-phase synthesis: Colloidal methods: Metal and semiconducting nanoparticles, Solution precipitation, Electrodeposition, Sol-gel technique: Introduction. Sol-gel process: synthesis of Aerogel, Xerogel, sol-gel coating processes. Hydrothermal synthesis, Dip coating, spin coating, flow coating etc. Template synthesis of nano patterning. Advantages and Disadvantages of Top down approaches.

Visualization and manipulation tools Microscopy: Basics, Working principle and applications. Optical microscopy, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM). Difference between SEM and TEM. Scanning Probe Microscope (SPM) techniques: Scanning Tunneling Microscopy (STM) and Atomic force microscopy. Optical Tweezers: Basics, Working principles and applications.

Phy. & Chem. Prop. of Nanomat.: Physical and Chemical Properties of Nanomaterials

Physical Properties of Nanomaterials Mechanical Characterization – Plastic deformation, Toughness, Stiffness, Ductility, modulus and load carrying capability, fatigue – abrasion and wear resistance etc. Stress-Strain Curve. Hardness of nanomaterials: Nanoindentation, Nanomachines, Mechanical properties of CNT. Micro Electromechanical Systems (MEMS), Nano Electromechanical Systems (NEMS). Thermodynamics of Nanomaterials: Melting point and phase transition processes at nanoscale materials. Classical thermodynamics Vs Nano thermodynamics.

Electronic Properties of Nanomaterials: Density of states of 3D, 2D, 1D and 0D dimensional nanostructures. Clusters of metals and semiconductors, nanowires. Size-induced metal insulator transition (SMIT). Electronic transport in 1, 2 and 3 dimensions. Effective mass, Drude conduction of metals - mean free path in 3D-diffusive transport and ballistic conduction. Coulomb blockade. Single electron transistors (SET), Tunnel diodes: Esaki tunneling diode (ETD), Resonant tunneling diode (RTD). Fundamentals of electrical conductivity in carbon nanotubes. CNT based 15 transistor, electrical conductivity of nanocomposites.

Optical properties of Nanomaterials Interaction of light with matter: Absorption-Emission. Direct and indirect band gap transitions, radiative - nonradiative process, photoluminescence. Surface Plasmon: Interaction of light with metal, scattering, extinction. Difference between Surface Plasmon Resonance (SPR) and Localized Surface Plasmon Resonance (LSPR). Origin of color generation from metal nanoparticles, Size and Shape dependent optical properties of metal nanoparticles. Applications of nano plasmonics. Quantum dots (QDs): optical properties of QD nanomaterials. Size dependent band gap tuning: optical absorption and optical emission. Optical properties of core-shell nanomaterials. Optoelectronic applications of nanomaterials: detection, PV solar cells, photoelectrochemical cells, light emitting diodes etc.

Magnetic properties of nanomaterials: Origin of magnetism in materials, Classification into Dia-, Para- and Ferro- magnetic materials, Hysteresis in ferromagnetic materials, domains, soft and hard magnetic materials, Coercivity vs particle size, Single domain particles, superparamagnetism, Exchange coupling in magnetic multilayers (RKKY Coupling), Giant Magnetoresistance (GMR), Origin of GMR, Oscillatory exchange coupling, spin valve, Magnetic Tunnel Junction (MTJ), Spin Field Effect Transistor (SFET).

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