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YVUCET-2019: SYLLABUS
TEST-103: CHEMISTRY
COMMON ENTRANCE EXAMINATION – 2019 FOR ADMISSION INTO
(M.Sc., Chemistry/M.Sc. Environmental Science)
SECTION-A (30-Marks)

INORGANIC CHEMISTRY

p-block elements –I

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.

p-block elements -II

Group - 16: Classifications of oxides based on (i) Chemical behaviour and (ii) Oxygen content.

Group-17: Inter halogen compounds and pseudo halogens.

Organometallic Chemistry

Definition - classification of Organometallic compounds - nomenclature, preparation, properties and applications of alkyls of Li and Mg.

Chemical Bonding

Valence bond theory, hybridization, VB theory as applied to ClF_3 , $Ni(CO)_4$, Molecular orbital theory - LCAO method, construction of M.O. diagrams for homo-nuclear and hetero-nuclear diatomic molecules (N_2 , O_2 , CO and NO).

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 lanthanides - electronic structure, oxidation states, lanthanide contraction, consequences of lanthanide contraction, magnetic properties. Chemistry of actinides - electronic configuration, oxidation states, 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 - merits of crystal-field theory. Isomerism in coordination compounds - structural isomerism and stereo isomerism, stereochemistry of complexes with 4 and 6 coordination numbers.

Magnetic properties of metal complexes:

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

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.

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.

Bioinorganic chemistry:

Essential elements, biological significance of Na, K, Mg, Ca, Fe, Co, Ni, Zn .

Metalloporphyrins – Structure and functions of hemoglobin, and Chlorophyll.

SECTION-B (30 Marks)**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. Defects in crystals.

Gaseous state

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. Non-ideal 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.

Surface chemistry

Definition of colloids. SOLS- properties - kinetic, optical, electrical. Stability of colloids, Hardy-Schulze law, protective colloid.

Liquids in liquids (emulsions)-properties and uses. Liquids in solids (gels) uses.

Adsorption: Physical adsorption, chemisorption. Freundlich, Langmuir adsorption isotherms. Applications of adsorption

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 Hittorf's method. Application of conductivity measurements- conductometric titrations.

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.

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.

Thermodynamics

The first law of thermodynamics-statement, definition of internal energy and enthalpy. Heat capacities and their relationship. Joule-Thomson effect- coefficient. Calculation of w , 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 reversible and irreversible processes. Entropy changes in spontaneous and equilibrium processes.

Chemical kinetics

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

SECTION-C(40 Marks)

ORGANIC CHEMISTRY

Structural theory in Organic Chemistry

Types of bond fission type of organic reagents (Electrophilic, Nucleophilic, and free radical reagents including neutral molecules like H_2O , NH_3 & $AlCl_3$).

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,

Types of Organic reactions : Addition - electrophilic, nucleophilic and free radical. Substitution - electrophilic, nucleophilic and free radical reactions. Elimination- Examples.

Acyclic Hydrocarbons

Alkenes - Addition of halogen. Addition of HX, Markonikov's rule (with mechanism), addition of H_2O , HOX, H_2SO_4 and addition of HBr in the presence of peroxide (anti - Markonikov's addition). 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 – Terminal and non terminal Alkynes, Properties; Acidity of acetylenic hydrogen (formation of Metal acetylides). Electrophilic addition of X_2 , HX, H_2O (Tautomerism), Oxidation with $KMnO_4$, OsO_4 , Metal Ammonia reduction and Polymerisation reaction of acetylene.

(Cycloalkanes)

Nomenclature, Preparation by Freund's method, Wislicenus method. Properties - Stability of cycloalkanes - Baeyer's strain theory, Sachse and Mohr predictions and Pitzer's strain theory.

Benzene and its reactivity

Concept of aromaticity - aromaticity (definition), Huckel's rule - application to Benzenoid (Benzene, Naphthalene) and Non - Benzenoid compounds (cyclopropenyl cation, cyclopentadienyl anion and tropylium cation), Molecular structure of Benzene based on modern concepts (VBT and MOT).

Reactions - 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 (i) Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, carbonyl and sulphonic acid groups (iii) Halogens

Stereochemistry of carbon compounds

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.

SN^1 and SN^2 - reaction mechanism with optically active alkyl halide 2-bromobutane.

Hydroxy compounds

Nomenclature and classification of Alcohols: Preparation with hydroboration reaction and Grignard synthesis. Physical properties- Hydrogen bonding (intermolecular and intramolecular). Effect of hydrogen bonding on boiling point and solubility in water. Chemical properties:

- a) Dehydration of alcohols.
- b) Oxidation of alcohols by CrO_3 , $KMnO_4$.

Identification of alcohols by oxidation with $KMnO_4$, Ceric ammonium nitrate, Luca's reagent .

Phenols: Preparation i) from diazonium salt, ii) from cumene.

Chemical Properties: a) Bromination, b) Kolbe-Schmidt reaction (with mechanism)

c) Reimer-Tiemann reaction, (with mechanism), d) azocoupling,

Identification of Phenol with neutral $FeCl_3$

Carbonyl compounds

Nomenclature of aliphatic and aromatic carbonyl compounds, Synthesis of aldehydes from acid chlorides, synthesis of ketones from nitriles. Physical properties: Reactivity of carbonyl group in aldehydes and ketones.

Nucleophilic addition reaction with a) NaHSO_3 , b) HCN , c) RMgX , d) NH_2OH , e) PhNHNH_2 , f) 2,4-DNPH, With mechanism a) Aldol, b) Cannizzaro's reaction, c) Perkin reaction, d) Benzoin condensation, Reduction: Clemmensen reduction, Wolf-Kishner reduction, MPV reduction, reduction with LiAlH_4 and NaBH_4 . 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)

Carboxylic acids and derivatives

Nomenclature, classification of carboxylic acids. Methods of preparation by Hydrolysis of nitriles, amides and esters (by acids and bases), 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, **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 Schmidt reaction, halogenation by Hell-Volhard-Zelinsky reaction.

Active methylene compounds

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

Malonic ester: preparation. **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.

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 Micheal addition and reduction.

Nitrogen compounds :

Amines (Aliphatic and Aromatic): Nomenclature, Classification into 1°, 2°, 3° 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.

Chemical properties: a) Alkylation b) Acylation c) Carbylamine reaction d) Hinsberg separation e) Reaction with Nitrous acid of 1°, 2°, 3° (Aliphatic and aromatic amines). Electrophilic substitution of Aromatic amines – Bromination and Nitration. Oxidation of aryl and Tertiary amines, Diazotization.

Heterocyclic Compounds

Introduction and definition: Simple five membered ring compounds with one hetero atom
Ex. Furan. Thiophene and pyrrole - Aromatic character – Preparation from 1,4,-dicarbonyl compounds, Paul-Knorr synthesis.

Properties : Acidic character of pyrrole - electrophilic substitution at 2 or 5 position, Halogenation, Nitration and Sulphonation under mild conditions - Diels Alder reaction in furan.

Pyridine – Structure - Basicity - Aromaticity - Comparison with pyrrole - one method of preparation and properties - Reactivity towards Nucleophilic substitution reaction.

Carbohydrates

Monosaccharides: (+) Glucose (aldo hexose) - Evidence for cyclic structure of glucose (some negative aldehydes tests and mutarotation) - Proof for the ring size (methylation, hydrolysis and oxidation reactions) - Pyranose structure (Haworth formula and chair conformational formula).

(-) Fructose (ketohexose) - Evidence of 2 - ketohexose structure (formation of pentaacetate, formation of cyanohydrin its hydrolysis and reduction by HI). Cyclic structure for fructose (Furanose structure and Haworth formula) - osazone formation from glucose and fructose – Definition of anomers with examples.

Interconversion of Monosaccharides: Aldopentose to Aldohexose (Arabinose to D- Glucose, D-Mannose) (Kiliani - Fischer method). Epimers, Epimerisation - Lobry de bruyn van Ekenstein rearrangement. Aldohexose to Aldopentose (D-Glucose to D- Arabinose) by Ruff degradation. Aldohexose to Ketohexose [(+) Glucose to (-) Fructose] and Ketohexose to Aldohexose (Fructose to Glucose)

Amino acids and proteins

Introduction: Definition of Amino acids, classification of Amino acids into alpha, beta, and gamma amino acids. Natural and essential amino acids - definition and examples, classification of alpha amino acids into acidic, basic and neutral amino acids with examples. Methods of synthesis: General methods of synthesis of alpha amino acids (specific examples - Glycine, Alanine, valine and leucine) by following methods: a) from halogenated carboxylic acid b) Malonic ester synthesis c) strecker's synthesis.

Physical properties: Zwitter ion structure - salt like character - solubility, melting points, amphoteric character, definition of isoelectric point.

Chemical properties: General reactions due to amino and carboxyl groups - lactams from gamma and delta amino acids by heating peptide bond (amide linkage). Structure and nomenclature of peptides and proteins.

