CHEMISTR SYLABUS

Physical Chemistry

Chemical Kinetics

Factors influencing the rate of reactions – concentration, temperature, pressure, solvent, light and catalyst.Order and molecularity of reactions, mathematical expressions for rate constants of first order,second order and n^{th} order reactions.Expression for half life of first order,second order and n^{th} order reactions. Arrhenius equation, energy of activation, simple collision theory, mechanism of bimolecular reaction, Lindeman's theory, Hinshelwood's theory for unimolecular reaction, Activatedcomplex theory of reaction rate, classical thermodynamic treatment.

Gaseous State

Maxwell – Boltzmann distribution law, mathematical expression for mole and molecule, mean free path, collision frequency and collision number, Definition and expressions using SI units, Definition and expression for rms velocity and average velocity and relationship between them.

Laws of corresponding states – Statements reduced equation of state and explanation, Joule's Thomson effect, Joule – Thomson Co – efficient inversion temperature definition. Applications of Joule Thomson affect to the liquifaction of air.

Solid State

Structural difference between solid, liquid and gases.Space lattice definition, Laws of Crystallography – (Law of constancy of interfacial angles, Law of rationality of indices,Law of symmetry), Symmetry of elements in crystals, crystal systems, Miller indices, Bravais lattices, X-ray diffraction study of crystals.Bragg's Law, Co-ordination number in ionic solids, study of structures of NaCl, CsCl, ZnS, CaF_2 crystals, liquid crystals – classification and applications.

Photochemistry

Introduction to photochemistry, quantum yield and its determination, factors affecting quantum yield, Actinometry-Uranyloxalate and potassium ferrioxalateactinometers, acetone and diethylketoneactinometers. Term symbols and significance.Photosensitization by mercury, dissociation of H_2. Photochemical kinetics of: Decomposition of CH_3CHO, formation of HCl. Photodegradation, Photocatalyst – ZnO, TiO_2, Principle, application of ZnO/TiO_2 in the photo degradation of dyes (IC), pesticides (DDT) and in industrial effluents. Effect of photodegradation on COD value.

Radiation Chemistry

Introduction, units, interaction of electromagnetic radiation with matter, G-vale, LET of radiation, dosimetry, Fricke and cericsulfate dosimeters. Radiolysis – cysteine, and biphenyl. Radioisotopes as tracers, use of isotopic tracers in the elucidation of reaction mechanism, structure determination and solubility of sparingly soluble substances. Carbon dating, isotope dilution, neutron activation analysis, radiometric titrations and medicinal applications of isotopic tracers.Hazards in radiochemical work and radiation protection.

Surface chemistry

Types of adsorption isotherms, effect of temperature on adsorption, mechanical adsorption, estimation of surface area using BET equation, Gibbs adsorption isotherm, surface tension and surface energy, pressure difference across curved surface(Laplace equation). Kelvin equation, electro-kinetic Phenomenon) catalytic activity of surfaces.

Solutions

Types of solutions, Raoult's law, ideal and non ideal solutions. Vapors Pressure – composition and boiling point – composition diagrams for above types principles of fractional distillation. Azeotropic mixtures.CST with respect to water – phenol system and nicotine water system.Solution of gases in liquids. Henry's Law

Electrochemistry

Arrhenius theory of strong and weak electrolytes and its limitations, Lewis acids and bases, Acid-base concept in non-aqueous media, leveling effect, super acids.Debye-Huckel theory of strongelectrolytes, Debye Huckel-Onsager equation, Debye-Huckel limiting equation for activitycoefficients, Debye-Huckel equation for appreciable concentrations.A brief survey of Helmholtz-Perrin, Gouy-Chapman and Stern electrical double layer.Liquid junction potential and itsdetermination. Transport Number**:** Determination of transport number by Hittorf method and emfmethod. True and apparent transport numbers. Abnormal transport numbers, effect of temperatureand concentration on transport number. Energetics of cell reactions, effect of temperature, pressure andconcentration on energetics of cell reactions (calculation of ΔG, ΔH and ΔS).Electrochemical energysources –Batteries, classification, characteristics, primary, secondary and lithium batteries, super capacitors and fuel cells.

Irrversible electrode process- Introduction, reversible and irreversible electrodes reversible andirreversible cells. Polarization, over voltage-types, Equations for concentration over potential,diffusion current –stationary current, potential curves, thickness of diffusion layer, diffusion controlledcurrent –potential curves at a dropping mercury electrode, polarography, half wave potential,application in qualitative and quantitative analysis. Energy barrier and electrode kinetics, Butler-Volmer equation, Tafel equation.Hydrogen over voltage-mechanism, bubble formation

theory,Tafel'stheory, Gurney's quantum mechanical theory.Eyring- Laidler-Glasstone theory, Oxygen overvoltage.Effect of temperature, current density and pH on over voltage.

Corrosion:

Manifestations of corrosion, types of corrosion, basis of electrochemical corrosion,theories of corrosion. Local cell theory (Wagner and Traud theory) Current –potential relations (Evandiagram) in corrosion cells.Effect of pH, nature of metal and dissolved oxygen (principle ofdifferential aeration) on corrosion.Corrosion inhibition and prevention by painting, phosphating,corrosion protection by Anodic (passivation) and cathodic protection.

Ionic Equilibrium:

Hydrolysis of salts of weak acids and weak bases, Ionic product of water, relationship between Kh, Kw, Ka& Kb Buffers, buffer action and buffer capacity, PH of buffers, solubility product & ionic product in precipitation in qualitative analysis, Analytical and biological applications of buffers.

Thermodynamics

First law of thermodynamics:

Statement, definition of internal energy and enthalpy.Heat capacity, heat capacities at constant volume and pressure and their relationship.Joule's law – Joule-Thomson coefficient and inversion temperature.

Bond dissociation energy and its calculation from thermo-chemical data, temperature dependence of enthalpy.Kirchhoff's equation.

Second law of thermodynamics:

Need for the law, different statements of the law. Carnot cycle and its efficiency, Carnot theorem.Thermodynamic scale of temperature.

Concept of entropy, entropy as a state function, entropy as a function of V & T, entropy as a function of P & T, entropy change in physical change, Clausius inequality, entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases.

Third laws of thermodynamics:

Gibbs and Helmholtz functions; Gibbs function(G) and Helmholtz function (A) as thermo-dynamic quantities A &G as criteria for thermodynamic equilibrium and spontaneity, their advantage over entropy change. Variation of G with PVT.

Chemical Equilibrium

Equilibrium constant and free energy.Thermodynamic derivation of law of mass action, Le Chatelier's principle.Reaction isotherm and reaction isochore-Clapeyron equation and Clausius-Clapeyron equation, applications.

Phase Equilibrium

Statement and meaning of the terms – phase, component and degree of freedom, derivation of Gibbs phase rule, phase equilibria of one component system-water, and S systems. Phase equilibria of two component system : simple eutectic- Pb-Ag system, desilverisation of lead. Solid solutions: Compound formation with congruent melting point (Mg-Zn) and incongruent melting point, (NaCI-H2O), Freezing mixtures, acetone-dry ice.

Nuclear chemistry:

Radioactive laws, Radioactive decay – general characteristics, decay kinetics, parent – daughter decay growth relationships, determination of half-lives, Nuclear models- shell model, liquid drop model, Fermi gas model, Collective model and optical model, Nuclear stability – packing fraction, binding energy, proton-neutron ration, magic number, nuclear stability with respect to beta decay. Theories of alpha, beta and gamma decays. Nuclear reactions – Bethe's notation, types of nuclear reactions – specific nuclear reactions, photonuclear reactions, fission and fusion reactions, Oppenheimer – Phillips process, spallation reactions, conservation in nuclear reactions, reaction cross section.

Definition of curie and related calculations, preparation of artificial radionuclides by bombardment radiochemical separation techniques (carriers, solvent extraction and ion exchange), Szilard-Chalmers process.

Experimental techniques in the assay of radio isotopes, gas filled detectors-ionization chamber, proportional and Geiger-Muller counter-G.M Plateau, dead time, coincidence loss, determination of dead time, scintillation counters, solid state detectors.

Colloidal State:

Colloidal solutions – Types, preparation, examples. electrical concept of sols, Zeta potential, Electro-osmosis, Coagulation of colloids, Gold number, Kinetic properties- Tyndall effect, Brownian movement, Electrophoresis, general applications of colloids emulsions-types, preparation, emulsifying agent and applications.Methods of purification of sols, dialysis, electrodialysis, ultrafilteration.

Spectroscopy:

Ultraviolet, visible and vibration spectroscopy, application of IR in the study for H – bonding, stercoisormerism and Tautomerism. Identification of organic-compounds by IR, NMR Spertoscopy

Industrial Chemistry

1) Fuels :- calorific value, gaseous fuels –production, composition and applications of water gas, producer gas, natural gas, liquid petroleum gas, biogas.
2) Explosives:- TNT, Nitroglycerine, Propellants- Composition, types.
3) Glass:- Raw materials, types of glasses, composition, uses. Annealing of glass.
4) Cement:- Raw materials, manufacture, setting mechanism, grade of cements.

5) Ceramics:- Production and applications of ceramics, Insulators,High temperature Super-conductors-preparation and applications, Meissner effect.
6) Paints:- Constituents of paints and their functions, White lead and litho phone.
7) Refractories and abrasives:- Definition, manufacture (silicon carbide) and uses.
8) Chemical Fertilizers:- Definition, types, composition and uses. Manufacture of urea, superphosphate of lime.
9) Paper:-Raw materials and production of paper.
10) Fats, oils & detergents:- Natural fats, edible and industrial oils of vegetable origin, hydrogenation of unsaturated oils. Saponification number, Iodine value, acid value, soaps and syndets, manufacture, cleansing action of soaps.
11) Synthetic Polymers:- Definition, ionic vinyl-polymerization, Ziegler-Natta Polymerization and vinyl-polymers. Polyesters, phenol formaldehyde resins, epoxy resins. Natural and synthetic rubbers and uses. Conducting polymers.
12) Inorganic polymers- Definition, differences between inorganic and organic polymers, glass transition temperature (Tg), Fluorocarbon polymers- Definition- examples- preparation, properties and uses of freon12, Freon 22, PTFE and polyperfluorovinyl chloride, Phosphorous based polymers- phosphazenes (chain and cyclic polymers)- Definition types and structures, crystalline polymetaphosphates, Maddrell's salts, Kuroll's salts, application of phosphorous-based polymers, Sulphur based polymers-polymeric sulphurnitride $(SN)_n$ and Chalcogenide glasses, preparation, properties, structure and applications- Silicone based polymers-types, preparation, properties and uses of sililcones. rubbers or elastomers, silicone resins, metal co-ordination polymers.

Environmental Chemistry

a) Ecosystem:- The atmosphere, lithosphere, hydrosphere biosphere.
b) Air pollution:- Air pollutants-examples, their sources effect and control
c) Water Pollution:- Types of water Pollutants, Biodegradation, dissolved oxygen level of water, COD of water, Industrial effluents, their effects, sewage water treatment
d) Soil Pollution:- Pollutants – examples, study of their effects.
e) Effects of toxic pollutants on biosphere
f) Formation of ozone layer in atmosphere, effects of pollutants on ozone layer.
g) Disposal mechanism of solid wastes and nuclear wastes.

Biochemistry

a) **Carbohydrates**:- Classification, Examples, Biological importance. Configuration, relationship of D-aldoses, D- ketoses. General properties of aldoses and ketoses- oxidation, reduction, reducing property, formation of glycosides, acylation, methylation, condensation with phenylhydrazine, addition of HCN,

interconversion of aldoses and ketoses by chemical method. Stereochemistry of Monosaccharides (+) and (-), d and l, epimers, anomers and diastereoisomers.

b) **Vitamins**:- Classification-water soluble and fat soluble. Structural formula and coenzymic forms of vitamin B_1, B_2, B_6 and niacin, vitamin C as a redox reagent, properties and chemical synthesis. Structural formula of vitamin A,D,E& K.

c) **Nueleic acid**:- Isolation of DNA & RNA, composition of DNA- Nucleosides and Nucleotides, Chargaff's rule, Watson and Crick model of DNA, melting of DNA.

RNA Composition, Types of RNA.Colour reactions of DNA & RNA. Chemical reactions of RNA & DNA with acid and alkali

d) **Amino acids and Proteins**:-Properties of amino acids, peptides and peptide bond, biological applications.Proteins- Biological importance, classification based on structure, composition and biological functions.

Enzymes- Classification with examples, Theories of enzyme catalysis, RNA as an enzyme.

e) **Hormones**:- Definition, Classification with examples. Role of insulin and glucagon in glucose metabolism

f) **Lipids**:- CMC (critical micellar concentration), Liposome's definition and applications. Clinical significance of lipoproteins and cholesterol.

Inorganic Chemistry

Quantum Mechanics and Atomic structure

Prograssive and stationary waves, wave equation for a stationary wave (stretched ring) Dual nature of wave particle, debroglie relation, physical interpretation of wave function, concept of operators, Algebra of operators, commutative and non commutative operators, laplacian operator, Eigen value, Eigen function.

Schrodinger equation for particles, Application of Schrodinger equation to a free particle and to a particle trapped in a potential field.

Wave nature of electron, wave equation for H-atom,Heisenberg's uncertainty principle, quantum numbers, Paul's exclusion principle, Aufbau principle, Hund's rule, shapes of orbital's, p,d and f. Electronic configuration of elements.

Chemical bonding

Ionic bond-Lattice energy, Born Haber cycle, Covalent bond, Concept of resonance and resonance energy, hybridization, VSEPR theory, shapes of molecules, Electronegativity and partial ionic character,Fajans rule, molecular orbital theory of simple diatomic molecules.

Co-ordinate bond, hydrogen bond,metallic bond.

s-andp-block Elements

Structure and bonding in boranes, carboranes, borazines. Oxyacids of nitrogen, phosphorous, sulphur and halogens. Nobel gases and their importance, structure and applications of xenon and krypton compounds XeF_2, XeF_4, XeF_6, KrF_2, KrF_4.Classification of silicates. Importance of phosphorous,sulphurand selenium compounds in biological system.

d-andf-block Elements

Comparative study of properties of transitional elements of 3d-series with respect to oxidation states, ionization energy, colour, magnetic properties and complex formation.

Lanthanides- oxidation states, colour, magnetic properties and complex formation, separation of lanthanides by ion exchange method, lanthanide contraction and its consequences.

Actinides – General features, chemistry of separation of Np,Pu& Am from Uranium, similarities between the later actinides and the later Lanthanides.

Uranium – Isotope separation/ enrichment, Chemical properties, hydrides,Oxides and halides,Chemistry of Trans uranium elements.

Co-ordination compounds

Nomenclature of co-ordination compounds, Isomerism- Structural, geometrical and optical isomerism, Theory of complexes- VBT, CFT and LFT of transition metal complexes, applications of complexes.

Metallurgy

Types of metallurgy, Pyrometallurgy- Extraction of Nickel from sulphide ore, Iron from oxide ore

Hydrometallurgy- Extraction of gold from native ore by cyanide process and refining by quartation process.

Electrometallurgy-extraction of lithium.Powder metallurgy- production of tungsten powder, application of powder metallurgy.Extraction of thorium from monozite sand, uranium from pitch blende.

Steel-ferroalloys- production and properties of ferrosilicones, ferrochrome, ferromanganese. Influence of Si, Mn, Cr, Ni, Ti, V, Mo and W on the properties of steel. Heat treatment of steel, hardening, case hardening, carbiding, nitriding, tempering and annealing.

Metal carbonyls: General methods of preparation, general properties, classification structures of mononuclear carbonyls. Example: $[Fe(CO)_5]$,$[Ni(CO)_4]$.18 e^- rule as applied to the metal carbonyls.

Organic Chemistry

Organic reaction mechanisms

Structural effects on acidity and basicity, hydrogen bonding, resonance, inductive and hyper conjugation effects.Reaction intermediates – formation, structure stability, detection and reactions of carbocations,carbanions, free radicals, carbenes, nitrenes,nitrile amines.

Reaction mechanism

Classification of reactions.Eliminationreactions – $E_1$and E_2 mechanisms,cis- elimination, Hoffman and saytzeffeliminations, competition between elimination and substitution, chugaer reaction, Addition reactions – mechanism of addition to c-c multiple bonds involving electrophiles, nucleophiles and free radicals Markownikoff's rule and antiMarkowrikoff's rule, hydroboration and its application.Substitution reaction– mechanism electrophilic and nucleophilicsubstitutions – Nitration, halogenation, sulphonation, FriedelCraft- alkylation, acylation,chloromethylationvilsmeier-Haack reaction.

Alkanes and cycloalkanes

Isomerism in alkanes, Synthesis by wurtz reaction, kolbe's reaction, corey house reaction, Nomenclature of cycloalkanes, Bayer's strain theory and its limitations. Sachse-Mohr theory.

Alkenes, Dienes and Alkynes

Mechanism of dehydration of alcohols and dehydrohalogenation of alkyl halides.Saytzeff rule Hofman elimination, Polymerization of alkenes.

Nomenclature and classification of dienes, polymerization, Diels-Alder reaction.

Acidity of Alkynes, Ozonolysis, Nucleophilic addition of methanol and ammonia, polymerization.

Arenes and Aromaticity

a) Arenes:- Introduction, nomenclature of benzene derivatives, modern concept of structure of benzene, Resonance energy. Mechanism of electrophilic substitution reactions of benzene(Nitration, Halogenation, Sulphonation and Friedle-Craft reaction)

b) Aromaticity :- Definition, Huckel rule with examples

Heterocyclic compounds

Nomenclature of Heterocyclic compounds, structure reactivity, synthesis and reactions of pyrazole, midazole, oxazole, isoxazole, thiazole, isothiazole, pyrimidine and purine, preparation and reactions of coumarins, chromones, flavones and isoflavones.

Alcohols and Thiols

Alcohols – synthesis by reduction of aldehydes, ketones, acids, esters and by hydration of alkenes,oxidation of alcohol with $KMnO_4$& $K_2Cr_2O_7$.Glycol – Preparation from alkenes, oxidation of glycol by periodicacid. Glycerol – Preparation from propene. Thiols – Uses of dithianes.

Phenols

Acid nature of phenol, effect of substituents on acidity of phenols, Riemer-Tiemann's and Kolbe- Schmidt reactions, industrial applications of phenols.

Carbonyl compounds:

Aldehydes and Ketones- structure, nomenclature, addition reaction -HCN, $NaHSO_3$, condensation reaction with 2, 4-dinitrophenyl hydrazine, NH_2OH. Reactions-Aldol condensation, Perkin's reaction, Cannizzaro's reaction and Claisen reaction, Clemmensen reduction, benzoin condensation

Carboxylic acids & their derivatives

Definition, Classification, Examples, synthesis of fattyacids by alcohols, cyanides and Grignard reagent.Acidity of carboxylic acids, effect of substitution on acid strength.Structure and nomenclature of acid chlorides, esters, amides and acid-anhydrides.Mechanism of esterfication and hydrolysis.

Nitro compounds

Nitroalkanes,nitroarenes, reduction of nitrobenzene in acid, alkaline and neutral medium.Electrophilic substitution reactions in nitrobenzene.Amines – definition, Classification with examples methylamine and aniline. Basic character of amines, synthetic applications of benzene,diazonium chloride.

Reagents in organic synthesis:

Use of following reagents in organic synthesis: Lithium disopropylamide(LDA), Gilmann reagent, dicyclohexylcarbodimide (DCC), dichlorodicyano quinine(DDQ), trialkylsilyl halides, trimethylsilyl cyanide, phase transfer catalyst, crown ethers, cyclodextrins, Fenton's reagent, Ziegler-Natta catalyst, diazomethane, tributyltinhydride, stannous chloride, Lawesson reagent, thiourea, Sharplessepoxidation, Woodward and Prevost hydroxylation, Stark enamine reaction, Phosphorus ylides-Wittig and related reactions, 1, 3-dithiane anions-Umpolung reaction, sulphurylides-reactions with aldehydes and ketones, Peterson reactions-synthesis of alkenes.

Microwave induced organic synthesis, ionic liquids in organic synthesis, polymer supported reagents and synthesis, the use of ultra sound in organic synthesis.

Stereochemistry

Fischer, Newman, Sawhorse and flying wedge projections and their interconversions.Optical isomerism- Elements of symmetry and chirality.D-L conventions. CIP rules, R-S and M-P conventions. Chirality in compounds with a stereogeniccentre, and in allenes, alkylidene cycloalkanes and spiranes(with a stereogenic axis).Cram's and Prelog's rules.

Conformational analysis:

Conformational analysis of cycloalkanes-cyclobutane, cyclopentane, cyclohexanes (monosubstituted e.g., methyl, iso-propyl, tert-butyl and di-substituted cyclohexanes e.g., dialkyl, dihalo, diols), and cycloheptane.Nomenclature and conformations of fused rings and bridged ring systems.

Prochirality: Enantiotopic and diastereotopic atoms, groups and faces.