

SVUCET-2018: SYLLABUS
SECTION- A
INORGANIC CHEMISTRY

Unit – I: P-block elements:

General characteristics of elements of groups 13, 14, 15, 16 and 17

Group – 13: Synthesis and structure of diborane and higher boranes (B_4H_{10} and B_5H_9), boron-nitrogen compounds ($B_3N_3H_6$ and BN)

Group – 14: Preparation and applications of silanes and silicones.

Group – 15: Preparation and reactions of hydrazine, hydroxylamine.

Unit – II: P-block elements:

General characteristics of elements of groups 16 and 17

Group – 16: Classifications of oxides based on (i) Chemical behavior and (ii) Oxygen Content.

Group – 17: Inter halogen compounds and pseudo halogens

Chemistry of d-block elements:

Characteristics of d-block elements with special reference to electronic configuration, variable valence, magnetic properties, catalytic properties and ability to form complexes. Stability of various oxidation states

Theories of bonding in metals:

Metallic properties and its limitations, Valence bond theory, Free electron theory, Explanation of thermal and electrical conductivity of metals, limitations, Band theory, formation of bands, explanation of conductors, semiconductors and insulators.

Metal carbonyls :

EAN rule, classification of metal carbonyls, structures and shapes of metal carbonyls of V, Cr, Mn, Fe, Co and Ni.

Chemistry of f-block elements:

Chemistry of lanthanides - electronic structure, oxidation states, lanthanide contraction, consequences of lanthanide contraction, magnetic properties. Chemistry of actinides - electronic configuration, oxidation states, actinide contraction, comparison of lanthanides and actinides.

Coordination Chemistry:

IUPAC nomenclature, bonding theories – review of Werner's theory and Sidgwick's concept of coordination, Valence bond theory, geometries of coordination numbers 4-tetrahedral and square planar and 6-octahedral and its limitations, crystal field theory, splitting of d-orbitals in octahedral, tetrahedral and square-planar complexes – low spin and high spin complexes – factors affecting crystal-field splitting energy, merits and demerits of crystal-field theory. Isomerism in coordination compounds – structural isomerism and stereo isomerism, stereochemistry of complexes with 4 and 6 coordination numbers.

Spectral and magnetic properties of metal complexes:

Types of magnetic behaviour, spin-only formula, calculation of magnetic moments, experimental determination of magnetic susceptibility – Gouy method.

Reactivity of metal complexes:

Labile and inert complexes, ligand substitution reactions – SN_1 and SN_2 , substitution reactions of square planar complexes – Trans effect and applications of trans effect.

Stability of metal complexes:

Thermodynamic stability and kinetic stability, factors affecting the stability of metal complexes, chelate effect, determination of composition of complex by Job's method and mole ratio method.

Section – B**PHYSICAL CHEMISTRY****Solidstate**

Symmetry in crystals. Law of constancy of interfacial angles. The law of rationality of indices. The law of symmetry. Definition of lattice point, space lattice, unit cell. Bravais lattices and crystal systems. X-ray diffraction and crystal structure. Bragg's law. Determination of crystal structure by Bragg's method. Indexing of planes and structure of NaCl and KCl crystals. Defects in crystals. Stoichiometric and non-stoichiometric defects.

Gaseous state

Compression factors, deviation of real gases from ideal behavior. Vander Waal's equation of state. P-V Isotherms of real gases, Andrew's isotherms of carbon dioxide, continuity of state. Critical phenomena. The vander Waal's equation and the critical state. Law of corresponding states. Relationship between critical constants and vander Waal's constants. Joule Thomson effect.

Liquid state

Structural differences between solids, liquids and gases. Liquid crystals, the mesomorphic state. Classification of liquid crystals into Smectic and Nematic. Differences between liquid crystal and solid/liquid. Application of liquid crystals as LCD devices.

Solutions

Liquid-liquid - ideal solutions, Raoult's law. Ideally dilute solutions, Henry's law. Nonideal solutions. Vapour pressure - composition and vapour pressure- temperature curves. Azeotropes-HCl-H₂O, ethanol-water systems and fractional distillation. Partially miscible liquids-phenol-water, trimethylamine-water, nicotine-water systems. Effect of impurity on consolute temperature. Immiscible liquids and steam distillation. Nernst distribution law. Calculation of the partition coefficient. Applications of distribution law.

SPECTROSCOPY**UNIT-I**

General features of absorption - Beer-Lambert's law and its limitations, transmittance, absorbance, and molar absorptivity. Single and double beam spectrophotometers. Application of Beer-Lambert law for quantitative analysis of 1. Chromium in K₂Cr₂O₇ 2. Manganese in Manganous sulphate

Electronic spectroscopy:

Interaction of electromagnetic radiation with molecules and types of molecular spectra. Energy levels of molecular orbitals (σ , π , n). Selection rules for electronic spectra. Types of electronic transitions in molecules effect of conjugation. Concept of chromophore and auxochrome.

PHYSICAL CHEMISTRY

Dilute solutions

Colligative properties. Raoult's law, relative lowering of vapour pressure, its relation to molecular weight of non-volatile solute. Elevation of boiling point and depression of freezing point. Derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods of determination. Osmosis, osmotic pressure, experimental determination. Theory of dilute solutions. Determination of molecular weight of non-volatile solute from osmotic pressure. Abnormal Colligative properties- Van't Hoff factor.

Electrochemistry-I

Specific conductance, equivalent conductance. Variation of equivalent conductance with dilution. Migration of ions, Kohlrausch's law. Arrhenius theory of electrolyte dissociation and its limitations. Ostwald's dilution law. Debye- Huckel-Onsager's equation for strong electrolytes (elementary treatment only). Definition of transport number, determination by Hittorfs method. Application of conductivity measurements- conductometric titrations.

1. Electrochemistry-II

Single electrode potential, sign convention, Reversible and irreversible cells Nernst Equation- Reference electrode, Standard Hydrogen electrode, calomel electrode, Indicator electrode, metal – metal ion electrode, Inert electrode, Determination of EMF of cell, Applications of EMF measurements - Potentiometric titrations.

2.Phase rule

Concept of phase, components, degrees of freedom. Thermodynamic Derivation of Gibbs phase rule. Phase equilibrium of one component system – water system. Phase equilibrium of two- component system, solid-liquid equilibrium. Simple eutectic diagram of Pb-Ag system, simple eutectic diagram, desilverisation of lead., NaCl-Water system, Freezing mixtures.

Thermodynamics

The first law of thermodynamics-statement, definition of internal energy and enthalpy. Heat capacities and their relationship. Joule's law-Joule-Thomson coefficient. Calculation of w , q , dU and dH for the expansion of perfect gas under isothermal and adiabatic conditions for reversible processes. State function. Temperature dependence of enthalpy of formation-Kirchoff's equation.

Second law of thermodynamics. Different Statements of the law. Carnot cycle and its efficiency. Carnot theorem. Concept of entropy, entropy as a state function, entropy changes in cyclic, reversible, and irreversible processes. Entropy changes in spontaneous and equilibrium processes.

Chemical kinetics

Rate of reaction, factors influencing the rate of a reaction-concentration, temperature, pressure, solvent, light, catalyst. Definition of order and molecularity. Derivation of rate constants for first, second, third and zero order reactions and examples. Derivation for time half change. Methods to determine the order of reactions. Kinetics of complex reactions (first order only): opposing reactions, parallel reactions, consecutive reactions and chain reactions. Effect of temperature on rate of reaction, Arrhenius equation, concept of activation energy.

Photochemistry

Difference between thermal and photochemical processes. Laws of photochemistry-Grothus-Draper's law and Stark-Einstein's law of photochemical equivalence. Quantum yield. Photochemical hydrogen-

chlorine, hydrogen-bromine reaction. qualitative description of fluorescence, phosphorescence, Photosensitized reactions- energy transfer processes (simple example)

SECTION - C ORGANIC CHEMISTRY

Structural theory in Organic Chemistry

Types of bond fission and organic reagents (Electrophilic, Nucleophilic, and free radical reagents including neutral molecules like H₂O, NH₃ & AlCl₃).

Bond polarization : Factors influencing the polarization of covalent bonds, electro negativity – inductive effect. Application of inductive effect (a) Basicity of amines (b) Acidity of carboxylic acids (c) Stability of carbonium ions. Resonance or Mesomeric effect, application to (a) acidity of phenol, and (b) acidity of carboxylic acids. Hyper conjugation and its application to stability of carbonium ions, Free radicals and alkenes, carbanions, carbenes.

Types of Organic reactions : Addition – electrophilic, nucleophilic and free radical. Substitution – electrophilic, nucleophilic and free radical. Elimination- Examples (mechanism not required).

2. Acyclic Hydrocarbons

Alkanes– IUPAC Nomenclature of Hydrocarbons. Methods of preparation: Hydrogenation of alkynes and alkenes, Wurtz reaction, Kolbe's electrolysis, Corey- House reaction. Chemical reactivity – inert nature, free radical substitution mechanism. Halogenation example. Alkenes – Preparation of alkenes (a) by dehydration of alcohols (b) by dehydrohalogenation of alkyl halides (c) by dehalogenation of 1,2 dihalides (brief mechanism), Saytzev's rule. Properties: Addition of hydrogen – heat of hydrogenation and stability of alkenes. Addition of halogen and its mechanism. Addition of HX, Markonikov's rule, addition of H₂O, HOX, H₂SO₄ with mechanism and addition of HBr in the presence of peroxide (anti – Markonikov's addition). Oxidation – hydroxylation by KMnO₄ , Dienes – Types of dienes, reactions of conjugated dienes – 1,2 and 1,4 addition of HBr to 1,3 – butadiene and Diel's – Alder reaction. Alkynes – Preparation by dehydrohalogenation of dihalides, dehalogenation of tetrahalides, Properties; Acidity of acetylenic hydrogen (formation of Metal acetylides). Preparation of higher acetylenes, Physical properties. Chemical reactivity – electrophilic addition of X₂, HX, H₂O (Tautomerism), Oxidation with KMnO₄, OsO₄, reduction and Polymerisation reaction of acetylene.

3. Alicyclic hydrocarbons (Cycloalkanes)

Nomenclature, Preparation by Freund's methods, heating dicarboxylic metal salts. Properties – reactivity of cyclopropane and cyclobutane by comparing with alkanes, Stability of cycloalkanes – Baeyer's strain theory, Sachse and Mohr predictions and Pitzer's strain theory. Conformational structures of cyclohexane.

Benzene and its reactivity

Concept of resonance, resonance energy. Heat of hydrogenation, heat of combustion of Benzene, mention of C-C bond lengths and orbital picture of Benzene. Concept of aromaticity – aromaticity (definition), Huckel's rule – application to Benzenoid (Benzene, Napthalene) and Non – Benzenoid compounds (cyclopropenyl cation, cyclopentadienyl anion and tropylium cation) Reactions – General mechanism of electrophilic substitution, mechanism of nitration. Friedel Craft's alkylation and acylation. Orientation of aromatic substitution – Definition of ortho, para and meta directing groups. Ring activating and deactivating groups with examples (Electronic interpretation of various groups like NO₂ and Phenolic). Orientation of (i). Amino, methoxy and methyl groups (ii). Carboxy, nitro, nitrile, carbonyl and Sulfonic acid groups. (iii). Halogens (Explanation by taking minimum of one example from each type).

Stereochemistry of carbon compounds 15 h

Molecular representations- Wedge, Fischer, Newman and Saw-Horse formulae. Optical isomerism: Optical activity- wave nature of light, plane polarised light, optical rotation and specific rotation. Chiral molecules- definition and criteria(Symmetry elements)- Definition of enantiomers and diastereomers – Explanation of optical isomerism with examples Glyceraldehyde, Lactic acid, Alanine, Tartaric acid, 2,3-dibromopentane. D,L and R,S configuration methods and E,Z- configuration with examples.

Halogen compounds

Nomenclature and classification of alkyl (into primary, secondary, tertiary), aryl, aryl alkyl, allyl, vinyl, benzyl halides. Nucleophilic aliphatic substitution reaction- classification into SN1 and SN2 – reaction mechanism with examples – Ethyl chloride, t-butyl chloride and optically active alkyl halide 2-bromobutane.

Hydroxy compounds

Nomenclature and classification of hydroxy compounds. Alcohols: Preparation with hydroboration reaction, Grignard synthesis of alcohols. Phenols: Preparation i) from diazonium salt, ii) from aryl sulphonates, iii) from cumene. Physical properties- Hydrogen bonding (intermolecular and intramolecular). Effect of hydrogen bonding on boiling point and solubility in water. Identification of alcohols by oxidation with KMnO₄, Ceric ammonium nitrate, Luca's reagent and phenols by reaction with FeCl₃. Chemical properties:

a) Dehydration of alcohols.

b) Oxidation of alcohols by CrO₃, KMnO₄.

c) Special reaction of phenols: Bromination, Kolbe-Schmidt reaction, Reimer-Tiemann reaction, Fries rearrangement, azocoupling, Pinacol-Pinacolone rearrangement.

Carbonyl compounds

Nomenclature of aliphatic and aromatic carbonyl compounds, structure of the carbonyl group. Synthesis of aldehydes from acid chlorides, synthesis of aldehydes and ketones using 1,3- dithianes, synthesis of ketones from nitriles and from carboxylic acids. Physical properties: Reactivity of carbonyl group in aldehydes and ketones. Nucleophilic addition reaction with a) NaHSO₃, b) HCN, c) RMgX, d) NH₂OH, e) PhNHNH₂, f) 2,4 DNPH, g) Alcohols-formation of hemiacetal and acetal. Base catalysed reactions: a) Aldol, b) Cannizzaro's reaction, c) Perkin reaction, d) Benzoin condensation, e) Haloform reaction, f) Knoevenagel reaction. Oxidation of aldehydes- Baeyer-Villiger oxidation of ketones.Reduction: Clemmensen reduction, Wolf-Kishner reduction, MPV reduction, reduction with LiAlH₄ and NaBH₄. Analysis of aldehydes and ketones with a) 2,4-DNPH test, b) Tollen's test, c) Fehling test, d) Schiff's test e) Haloform test (with equation)

UNIT-V

Carboxylic acids and derivatives

Nomenclature, classification and structure of carboxylic acids. Methods of preparation by a) Hydrolysis of nitriles, amides b) Hydrolysis of esters by acids and bases with mechanism c) Carbonation of Grignard reagents. Special methods of preparation of aromatic acids by a) Oxidation of side chain. b) Hydrolysis by benzotrichlorides. c) Kolbe reaction. **Physical properties:** Hydrogen bonding, dimeric association, acidity- strength of acids with examples of trimethyl acetic acid and trichloroacetic acid. Relative differences in the acidities of aromatic and aliphatic acids. **Chemical properties:** Reactions involving H, OH and COOH groups- salt formation, anhydride formation, acid chloride formation, amide formation and esterification (mechanism).

Degradation of carboxylic acids by Huns-Diecker reaction, decarboxylation by Schimdt reaction, Arndt-Eistert synthesis, halogenation by Hell- Volhard- Zelinsky reaction.

Active methylene compounds

Acetoacetic ester: keto-enol tautomerism, preparation by Claisen condensation, Acid hydrolysis and ketonic hydrolysis. Preparation of a) monocarboxylic acids. b) Dicarboxylic acids. c) Reaction with urea

Malonic ester: preparation from acetic acid. **Synthetic applications:** Preparation of a) monocarboxylic acids (propionic acid and n-butyric acid). b) Dicarboxylic acids (succinic acid and adipic acid) c) α,β -unsaturated carboxylic acids (crotonic acid). d) Reaction with urea.

Infra red spectroscopy

Different Regions in Infrared radiations. Modes of vibrations in diatomic and polyatomic molecules. Characteristic absorption bands of various functional groups. Interpretation of spectra-Alkanes, Aromatic, Alcohols Carbonyls, and amines with one example to each.

Proton magnetic resonance spectroscopy (1H-NMR)

Principles of nuclear magnetic resonance, equivalent and non-equivalent protons, position of signals. Chemical shift, NMR splitting of signals - spin-spin coupling, coupling constants. Applications of NMR with suitable examples - ethyl bromide, ethanol, acetaldehyde, 1,1,2-tribromo ethane, ethyl acetate, toluene and acetophenone.

Nitro hydrocarbons

Nomenclature and classification-nitro hydrocarbons, structure – Tautomerism of nitroalkanes leading to aci and keto form, preparation of nitroalkanes, reactivity - halogenations, reaction with HONO (Nitrous acid), Nef reaction and mannich reaction leading to Michael addition and reduction.

Nitrogen compounds

Nitro hydrocarbons: Nomenclature and classification – nitro hydrocarbons – structure. Tautomerism of nitroalkanes leading to aci and keto form. Preparation of Nitroalkanes. Reactivity – halogenation, reaction with HONO (Nitrous acid), Nef reaction and Mannich reaction leading to Michael addition and reduction. Amines (Aliphatic and Aromatic): Nomenclature, Classification into 1^o, 2^o and 3^o Amines and Quarternary ammonium compounds. Preparative methods -1. Ammonolysis of alkyl halides 2. Gabriel synthesis 3. Hoffman's bromamide reaction (mechanism). Reduction of Amides and Schmidt reaction. Physical properties and basic character – Comparative basic strength of Ammonia, methyl amine, dimethyl amine, trimethyl amine and aniline – comparative basic strength of aniline, N-methylaniline and N,N-dimethyl aniline (in aqueous and non-aqueous medium), steric effects and substituent effects. Use of amine salts as phase transfer catalysts. Chemical properties: **a)** Alkylation **b)** Acylation **c)** Carbylamine reaction **d)** Hinsberg separation **e)** Reaction with Nitrous acid of 1^o, 2^o and 3^o (Aliphatic and aromatic amines). Electrophilic substitutions of Aromatic amines – Bromination and Nitration. oxidation of aryl and 3^o Amines. Diazotization