



43 Years' Chapterwise Topicwise Solved Papers

2021-1979

IIT JEE
JEE Main & Advanced

Chemistry

Ranjeet Shahi



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SYLLABUS

JEE MAIN

Section A : PHYSICAL CHEMISTRY

UNIT I Some Basic Concepts in Chemistry

Matter and its nature, Dalton's atomic theory; Concept of atom, molecule, element and compound; Physical quantities and their measurements in Chemistry, precision and accuracy, significant figures, S.I. Units, dimensional analysis; Laws of chemical combination; Atomic and molecular masses, mole concept, molar mass, percentage composition, empirical and molecular formulae; Chemical equations and stoichiometry.

UNIT II States of Matter

Classification of matter into solid, liquid and gaseous states.

Gaseous State Measurable properties of gases; Gas laws - Boyle's law, Charle's law, Graham's law of diffusion, Avogadro's law, Dalton's law of partial pressure; Concept of Absolute scale of temperature; Ideal gas equation, Kinetic theory of gases (only postulates); Concept of average, root mean square and most probable velocities; Real gases, deviation from Ideal behaviour, compressibility factor, van der Waals' equation, liquefaction of gases, critical constants.

Liquid State Properties of liquids - vapour pressure, viscosity and surface tension and effect of temperature on them (qualitative treatment only).

Solid State Classification of solids: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea); Bragg's Law and its applications, Unit cell and lattices, packing in solids (fcc, bcc and hcp lattices), voids, calculations involving unit cell parameters, imperfection in solids; electrical, magnetic and dielectric properties.

UNIT III Atomic Structure

Discovery of sub-atomic particles (electron, proton and neutron); Thomson and Rutherford atomic models and their limitations; Nature of electromagnetic radiation, photoelectric effect; spectrum of hydrogen atom, Bohr model of hydrogen atom - its postulates, derivation of the relations for energy of the electron and radii of the different orbits, limitations of Bohr's model; dual nature of matter, de-Broglie's relationship, Heisenberg uncertainty principle.

Elementary ideas of quantum mechanics, quantum mechanical model of atom, its important features, ψ and ψ_2 , concept of atomic orbitals as one electron wave functions; Variation of ψ and ψ_2 with r for $1s$ and $2s$ orbitals; various quantum numbers (principal, angular momentum and magnetic quantum numbers) and their significance; shapes of s , p and d - orbitals, electron spin and spin quantum number; rules for filling electrons in orbitals – aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of elements, extra stability of half-filled and completely filled orbitals.

UNIT IV Chemical Bonding and Molecular Structure

Kossel Lewis approach to chemical bond formation, concept of ionic and covalent bonds.

Ionic Bonding Formation of ionic bonds, factors affecting the formation of ionic bonds; calculation of lattice enthalpy.

Covalent Bonding Concept of electronegativity, Fajan's rule, dipole moment; Valence Shell Electron Pair Repulsion (VSEPR) theory and shapes of simple molecules.

Quantum mechanical approach to covalent bonding Valence bond theory - Its important features, concept of hybridization involving s , p and d orbitals; Resonance.

Molecular Orbital Theory Its important features, LCAOs, types of molecular orbitals (bonding, antibonding), sigma and pi-bonds, molecular orbital electronic configurations of homonuclear diatomic molecules, concept of bond order, bond length and bond energy.

Elementary idea of metallic bonding. Hydrogen bonding and its applications.

UNIT V Chemical Thermodynamics

Fundamentals of thermodynamics System and surroundings, extensive and intensive properties, state functions, types of processes.

First law of thermodynamics Concept of work, heat internal energy and enthalpy, heat capacity, molar heat capacity, Hess's law of constant heat summation; Enthalpies of bond dissociation, combustion, formation, atomization, sublimation, phase transition, hydration, ionization and solution.

Second law of thermodynamics Spontaneity of processes; ΔS of the universe and ΔG of the system as criteria for spontaneity, ΔG° (Standard Gibb's energy change) and equilibrium constant.

UNIT VI Solutions

Different methods for expressing concentration of solution - molality, molarity, mole fraction, percentage (by volume and mass both), vapour pressure of solutions and Raoult's Law - Ideal and non-ideal solutions, vapour pressure - composition plots for ideal and non-ideal solutions.

Colligative properties of dilute solutions - relative lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure; Determination of molecular mass using colligative properties; Abnormal value of molar mass, van't Hoff factor and its significance.

UNIT VII Equilibrium

Meaning of equilibrium, concept of dynamic equilibrium.

Equilibria involving physical processes Solid -liquid, liquid - gas and solid - gas equilibria, Henry's law, general characteristics of equilibrium involving physical processes.

Equilibria involving chemical processes Law of chemical equilibrium, equilibrium constants (K and K') and their significance, significance of ΔG and ΔG° in chemical equilibria, factors affecting equilibrium concentration, pressure, temperature, effect of catalyst; Le - Chatelier's principle.

Ionic equilibrium Weak and strong electrolytes, ionization of electrolytes, various concepts of acids and bases (Arrhenius, Bronsted - Lowry and Lewis) and their ionization, acid-base equilibria (including multistage ionization) and ionization constants, ionization of water, pH scale, common ion effect, hydrolysis of salts and pH of their solutions, solubility of sparingly soluble salts and solubility products, buffer solutions.

UNIT VIII Redox Reactions and Electrochemistry

Electronic concepts of oxidation and reduction, redox reactions, oxidation number, rules for assigning oxidation number, balancing of redox reactions.

Electrolytic and metallic conduction, conductance in electrolytic solutions, specific and molar conductivities and their variation with concentration: Kohlrausch's law and its applications.

Electrochemical cells - Electrolytic and Galvanic cells, different types of electrodes, electrode potentials including standard electrode potential, half-cell and cell reactions, emf of a Galvanic cell and its measurement; Nernst equation and its applications; Relationship between cell potential and Gibbs' energy change; Dry cell and lead accumulator; Fuel cells; Corrosion and its prevention.

UNIT IX Chemical Kinetics

Rate of a chemical reaction, factors affecting the rate of reactions concentration, temperature, pressure and catalyst; elementary and complex reactions, order and molecularity of reactions, rate law, rate constant and its units, differential and integral forms of zero and first order reactions, their characteristics and half-lives, effect of

temperature on rate of reactions - Arrhenius theory, activation energy and its calculation, collision theory of bimolecular gaseous reactions (no derivation).

UNIT X Surface Chemistry

Adsorption - Physisorption and chemisorption and their characteristics, factors affecting adsorption of gases on solids-Freundlich and Langmuir adsorption isotherms, adsorption from solutions.

Catalysis Homogeneous and heterogeneous, activity and selectivity of solid catalysts, enzyme catalysis and its mechanism.

Colloidal state distinction among true solutions, colloids and suspensions, classification of colloids - lyophilic, lyophobic; multi-molecular, macromolecular and associated colloids (micelles), preparation and properties of colloids Tyndall effect, Brownian movement, electrophoresis, dialysis, coagulation and flocculation; Emulsions and their characteristics.

Section B : INORGANIC CHEMISTRY

UNIT XI Classification of Elements and Periodicity in Properties

Periodic Law and Present Form of the Periodic Table, s, p, d and f Block Elements, Periodic Trends in Properties of Elements atomic and ionic radii, Ionization Enthalpy, Electron Gain Enthalpy, Valence, Oxidation States and Chemical Reactivity.

Group 16 Preparation, properties, structures and uses of dioxygen and ozone; Allotropic forms of sulphur; Preparation, properties, structures and uses of sulphur dioxide, sulphuric acid (including its industrial preparation); Structures of oxoacids of sulphur.

Group 17 Preparation, properties and uses of chlorine and hydrochloric acid; Trends in the acidic nature of hydrogen halides; Structures of interhalogen compounds and oxides and oxoacids of halogens.

Group 18 Occurrence and uses of noble gases; Structures of fluorides and oxides of xenon.

UNIT XVI d-and f-Block Elements

Transition Elements General introduction, electronic configuration, occurrence and characteristics, general trends in properties of the first row transition elements - physical properties, ionization enthalpy, oxidation states, atomic radii, colour, catalytic behaviour, magnetic properties, complex formation, interstitial compounds, alloy formation; Preparation, properties and uses of $K_2Cr_2O_7$ and $KMnO_4$.

Inner Transition Elements

Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction. Actinoids - Electronic configuration and oxidation states.

UNIT XVII Coordination Compounds

Introduction to coordination compounds, Werner's theory; ligands, coordination number, denticity, chelation; IUPAC nomenclature of mononuclear coordination compounds, isomerism; Bonding Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties; importance of coordination compounds (in qualitative analysis, extraction of metals and in biological systems).

UNIT XVIII Environmental Chemistry

Environmental pollution Atmospheric, water and soil.

Atmospheric pollution - Tropospheric and stratospheric.

Tropospheric pollutants Gaseous pollutants Oxides of carbon, nitrogen and sulphur, hydrocarbons; their sources, harmful effects and prevention; Green house effect and Global warming; Acid rain; Particulate pollutants Smoke, dust, smog, fumes, mist; their sources, harmful effects and prevention.

Stratospheric pollution Formation and breakdown of ozone, depletion of ozone layer - its mechanism and effects.

Water pollution Major pollutants such as, pathogens, organic wastes and chemical pollutants their harmful effects and prevention.

Soil pollution Major pollutants such as: Pesticides (insecticides, herbicides and fungicides), their harmful effects and prevention. Strategies to control environmental pollution.

UNIT XII General Principles and Processes of Isolation of Metals

Modes of occurrence of elements in nature, minerals, ores; steps involved in the extraction of metals - concentration, reduction (chemical and electrolytic methods) and refining with special reference to the extraction of Al, Cu, Zn and Fe; Thermodynamic and electrochemical principles involved in the extraction of metals.

UNIT XIII Hydrogen

Position of hydrogen in periodic table, isotopes, preparation, properties and uses of hydrogen; physical and chemical properties of water and heavy water; Structure, preparation, reactions and uses of hydrogen peroxide; Classification of hydrides ionic, covalent and interstitial; Hydrogen as a fuel.

UNIT XIV s-Block Elements (Alkali and Alkaline Earth Metals)

Group 1 and 2 Elements

General introduction, electronic configuration and general trends in physical and chemical properties of elements, anomalous properties of the first element of each group, diagonal relationships.

Preparation and properties of some important compounds - sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate; Industrial uses of lime, limestone, Plaster of Paris and cement; Biological significance of Na, K, Mg and Ca.

UNIT XV p-Block Elements

Group 13 to Group 18 Elements

General Introduction Electronic configuration and general trends in physical and chemical properties of elements across the periods and down the groups; unique behaviour of the first element in each group. Group wise study of the p-block elements

Group 13 Preparation, properties and uses of boron and aluminium; structure, properties and uses of borax, boric acid, diborane, boron trifluoride, aluminium chloride and alums.

Group 14 Tendency for catenation; Structure, properties and uses of allotropes and oxides of carbon, silicon tetrachloride, silicates, zeolites and silicones.

Group 15 Properties and uses of nitrogen and phosphorus; Allotropic forms of phosphorus; Preparation, properties, structure and uses of ammonia, nitric acid, phosphine and phosphorus halides (PCl_3 , PCl_5); Structures of oxides and oxoacids of nitrogen and phosphorus.

Section C : ORGANIC CHEMISTRY

UNIT XIX Purification & Characterisation of Organic Compounds

Purification Crystallisation, sublimation, distillation, differential extraction and chromatography principles and their applications. Qualitative analysis Detection of nitrogen, sulphur, phosphorus and halogens.

Quantitative analysis (basic principles only) Estimation of carbon, hydrogen, nitrogen, halogens, sulphur, phosphorus.

Calculations of empirical formulae and molecular formulae; Numerical problems in organic quantitative analysis.

UNIT XX Some Basic Principles of Organic Chemistry

Tetravalency of carbon; Shapes of simple molecules hybridization (*s* and *p*); Classification of organic compounds based on functional groups: —C=C—, —C=C— and those containing halogens, oxygen, nitrogen and sulphur, Homologous series; Isomerism - structural and stereoisomerism.

Nomenclature (Trivial and IUPAC)

Covalent bond fission Homolytic and heterolytic free radicals, carbocations and carbanions; stability of carbocations and free radicals, electrophiles and nucleophiles.

Electronic displacement in a covalent bond Inductive effect, electromeric effect, resonance and hyperconjugation.

Common types of organic reactions Substitution, addition, elimination and rearrangement.

UNIT XXI Hydrocarbons

Classification, isomerism, IUPAC nomenclature, general methods of preparation, properties and reactions.

Alkanes Conformations: Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes.

Alkenes Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's and peroxide effect); Ozonolysis, oxidation, and polymerization.

Alkenes acidic character; addition of hydrogen, halogens, water and hydrogen halides; polymerization.

Aromatic hydrocarbons Nomenclature, benzene structure and aromaticity; Mechanism of electrophilic substitution: halogenation, nitration, Friedel – Craft's alkylation and acylation, directive influence of functional group in mono-substituted benzene.

UNIT XXII Organic Compounds Containing Halogens

General methods of preparation, properties and reactions; Nature of C—X bond; Mechanisms of substitution reactions.

Uses/environmental effects of chloroform, iodoform, freons and DDT.

UNIT XXIII Organic Compounds Containing Oxygen

General methods of preparation, properties, reactions and uses.

Alcohols, Phenols and Ethers

Alcohols Identification of primary, secondary and tertiary alcohols; mechanism of dehydration.

Phenols Acidic nature, electrophilic substitution reactions: halogenation, nitration and sulphonation, Reimer - Tiemann reaction.

Ethers: Structure

Aldehyde and Ketones Nature of carbonyl group;

Nucleophilic addition to >C=O group, relative reactivities of aldehydes and ketones; Important reactions such as - Nucleophilic addition reactions (addition of HCN, NH₃, and its derivatives), Grignard reagent; oxidation; reduction (Wolff Kishner and Clemmensen); acidity of α-hydrogen, aldol condensation, Cannizzaro reaction, Haloform reaction; Chemical tests to distinguish between aldehydes and Ketones.

Carboxylic Acids Acidic strength & factors affecting it.

UNIT XXIV Organic Compounds Containing Nitrogen

General methods of preparation, properties, reactions and uses.

Amines Nomenclature, classification, structure basic character and identification of primary, secondary and tertiary amines and their basic character.

Diazonium Salts Importance in synthetic organic chemistry.

UNIT XXV Polymers

General introduction and classification of polymers, general methods of polymerization-addition and condensation, copolymerization; Natural and synthetic rubber and vulcanization; some important polymers with emphasis on their monomers and uses - polythene, nylon, polyester and bakelite.

UNIT XXVI Biomolecules

General introduction and importance of biomolecules.

Carbohydrates Classification aldoses and ketoses; monosaccharides (glucose and fructose), constituent monosaccharides of oligosaccharides (sucrose, lactose, maltose) and polysaccharides (starch, cellulose, glycogen).

Proteins Elementary idea of α-amino acids, peptide bond, polypeptides; proteins: primary, secondary, tertiary and quaternary structure (qualitative idea only), denaturation of proteins, enzymes. Vitamins Classification and functions.

Nucleic Acids Chemical constitution of DNA and RNA. Biological functions of Nucleic acids.

UNIT XXVII Chemistry in Everyday Life

Chemicals in medicines Analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines - their meaning and common examples.

Chemicals in food Preservatives, artificial sweetening agents - common examples.

Cleansing agents Soaps and detergents, cleansing action.

Unit XXVIII Principles Related to Practical Chemistry

Practical Chemistry

- Detection of extra elements (N, S, halogens) in organic compounds; Detection of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl and amino groups in organic compounds.
- Chemistry involved in the preparation of the following
- Inorganic compounds Mohr's salt, potash alum.
- Organic compounds Acetanilide, *p*-nitroacetan ilide, aniline yellow, iodoform.
- Chemistry involved in the titrimetric exercises - Acids bases and the use of indicators, oxali acid vs KMnO₄, Mohr's salt vs KMnO₄.
- Chemical principles involved in the qualitative salt analysis
- Cations — Pb²⁺, Cu²⁺, Al³⁺, Fe³⁺, Zn²⁺, Ni²⁺, Ca²⁺, Ba²⁺, Mg²⁺, NH⁴⁺. Anions — CO₃²⁻, S²⁻, SO₄²⁻, NO₂, NO₃⁻, Cl⁻, Br⁻, I⁻ (Insoluble salts excluded).
- Chemical principles involved in the following experiments
 1. Enthalpy of solution of CuSO₄
 2. Enthalpy of neutralization of strong acid and strong base.
 3. Preparation of lyophilic and lyophobic sols.
 4. Kinetic study of reaction of iodide ion with hydrogen peroxide at room temperature.

JEE ADVANCED

PHYSICAL CHEMISTRY

General Topics Concept of atoms and molecules, Dalton's atomic theory, Mole concept, Chemical formulae, Balanced chemical equations, Calculations (based on mole concept) involving common oxidation-reduction, neutralisation, and displacement reactions, Concentration in terms of mole fraction, molarity, molality and normality.

Gaseous and Liquid States Absolute scale of temperature, ideal gas equation, Deviation from ideality, van der Waals' equation, Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature, Law of partial pressures, Vapour pressure, Diffusion of gases.

Atomic Structure and Chemical Bonding Bohr model, spectrum of hydrogen atom, quantum numbers, Wave-particle duality, de-Broglie hypothesis, Uncertainty principle, Qualitative quantum mechanical picture of hydrogen atom, shapes of s, p and d orbitals, Electronic configurations of elements (up to atomic number 36), Aufbau principle, Pauli's exclusion principle and Hund's rule, Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only, Orbital energy diagrams for homonuclear diatomic species, Hydrogen bond, Polarity in molecules, dipole moment (qualitative aspects only), VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

Energetics First law of thermodynamics, Internal energy, work and heat, pressure-volume work, Enthalpy, Hess's law, Heat of reaction, fusion and vaporization, Second law of thermodynamics, Entropy, Free energy, Criterion of spontaneity.

Chemical Equilibrium Law of mass action, Equilibrium constant, Le-Chatelier's principle (effect of concentration, temperature and pressure), Significance of DG and DGo in chemical equilibrium, Solubility product, common ion effect, pH and buffer solutions, Acids and bases (Bronsted and Lewis concepts), Hydrolysis of salts.

Electrochemistry Electrochemical cells and cell reactions, Standard electrode potentials, Nernst equation and its relation to DG, Electrochemical series, emf of galvanic cells, Faraday's laws of electrolysis, Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's law, Concentration cells.

Chemical Kinetics Rates of chemical reactions, Order of reactions, Rate constant, First order reactions, Temperature dependence of rate constant (Arrhenius equation).

Solid State Classification of solids, crystalline state, seven crystal systems (cell parameters a, b, c), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices, Nearest neighbours, ionic radii, simple ionic compounds, point defects.

Solutions Raoult's law, Molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point.

Surface Chemistry Elementary concepts of adsorption (excluding adsorption isotherms), Colloids, types, methods of preparation and general properties, Elementary ideas of emulsions, surfactants and micelles (only definitions and examples).

Nuclear Chemistry Radioactivity, isotopes and isobars, Properties of rays, Kinetics of radioactive decay (decay series excluded), carbon dating, Stability of nuclei with respect to proton-neutron ratio, Brief discussion on fission and fusion reactions.

INORGANIC CHEMISTRY

Isolation/Preparation and Properties of the following Non-metals Boron, silicon, nitrogen, phosphorus, oxygen, sulphur and halogens, Properties of allotropes of carbon (only diamond and graphite), phosphorus and sulphur.

Preparation and Properties of the following Compounds

Oxides, peroxides, hydroxides, carbonates, bicarbonates, chlorides and sulphates of sodium, potassium, magnesium and calcium, Boron, diborane, boric acid and borax, Aluminium, alumina, aluminium chloride and alums, Carbon, oxides and oxyacid (carbonic acid), Silicon, silicones, silicates and silicon carbide, Nitrogen, oxides, oxyacids and ammonia, Phosphorus, oxides, oxyacids (phosphorus acid, phosphoric acid) and phosphine, Oxygen, ozone and hydrogen peroxide, Sulphur, hydrogen sulphide, oxides, sulphurous acid, sulphuric acid and sodium thiosulphate, Halogens, hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder, Xenon fluorides.

Transition Elements (3d series) Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and

calculation of spin-only magnetic moment; Coordination compounds: nomenclature of mononuclear coordination compounds, cis-trans and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

Preparation and Properties of the following

Compounds Oxides and chlorides of tin and lead, Oxides, chlorides and sulphates of Fe^{2+} , Cu^{2+} and Zn^{2+} , Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate.

Ores and Minerals Commonly occurring ores and minerals of iron, copper, tin, lead, magnesium, aluminium, zinc and silver.

Extractive Metallurgy Chemical principles and reactions only (industrial details excluded), Carbon reduction method (iron and tin), Self reduction method (copper and lead), Electrolytic reduction method (magnesium and aluminium), Cyanide process (silver and gold).

Principles of Qualitative Analysis Groups I to V (only Ag^+ , Hg^{2+} , Cu^{2+} , Pb^{2+} , Bi^{3+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Mn^{2+} and Mg^{2+}), Nitrate, halides (excluding fluoride), sulphate and sulphide.

ORGANIC CHEMISTRY

Concepts Hybridisation of carbon, Sigma and pi-bonds, Shapes of simple organic molecules, Structural and geometrical isomerism, Optical isomerism of compounds containing up to two asymmetric centres, (R,S and E,Z nomenclature excluded), IUPAC nomenclature of simple organic compounds (only hydrocarbons, mono-functional and bi-functional compounds), Conformations of ethane and butane (Newman projections), Resonance and hyperconjugation, Keto-enol tautomerism, Determination of empirical and molecular formulae of simple compounds (only combustion method), Hydrogen bonds, definition and their effects on physical properties of alcohols and carboxylic acids, Inductive and resonance effects on acidity and basicity of organic acids and bases, Polarity and inductive effects in alkyl halides, Reactive intermediates produced during homolytic and heterolytic bond cleavage, Formation, structure and stability of carbocations, carbanions and free radicals.

Preparation, Properties and Reactions of Alkanes

Homologous series, physical properties of alkanes (melting points, boiling points and density), Combustion and halogenation of alkanes, Preparation of alkanes by Wurtz reaction and decarboxylation reactions.

Preparation, Properties and Reactions of Alkenes and Alkynes Physical properties of alkenes and alkynes

(boiling points, density and dipole moments), Acidity of alkynes, Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination), Reactions of alkenes with KMnO_4 and ozone, Reduction of alkenes and alkynes, Preparation of alkenes and alkynes by elimination reactions, Electrophilic addition reactions of alkenes with X_2 , HX , HOX and H_2O (X =halogen), Addition reactions of alkynes, Metal acetylides.

Reactions of Benzene Structure and aromaticity, Electrophilic substitution reactions, halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation Effect of o-, m- and p-directing groups in monosubstituted benzenes.

Phenols Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation), Reimer-Tiemann reaction, Kolbe reaction.

Characteristic Reactions of the following (including those mentioned above) Alkyl halides, rearrangement reactions of alkyl carbocation, Grignard reactions, nucleophilic substitution reactions, Alcohols, esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, ZnCl_2 /concentrated HCl, conversion of alcohols into aldehydes and ketones, Ethers, Preparation by Williamson's Synthesis, Aldehydes and Ketones, oxidation, reduction, oxime and hydrazone formation, aldol condensation, Perkin reaction, Cannizzaro reaction, haloform reaction and nucleophilic addition reactions (Grignard addition), Carboxylic acids, formation of esters, acid chlorides and amides, ester hydrolysis. Amines, basicity of substituted anilines and aliphatic amines, preparation from nitro compounds, reaction with nitrous acid, azo coupling reaction of diazonium salts of aromatic amines, Sandmeyer and related reactions of diazonium salts, carbylamine reaction, Haloarenes, nucleophilic aromatic substitution in haloarenes and substituted haloarenes (excluding Benzyne mechanism and Cine substitution).

Carbohydrates Classification, mono and disaccharides (glucose and sucrose), Oxidation, reduction, glycoside formation and hydrolysis of sucrose.

Amino Acids and Peptides General structure (only primary structure for peptides) and physical properties.

Properties and Uses of Some Important Polymers Natural rubber, cellulose, nylon, teflon and PVC.

Practical Organic Chemistry Detection of elements (N, S, halogens), Detection and identification of the following functional groups, hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro, Chemical methods of separation of mono-functional organic compounds from binary mixtures.

1

Some Basic Concepts of Chemistry

Topic 1 Mole Concept

Objective Questions I (Only one correct option)

1. 5 moles of AB_2 weight 125×10^{-3} kg and 10 moles of A_2B_2 weight 300×10^{-3} kg. The molar mass of $A(M_A)$ and molar mass of $B(M_B)$ in kg mol^{-1} are (2019 Main, 12 April I)
(a) $M_A = 10 \times 10^{-3}$ and $M_B = 5 \times 10^{-3}$
(b) $M_A = 50 \times 10^{-3}$ and $M_B = 25 \times 10^{-3}$
(c) $M_A = 25 \times 10^{-3}$ and $M_B = 50 \times 10^{-3}$
(d) $M_A = 5 \times 10^{-3}$ and $M_B = 10 \times 10^{-3}$
2. The minimum amount of $O_2(g)$ consumed per gram of reactant is for the reaction (Given atomic mass : Fe = 56, O = 16, Mg = 24, P = 31, C = 12, H = 1) (2019 Main, 10 April II)
(a) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
(b) $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$
(c) $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
(d) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
3. At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of O_2 for complete combustion and 40 mL of CO_2 is formed. The formula of the hydrocarbon is (2019 Main, 10 April I)
(a) C_4H_7Cl (b) C_4H_6 (c) C_4H_{10} (d) C_4H_8
4. 10 mL of 1 mM surfactant solution forms a monolayer covering 0.24 cm^2 on a polar substrate. If the polar head is approximated as a cube, what is its edge length? (2019 Main, 9 April II)
(a) 2.0 pm (b) 0.1 nm (c) 1.0 pm (d) 2.0 nm
5. For a reaction,
 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, identify dihydrogen (H_2) as a limiting reagent in the following reaction mixtures. (2019 Main, 9 April I)
(a) 56 g of N_2 + 10 g of H_2 (b) 35 g of N_2 + 8 g of H_2
(c) 14 g of N_2 + 4 g of H_2 (d) 28 g of N_2 + 6 g of H_2
6. The percentage composition of carbon by mole in methane is (2019 Main, 8 April II)
(a) 75% (b) 20% (c) 25% (d) 80%
7. 8 g of NaOH is dissolved in 18 g of H_2O . Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solution respectively are (2019 Main, 12 Jan II)
(a) 0.2, 11.11 (b) 0.167, 22.20
(c) 0.2, 22.20 (d) 0.167, 11.11
8. The volume strength of 1 M H_2O_2 is (Molar mass of H_2O_2 = 34 g mol^{-1}) (2019 Main, 12 Jan II)
(a) 16.8 (b) 22.4 (c) 11.35 (d) 5.6
9. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is (2019 Main, 10 Jan II)
(a) 17.1 g (b) 68.4 g (c) 136.8 g (d) 34.2 g
10. For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is :
 $2C_{57}H_{110}O_6(s) + 163O_2(g) \rightarrow 114CO_2(g) + 110H_2O(l)$ (2019 Main, 9 Jan II)
(a) 490 g (b) 495 g (c) 445 g (d) 890 g
11. A solution of sodium sulphate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is (2019 Main, 9 Jan I)
(a) 16 (b) 4 (c) 132 (d) 8
12. The most abundant elements by mass in the body of a healthy human adult are oxygen (61.4%), carbon (22.9%), hydrogen (10.0 %), and nitrogen (2.6%). The weight which a 75 kg person would gain if all ^1H atoms are replaced by ^2H atoms is (2017 JEE Main)
(a) 15 kg (b) 37.5 kg
(c) 7.5 kg (d) 10 kg
13. 1 g of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2 . The molar mass of M_2CO_3 in g mol^{-1} is (2017 JEE Main)
(a) 1186 (b) 84.3 (c) 118.6 (d) 11.86

2 Some Basic Concepts of Chemistry

- 14.** At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O₂ by volume for complete combustion. After combustion, the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is (2016 Main)
 (a) C₃H₈ (b) C₄H₈ (c) C₄H₁₀ (d) C₃H₆
- 15.** The molecular formula of a commercial resin used for exchanging ions in water softening is C₈H₇SO₃Na (molecular weight = 206). What would be the maximum uptake of Ca²⁺ ions by the resin when expressed in mole per gram resin? (2015 Main)
 (a) $\frac{1}{103}$ (b) $\frac{1}{206}$ (c) $\frac{2}{309}$ (d) $\frac{1}{412}$
- 16.** 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is (2015 Main)
 (a) 18 mg (b) 36 mg (c) 42 mg (d) 54 mg
- 17.** The ratio mass of oxygen and nitrogen of a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is (2014 Main)
 (a) 1 : 4 (b) 7 : 32 (c) 1 : 8 (d) 3 : 16
- 18.** The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be (2013 Main)
 (a) 0.875 M (b) 1.00 M (c) 1.75 M (d) 0.0975M
- 19.** Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is (2011)
 (a) 1.78 M (b) 2.00 M (c) 2.05 M (d) 2.22 M
- 20.** Given that the abundances of isotopes ⁵⁴Fe, ⁵⁶Fe and ⁵⁷Fe are 5%, 90% and 5%, respectively, the atomic mass of Fe is (2009)
 (a) 55.85 (b) 55.95
 (c) 55.75 (d) 56.05
- 21.** Mixture X = 0.02 mole of [Co(NH₃)₅SO₄]Br and 0.02 mole of [Co(NH₃)₅Br]SO₄ was prepared in 2 L solution.
 1 L of mixture X + excess of AgNO₃ solution \longrightarrow Y
 1 L of mixture X + excess of BaCl₂ solution \longrightarrow Z
 Number of moles of Y and Z are (2003, 1M)
 (a) 0.01, 0.01 (b) 0.02, 0.01
 (c) 0.01, 0.02 (d) 0.02, 0.02
- 22.** Which has maximum number of atoms? (2003, 1M)
 (a) 24 g of C (12) (b) 56 g of Fe (56)
 (c) 27 g of Al (27) (d) 108 g of Ag (108)
- 23.** How many moles of electron weighs 1 kg?
 (a) 6.023×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$ (2002, 3M)
 (c) $\frac{6.023}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^8$
- 24.** The normality of 0.3 M phosphorus acid (H₃PO₃) is (1999, 2M)
 (a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6
- 25.** In which mode of expression, the concentration of a solution remains independent of temperature? (1988, 1M)
 (a) Molarity (b) Normality (c) Formality (d) Molality
- 26.** A molal solution is one that contains one mole of solute in (1986, 1M)
 (a) 1000 g of solvent (b) 1.0 L of solvent
 (c) 1.0 L of solution (d) 22.4 L of solution
- 27.** If 0.50 mole of BaCl₂ is mixed with 0.20 mole of Na₃PO₄, the maximum number of moles of Ba₃(PO₄)₂ that can be formed is (1981, 1M)
 (a) 0.70 (b) 0.50 (c) 0.20 (d) 0.10
- 28.** 2.76 g of silver carbonate on being strongly heated yields a residue weighing (1979, 1M)
 (a) 2.16 g (b) 2.48 g (c) 2.32 g (d) 2.64 g
- 29.** When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is (1979, 1M)
 (a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4
- 30.** The largest number of molecules is in (1979, 1M)
 (a) 36 g of water
 (b) 28 g of CO
 (c) 46 g of ethyl alcohol
 (d) 54 g of nitrogen pentoxide (N₂O₅)
- 31.** The total number of electrons in one molecule of carbon dioxide is (1979, 1M)
 (a) 22 (b) 44 (c) 66 (d) 88
- 32.** A gaseous mixture contains oxygen and nitrogen in the ratio of 1:4 by weight. Therefore, the ratio of their number of molecules is (1979, 1M)
 (a) 1 : 4 (b) 1 : 8 (c) 7 : 32 (d) 3 : 16

Numerical Answer Type Questions

- 33.** A 100 mL solution was made by adding 1.43 g of Na₂CO₃ · xH₂O. The normality of the solution is 0.1 N. The value of x is
 (The atomic mass of Na is 23 g/mol) (2020 Main, 4 Sep II)
- 34.** Galena (an ore) is partially oxidised by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the content undergo self-reduction. The weight (in kg) of Pb produced per kg of O₂ consumed is
 (Atomic weights in g mol⁻¹ : O = 16, S = 32, Pb = 207) (2018 Adv.)
- 35.** To measure the quantity of MnCl₂ dissolved in an aqueous solution, it was completely converted to KMnO₄ using the reaction,
 MnCl₂ + K₂S₂O₈ + H₂O \longrightarrow KMnO₄ + H₂SO₄ + HCl
 (equation not balanced).

Some Basic Concepts of Chemistry 3

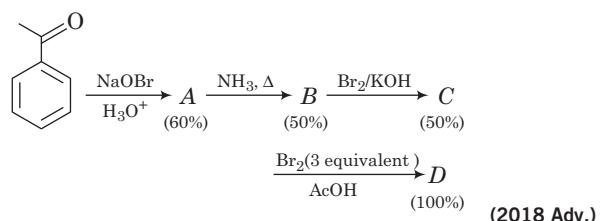
Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl₂ (in mg) present in the initial solution is

(Atomic weights in g mol⁻¹: Mn = 55, Cl = 35.5)

(2018 Adv.)

- 36.** In the following reaction sequence, the amount of *D* (in gram) formed from 10 moles of acetophenone is

(Atomic weights in g mol⁻¹ : H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)



Fill in the Blanks

- 37.** The weight of 1×10^{22} molecules of CuSO₄ · 5H₂O is (1991, 1M)
- 38.** 3.0 g of a salt of molecular weight 30 is dissolved in 250 g water. The molarity of the solution is (1983, 1M)
- 39.** The total number of electrons present in 18 mL of water is (1980, 1M)
- 40.** The modern atomic mass unit is based on the mass of (1980, 1M)

Integer Answer Type Questions

- 41.** The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm⁻³. The ratio of the molecular weights of the solute and solvent, $\left(\frac{m_{\text{solute}}}{m_{\text{solvent}}}\right)$ is ... (2016 Adv.)
- 42.** A compound H₂X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL⁻¹. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is (2014 Adv.)
- 43.** 29.2% (w/W) HCl stock solution has density of 1.25 g mL⁻¹. The molecular weight of HCl is 36.5 g mol⁻¹. The volume (mL) of stock solution required to prepare a 200 mL solution 0.4 M HCl is (2012)

Subjective Questions

- 44.** 20% surface sites have adsorbed N₂. On heating N₂ gas evolved from sites and were collected at 0.001 atm and 298

K in a container of volume is 2.46 cm³. Density of surface sites is $6.023 \times 10^{14} \text{ cm}^{-2}$ and surface area is 1000 cm², find out the number of surface sites occupied per molecule of N₂. (2005, 3M)

- 45.** In a solution of 100 mL 0.5 M acetic acid, one gram of active charcoal is added, which absorbs acetic acid. It is found that the concentration of acetic acid becomes 0.49 M. If surface area of charcoal is $3.01 \times 10^2 \text{ m}^2$, calculate the area occupied by single acetic acid molecule on surface of charcoal. (2003)
- 46.** Find the molarity of water. Given: $\rho = 1000 \text{ kg/m}^3$ (2003)
- 47.** A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm³/g. If the virus is considered to be a single particle, find its molar mass. (1999, 3M)
- 48.** 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm³ of solution of density 1077.2 kg m⁻³. Calculate the molality, molarity and mole fraction of Na₂SO₄ in solution. (1994, 3M)
- 49.** *A* is a binary compound of a univalent metal. 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid *B*, that forms a hydrated double salt, *C* with Al₂(SO₄)₃. Identify *A*, *B* and *C*. (1994, 2M)
- 50.** Upon mixing 45.0 mL 0.25 M lead nitrate solution with 25.0 mL of a 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1993, 3M)
- 51.** Calculate the molality of 1.0 L solution of 93% H₂SO₄, (weight/volume). The density of the solution is 1.84 g/mL. (1990, 1M)
- 52.** A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture. (1990, 4M)
- 53.** *n*-butane is produced by monobromination of ethane followed by Wurtz's reaction. Calculate volume of ethane at NTP required to produce 55 g *n*-butane, if the bromination takes place with 90% yield and the Wurtz's reaction with 85% yield. (1989, 3M)
- 54.** A sugar syrup of weight 214.2 g contains 34.2 g of sugar (C₁₂H₂₂O₁₁). Calculate (i) molal concentration and (ii) mole fraction of sugar in syrup. (1988, 2M)
- 55.** An unknown compound of carbon, hydrogen and oxygen contains 69.77% C and 11.63% H and has a molecular weight of 86. It does not reduce Fehling's solution but forms a bisulphite addition compound and gives a positive iodoform test. What is the possible structure(s) of unknown compound? (1987, 3M)
- 56.** The density of a 3 M sodium thiosulphate solution (Na₂S₂O₃) is 1.25 g per mL. Calculate (i) the percentage by weight of

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sodium thiosulphate (ii) the mole fraction of sodium thiosulphate and (iii) the molalities of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions.

(1983, 5M)

- 57.** (a) 1.0 L of a mixture of CO and CO₂ is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 L. The volumes are measured under the same conditions. Find the composition of mixture by volume.

(b) A compound contains 28 per cent of nitrogen and 72 per cent of a metal by weight. 3 atoms of metal combine with 2 atoms of nitrogen. Find the atomic weight of metal. **(1980, 5M)**

58. 5.00 mL of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 mL) and the mixture exploded by means of electric spark. After explosion, the volume of the mixed gases remaining was 25 mL.

On adding a concentrated solution of KOH, the volume further diminished to 15 mL, the residual gas being pure

Topic 2 Equivalent Concept, Neutralisation and Redox Titration

Objective Questions I (Only one correct option)

- 1.** An example of a disproportionation reaction is
(2019 Main, 12 April I)

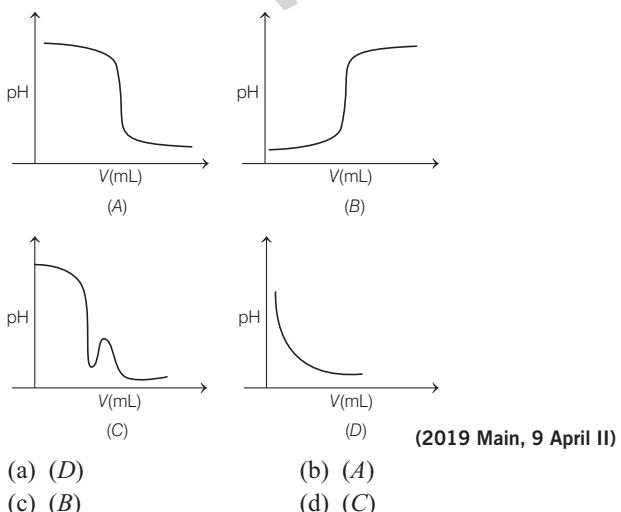
(a) $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$

(b) $2\text{NaBr} + \text{Cl}_2 \longrightarrow 2\text{NaCl} + \text{Br}_2$

(c) $2\text{KMnO}_4 \longrightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$

(d) $2\text{CuBr} \longrightarrow \text{CuBr}_2 + \text{Cu}$

2. In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment? **(2019 Main, 9 April II)**



3. 0.27 g of a long chain fatty acid was dissolved in 100 cm³ of hexane. 10 mL of this solution was added dropwise to the

oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas. (1979, 3M)

- 59.** In the analysis of 0.5 g sample of feldspar, a mixture of chlorides of sodium and potassium is obtained, which weighs 0.1180 g. Subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in the sample? **(1979, 5M)**

60. The vapour density (hydrogen = 1) of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g of the mixture. **(1979, 5M)**

61. Accounts for the following. Limit your answer to two sentences, "Atomic weights of most of the elements are fractional". **(1979, 1M)**

62. Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. **(1978, 2M)**

surface of water in a round watch glass. Hexane evaporates and a monolayer is formed. The distance from edge to centre of the watch glass is 10 cm. What is the height of the monolayer? [Density of fatty acid = 0.9 g cm⁻³; $\pi = 3$]

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8. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is (2019 Main, 10 Jan II)
 (a) 2 (b) 5 (c) 1 (d) 10

9. The ratio of mass per cent of C and H of an organic compound ($\text{C}_x\text{H}_y\text{O}_z$) is 6 : 1. If one molecule of the above compound ($\text{C}_x\text{H}_y\text{O}_z$) contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O . The empirical formula of compound $\text{C}_x\text{H}_y\text{O}_z$ is (2018 Main)
 (a) $\text{C}_3\text{H}_6\text{O}_3$ (b) $\text{C}_2\text{H}_4\text{O}$ (c) $\text{C}_3\text{H}_4\text{O}_2$ (d) $\text{C}_2\text{H}_4\text{O}_3$

10. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? (2018 Main)

Base	Acid	End point
(a) Weak	Strong	Colourless to pink
(b) Strong	Strong	Pinkish red to yellow
(c) Weak	Strong	Yellow to pinkish red
(d) Strong	Strong	Pink to colourless

11. From the following statements regarding H_2O_2 choose the incorrect statement. (2015 Main)
 (a) It can act only as an oxidising agent
 (b) It decomposed on exposure to light
 (c) It has to be stored in plastic or wax lined glass bottles in dark
 (d) It has to be kept away from dust

12. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is (2007, 3M)
 (a) 3 (b) 4 (c) 5 (d) 6

13. In the standardisation of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry, the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is (2001, 1M)
 (a) (molecular weight)/2 (b) (molecular weight)/6
 (c) (molecular weight)/3 (d) same as molecular weight

14. The reaction, $3\text{ClO}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + 2\text{Cl}^-(aq)$ is an example of (2001)
 (a) oxidation reaction
 (b) reduction reaction
 (c) disproportionation reaction
 (d) decomposition reaction

15. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is (2001, 1M)
 (a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

16. Among the following, the species in which the oxidation number of an element is + 6 (2000)
 (a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$
 (c) NiF_6^{2-} (d) CrO_2Cl_2

17. The oxidation number of sulphur in S_8 , S_2F_2 , H_2S respectively, are (1999)

- (a) 0, +1 and -2 (b) +2, +1 and -2
 (c) 0, +1 and +2 (d) -2, +1 and -2

18. The number of moles of KMnO_4 that will be needed to react completely with one mole of ferrous oxalate in acidic medium is (1997)

- (a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1

19. The number of moles of KMnO_4 that will be needed to react with one mole of sulphite ion in acidic solution is (1997)

- (a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1

20. For the redox reaction



The correct coefficients of the reactants for the balanced reaction are

MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+	
(a) 2	5	16	
(b) 16	5	2	
(c) 5	16	2	
(d) 2	16	5	

21. The volume strength of 1.5 N H_2O_2 is (1990, 1M)

- (a) 4.8 (b) 8.4 (c) 3.0 (d) 8.0

22. The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is

- (a) +3 (b) +2 (c) +1 (d) -1 (1988)

23. The equivalent weight of MnSO_4 is half of its molecular weight, when it converts to (1988, 1M)

- (a) Mn_2O_3 (b) MnO_2
 (c) MnO_4^- (d) MnO_4^{2-}

Objective Question II (More than one correct option)

24. For the reaction, $\text{I}^- + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$ the correct statement(s) in the balanced equation is/are

- (a) stoichiometric coefficient of HSO_4^- is 6 (2014 Adv.)
 (b) iodide is oxidised
 (c) sulphur is reduced
 (d) H_2O is one of the products

Numerical Answer Type Questions

25. 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink color is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution?

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Exp. No.	Vol. of NaOH (mL)
1	12.5
2	10.5
3	9.0
4	9.0
5	9.0

(2020 Adv.)

26. Aluminium reacts with sulphuric acid to form aluminium sulphate and hydrogen. What is the volume of hydrogen gas in litre (L) produced at 300 K and 1.0 atm pressure, when 5.4 g of aluminium and 50.0 mL of 5.0 M sulphuric acid are combined for the reaction?

(Use molar mass of aluminium as 27.0 g mol⁻¹, R = 0.082 atm L mol⁻¹ K⁻¹) (2020 Adv.)

27. A 20.0 mL solution containing 0.2 g impure H₂O₂ reacts completely with 0.316 g of KMnO₄ in acid solution. The purity of H₂O₂ (in%) is (molecular weight of H₂O₂ = 34; molecular weight of KMnO₄ = 158). (2020 Main, 4 Sep I)

28. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by NiCl₂ · 6H₂O to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of NiCl₂ · 6H₂O are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is _____

(Atomic weights in g mol⁻¹ : H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59) (2018 Adv.)

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
 (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
 (c) Statement I is true; Statement II is false.
 (d) Statement I is false; Statement II is true.
29. **Statement I** In the titration of Na₂CO₃ with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.

Statement II Two moles of HCl are required for the complete neutralisation of one mole of Na₂CO₃. (1991, 2M)

Fill in the Blanks

30. The compound YBa₂Cu₃O₇, which shows super conductivity, has copper in oxidation state Assume that the rare earth element yttrium is in its usual + 3 oxidation state. (1994, 1M)

Integer Answer Type Questions

31. The difference in the oxidation numbers of the two types of sulphur atoms in Na₂S₄O₆ is (2011)
 32. Among the following, the number of elements showing only one non-zero oxidation state is O, Cl, F, N, P, Sn, Ti, Na, Ti (2010)
 33. A student performs a titration with different burettes and finds titrate values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titrate value is (2010)

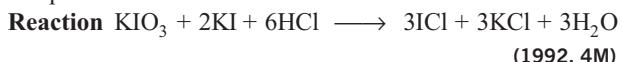
Subjective Questions

34. Calculate the amount of calcium oxide required when it reacts with 852 g of P₄O₁₀. (2005, 2M)
 35. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of KMnO₄ (20 mL) acidified with dilute H₂SO₄. The same volume of the KMnO₄ solution is just decolourised by 10 mL of MnSO₄ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO₂. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H₂SO₄. Write the balanced equations involved in the reactions and calculate the molarity of H₂O₂. (2001)
 36. How many millilitres of 0.5 M H₂SO₄ are needed to dissolve 0.5 g of copper (II) carbonate? (1999, 3M)
 37. An aqueous solution containing 0.10 g KIO₃ (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I₂ consumed 45.0 mL of thiosulphate solution decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. (1998, 5M)
 38. To a 25 mL H₂O₂ solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H₂O₂ solution. (1997, 5M)
 39. A 3.00 g sample containing Fe₃O₄, Fe₂O₃ and an inert impure substance, is treated with excess of KI solution in presence of dilute H₂SO₄. The entire iron is converted into Fe²⁺ along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M Na₂S₂O₃ solution to reduce the iodine present. A 50 mL of the dilute solution, after complete extraction of the iodine required 12.80 mL of 0.25 M KMnO₄ solution in dilute H₂SO₄ medium for the oxidation of Fe²⁺. Calculate the percentage of Fe₂O₃ and Fe₃O₄ in the original sample. (1996, 5M)
 40. A 20.0 cm³ mixture of CO, CH₄ and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm³. A further contraction of 14.0 cm³ occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. (1995, 4M)

Some Basic Concepts of Chemistry 7

- 41.** A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. (1995, 3M)

- 42.** One gram of commercial AgNO_3 is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in presence of 6 M HCl till all I^- ions are converted into ICl . It requires 50 mL of (M/10) KIO_3 solution, 20 mL of the same stock solution of KI requires 30 mL of (M/10) KIO_3 under similar conditions. Calculate the percentage of AgNO_3 in the sample.



- 43.** A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 mL . A 1.5 g of the same sample requires 150 mL of (M/10) HCl for complete neutralisation. Calculate the percentage composition of the components of the mixture. (1992, 5M)

- 44.** A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL . An aliquot of 25.0 mL of this solution requires for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (1991, 4M)

- 45.** A solution of 0.2 g of a compound containing Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions on titration with 0.02 M KMnO_4 in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralised with Na_2CO_3 , acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of $0.05\text{ M Na}_2\text{S}_2\text{O}_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titrations. (1991, 5M)

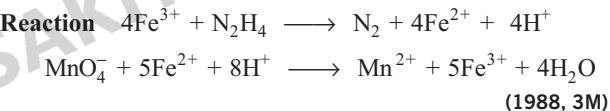
- 46.** A mixture of $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) and NaHC_2O_4 weighing 2.02 g was dissolved in water and the solution made up to one litre. Ten millilitres of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralisation. In another experiment, 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N potassium permanganate solution for complete reaction.

Calculate the amount of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 in the mixture. (1990, 5M)

- 47.** An organic compound X on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures Y and Z . Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structure of Y and Z . (1989, 5M)

- 48.** An equal volume of a reducing agent is titrated separately with 1 M KMnO_4 in acid, neutral and alkaline medium. The volumes of KMnO_4 required are 20 mL in acid, 33.3 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half-reactions. Find out the volume of $1\text{ M K}_2\text{Cr}_2\text{O}_7$ consumed, if the same volume of the reducing agent is titrated in acid medium. (1989, 5M)

- 49.** A sample of hydrazine sulphate ($\text{N}_2\text{H}_6\text{SO}_4$) was dissolved in 100 mL of water, 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it, required 20 mL of $M/50$ potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution.



- 50.** 5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L . 30 mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 100 mL of water. Calculate the amount in gram of the sulphate ions in solution. (1985, 4M)

- 51.** 2.68×10^{-3} moles of a solution containing an ion A^{n+} require 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to $A\text{O}_3^-$ in acidic medium. What is the value of n ? (1984, 2M)

- 52.** 4.08 g of a mixture of BaO and unknown carbonate $M\text{CO}_3$ was heated strongly. The residue weighed 3.64 g . This was dissolved in 100 mL of 1 N HCl . The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralisation. Identify the metal M . (1983, 4M)

Answers

Topic 1

- | | | | |
|--------|---------|---------|---------|
| 1. (d) | 2. (c) | 3. (b) | 4. (a) |
| 5. (d) | 6. (b) | 7. (d) | 8. (c) |
| 9. (b) | 10. (b) | 11. (b) | 12. (c) |

- | | | | |
|---------|---------|---------|---------|
| 13. (b) | 14. (*) | 15. (d) | 16. (d) |
| 17. (b) | 18. (a) | 19. (c) | 20. (b) |
| 21. (a) | 22. (a) | 23. (d) | 24. (d) |
| 25. (d) | 26. (a) | 27. (d) | 28. (a) |
| 29. (a) | 30. (a) | 31. (a) | 32. (c) |

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33. (10.00) 34. (6.47 kg) 35. (126 mg) 36. (495 g)
 37. (4.14 g) 38. (0.4) 39. (6.023×10^{24}) 40. C-12
 isotope
 41. (9) 42. (8) 43. (8 mL) 44. (2)
 45. ($5 \times 10^{-19} \text{ m}^2$) 46. (55.56 mol
 L^{-1}) 47. ($70.91 \times 10^6 \text{ g}$) 48. (4.3×10^{-3})
 51. (10.42) 52. (1.7 g) 53. (55.55 L) 54. (9.9×10^{-3})
 56. (i) (37.92), (ii) (0.065), (iii) (7.73 m) 57. (a) (0.6), (b) (24)
 59. (i) (0.0179 g), (ii) (10.6 %) 60. (0.437) 62. (20 %)

Topic 2

1. (d) 2. (b) 3. (a) 4. (a)

5. (d) 6. (*) 7. (b) 8. (c)
 9. (d) 10. (c) 11. (a) 12. (d)
 13. (b) 14. (c) 15. (a) 16. (d)
 17. (a) 18. (b) 19. (a) 20. (a)
 21. (b) 22. (c) 23. (b) 24. (a,b,d)
 25. (0.11) 26. (6.15) 27. (85)
 28. (2992) 29. (b) 30. 7/3 31. (5)
 32. (2) 33. (3) 34. (1008 g) 36. (8.096 mL)
 37. (0.062 M) 38. (1.334 V) 42. (85%) 44. (1.04)
 45. (1:2) 48. (16.67 mL) 49. (6.5 g L^{-1}) 50. (6.5376 g)
 51. (2) 52. (Ca)

Hints & Solutions

Topic 1 Mole Concept

1. **Key Idea** To find the mass of A and B in the given question, mole concept is used.

$$\text{Number of moles}(n) = \frac{\text{given mass}(w)}{\text{molecular mass}(M)}$$

Compound	Mass of A (g)	Mass of B (g)
AB_2	M_A	$2M_B$
A_2B_2	$2M_A$	$2M_B$

We know that,

$$\text{Number of moles}(n) = \frac{\text{given mass}(w)}{\text{molecular mass}(M)}$$

$$n \times M = w \quad \dots(A)$$

Using equation (A), it can be concluded that

$$5(M_A + 2M_B) = 125 \times 10^{-3} \text{ kg} \quad \dots(\text{i})$$

$$10(2M_A + 2M_B) = 300 \times 10^{-3} \text{ kg} \quad \dots(\text{ii})$$

From equation (i) and (ii)

$$\frac{1}{2} \frac{(M_A + 2M_B)}{(2M_A + 2M_B)} = \left(\frac{125}{300} \right)$$

On solving the equation, we obtain

$$M_A = 5 \times 10^{-3}$$

$$\text{and} \quad M_B = 10 \times 10^{-3}$$

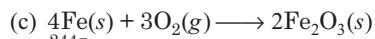
So, the molar mass of A(M_A) is

$$5 \times 10^{-3} \text{ kg mol}^{-1}$$

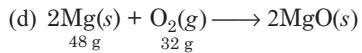
and B(M_B) is $10 \times 10^{-3} \text{ kg mol}^{-1}$.

2. (a) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
 $\frac{44\text{g}}{160\text{g}}$
 $\Rightarrow 1 \text{ g of reactant} = \frac{160}{44} \text{ g of } O_2 \text{ consumed} = 3.64 \text{ g}$

- (b) $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$
 $\frac{124\text{g}}{160\text{g}}$
 $\Rightarrow 1 \text{ g of reactant} = \frac{160}{124} \text{ g of } O_2 \text{ consumed} = 1.29 \text{ g}$



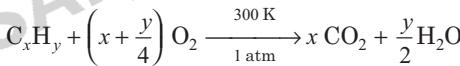
$$\Rightarrow 1 \text{ g of reactant} = \frac{96}{224} \text{ g of } O_2 \text{ consumed} = 0.43 \text{ g}$$



$$\Rightarrow 1 \text{ g of reactant} = \frac{32}{48} \text{ g of } O_2 \text{ consumed} = 0.67 \text{ g}$$

So, minimum amount of O_2 is consumed per gram of reactant (Fe) in reaction (c).

3. In eudiometry,



$$1 \text{ mol} \quad \left(x + \frac{y}{4} \right) \text{ mol} \quad x \text{ mol}$$

$$1 \text{ mL} \quad \left(x + \frac{y}{4} \right) \text{ mL} \quad x \text{ mL}$$

$$10 \text{ mL} \quad \left(x + \frac{y}{4} \right) \times 10 \text{ mL} \quad 10x \text{ mL}$$

$$\text{Given, (i)} \quad V_{CO_2} = 10x = 40 \text{ mL} \Rightarrow x = 4$$

$$\text{(ii)} \quad V_{O_2} = 10 \left(x + \frac{y}{4} \right) \text{ mL} = 55 \text{ mL}$$

$$\Rightarrow 10 \left(4 + \frac{y}{4} \right) = 55 \quad [\because x = 4]$$

$$\Rightarrow 40 + \frac{y \times 10}{4} = 55$$

$$\Rightarrow y \times \frac{10}{4} = 15 \Rightarrow y = 15 \times \frac{4}{10} = 6$$

So, the hydrocarbon (C_xH_y) is C_4H_6 .

4. Given, volume = 10 mL

$$\text{Molarity} = 1 \text{ mM} = 10^{-3} \text{ M}$$

$$\therefore \text{Number of millimoles} = 10 \text{ mL} \times 10^{-3} \text{ M} = 10^{-2}$$

$$\text{Number of moles} = 10^{-5}$$

Now, number of molecules

$$= \text{Number of moles} \times \text{Avogadro's number}$$

$$= 10^{-5} \times 6 \times 10^{23} = 6 \times 10^{18}$$

Surface area occupied by 6×10^{18} molecules = 0.24 cm^2

\therefore Surface area occupied by 1 molecule

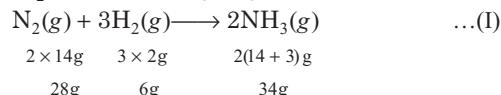
$$= \frac{0.24}{6 \times 10^{18}} = 0.04 \times 10^{-18} \text{ cm}^2$$

As it is given that polar head is approximated as cube. Thus, surface area of cube = a^2 , where

$$\begin{aligned} a &= \text{edge length} \\ \therefore a^2 &= 4 \times 10^{-20} \text{ cm}^2 \\ a &= 2 \times 10^{-10} \text{ cm} = 2 \text{ pm} \end{aligned}$$

5. **Key Idea** The reactant which is present in the lesser amount, i.e. which limits the amount of product formed is called limiting reagent.

When 56 g of N₂ + 10 g of H₂ is taken as a combination then dihydrogen (H₂) act as a limiting reagent in the reaction.



28 g N₂ requires 6 g H₂ gas.

$$56 \text{ g of N}_2 \text{ requires } \frac{6 \text{ g}}{28 \text{ g}} \times 56 \text{ g} = 12 \text{ g of H}_2$$

12 g of H₂ gas is required for 56 g of N₂ gas but only 10 g of H₂ gas is present in option (a).

Hence, H₂ gas is the limiting reagent.

In option (b), i.e. 35 g of N₂ + 8 g of H₂.

As 28 g N₂ requires 6 g of H₂,

$$35 \text{ g N}_2 \text{ requires } \frac{6 \text{ g}}{28 \text{ g}} \times 35 \text{ g H}_2 \Rightarrow 7.5 \text{ g of H}_2.$$

Here, H₂ gas does not act as limiting reagent since 7.5 g of H₂ gas is required for 35 g of N₂ and 8 g of H₂ is present in reaction mixture. Mass of H₂ left unreacted = 8 - 7.5 g of H₂.

$$= 0.5 \text{ g of H}_2.$$

Similarly, in option (c) and (d), H₂ does not act as limiting reagent.

For 14 g of N₂ + 4 g of H₂,

As we know 28 g of N₂ reacts with 6 g of H₂.

$$14 \text{ g of N}_2 \text{ reacts with } \frac{6}{28} \times 14 \text{ g of H}_2 \Rightarrow 3 \text{ g of H}_2.$$

For 28 g of N₂ + 6 g of H₂, i.e. 28 g of N₂ reacts with 6 g of H₂ (by equation I).

6. **Key Idea** The percentage composition of a compound is given by the formula.

% composition = [Composition of a substance in a compound / Total composition total of compound] × 100

In CH₄,

mole of carbon = 1

mole of hydrogen = 4

$$\therefore \% \text{ of carbon by mole in CH}_4 = \frac{1}{1+4} \times 100 = 20\%$$

7. Mole fraction of solute

$$= \frac{\text{number of moles of solute} + \text{number of moles solvent}}{\text{number of moles of solute}}$$

$$\chi_{\text{Solute}} = \frac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}} = \frac{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}} + \frac{w_{\text{Solvent}}}{Mw_{\text{Solvent}}}}$$

Given, $w_{\text{Solute}} = w_{\text{NaOH}} = 8 \text{ g}$

$$Mw_{\text{Solute}} = Mw_{\text{NaOH}} = 40 \text{ g mol}^{-1}$$

$$w_{\text{Solvent}} = w_{\text{H}_2\text{O}} = 18 \text{ g}$$

$$Mw_{\text{Solvent}} = 18 \text{ g mol}^{-1}$$

$$\therefore \chi_{\text{Solute}} = \chi_{\text{NaOH}} = \frac{8/40}{\frac{8}{40} + \frac{18}{18}} = \frac{0.2}{0.2 + 1} = \frac{0.2}{1.2} = 0.167$$

$$\text{Now, molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$\begin{aligned} &= \frac{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{w_{\text{Solvent}} \text{ (in g)}} \times 1000 = \frac{\frac{8}{40}}{\frac{18}{18}} \times 1000 \\ &= \frac{0.2}{18} \times 1000 = 11.11 \text{ mol kg}^{-1} \end{aligned}$$

Thus, mole fraction of NaOH in solution and molality of the solution respectively are 0.167 and 11.11 mol kg⁻¹.

8. Concentration of H₂O₂ is expressed in terms of volume strength, i.e. "volume of O₂ liberated by H₂O₂ at NTP". Molarity is connected to volume strength as:

$$\text{Molarity (M)} = \frac{x}{11.2} \text{ or } x = \text{Molarity} \times 11.2$$

where, x = volume strength

$$\text{So, for 1 M H}_2\text{O}_2, x = 1 \times 11.2 = 11.2$$

Among the given options, 11.35 is nearest to 11.2.

9. Molarity = $\frac{\text{Number of moles of solute (n)}}{\text{Volume of solution (in L)}}$

$$\text{Also, } n = \frac{w_B \text{ (g)}}{M_B \text{ (gmol}^{-1}\text{)}}$$

$$\therefore \text{Molarity} = \frac{w_B / M_B}{V}$$

Given, w_B = mass of solute (B) in g

$$M_B = \text{Gram molar mass of B (C}_{12}\text{H}_{22}\text{O}_{11}\text{)} = 342 \text{ g mol}^{-1}$$

$$\text{Molarity} = 0.1 \text{ M}$$

$$\text{Volume (V)} = 2 \text{ L}$$

$$\Rightarrow 0.1 = \frac{w_B / 342}{2} \Rightarrow w_B = 0.1 \times 342 \times 2 \text{ g} = 68.4 \text{ g}$$

10. $2 \text{ C}_{57}\text{H}_{110}\text{O}_6(s) + 163 \text{ O}_2(g) \longrightarrow 110\text{H}_2\text{O}(l) + 114 \text{ CO}_2(g)$

Molecular mass of C₅₇H₁₁₀O₆

$$= 2 \times (12 \times 57 + 1 \times 110 + 16 \times 6) \text{ g} = 1780 \text{ g}$$

Molecular mass of 110 H₂O = 110 (2 + 16) = 1980 g

1780 g of C₅₇H₁₁₀O₆ produced = 1980 g of H₂O.

$$445 \text{ g of C}_{57}\text{H}_{110}\text{O}_6 \text{ produced} = \frac{1980}{1780} \times 445 \text{ g of H}_2\text{O}$$

$$= 495 \text{ g of H}_2\text{O}$$

11. Molality (m) = $\frac{\text{Number of moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$

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$$= \frac{\text{Mass of solute (in g)} \times 1000}{\left[\frac{\text{Molecular weight of solute}}{\times \text{mass of solvent (in g)}} \right]} \\ = \frac{w_{\text{Na}^+} \times 1000}{M_{\text{Na}^+} \times w_{\text{H}_2\text{O}}} = \frac{92 \times 1000}{23 \times 1000} = 4 \text{ mol kg}^{-1}$$

12. Given, abundance of elements by mass
oxygen = 61.4%, carbon = 22.9%, hydrogen = 10% and
nitrogen = 2.6%

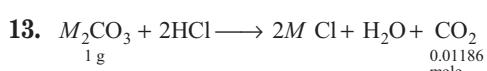
Total weight of person = 75 kg

$$\text{Mass due to } {}^1\text{H} = \frac{75 \times 10}{100} = 7.5 \text{ kg}$$

${}^1\text{H}$ atoms are replaced by ${}^2\text{H}$ atoms,

$$\text{Mass due to } {}^2\text{H} = (7.5 \times 2) \text{ kg}$$

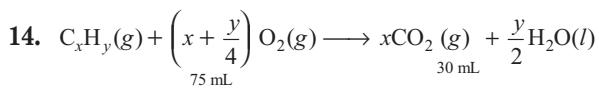
∴ Mass gain by person = 7.5 kg



Number of moles of $M_2\text{CO}_3$ reacted = Number of moles of CO_2 evolved

$$\frac{1}{M} = 0.01186 \quad [M = \text{molar mass of } M_2\text{CO}_3]$$

$$M = \frac{1}{0.01186} = 84.3 \text{ g mol}^{-1}$$



O_2 used = 20% of 375 = 75 mL

Inert part of air = 80% of 375 = 300 mL

Total volume of gases = CO_2 + Inert part of air
= 30 + 300 = 330 mL

$$\frac{x}{1} = \frac{30}{15} \Rightarrow x = 2$$

$$\frac{x + \frac{y}{4}}{1} = \frac{75}{15} \Rightarrow x + \frac{y}{4} = 5$$

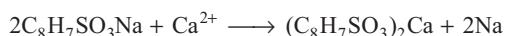
$$\Rightarrow x = 2, y = 12 \Rightarrow \text{C}_2\text{H}_{12}$$

15. We know the molecular weight of $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$
 $= 12 \times 8 + 1 \times 7 + 32 + 16 \times 3 + 23 = 206$

we have to find, mole per gram of resin.

∴ 1g of $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$ has number of mole
 $= \frac{\text{weight of given resin}}{\text{Molecular weight of resin}} = \frac{1}{206} \text{ mol}$

Now, reaction looks like



∴ 2 moles of $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$ combines with 1 mol Ca^{2+}

∴ 1 mole of $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$ will combine with $\frac{1}{2}$ mol Ca^{2+}

∴ $\frac{1}{206}$ mole of $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$ will combine with

$$\frac{1}{2} \times \frac{1}{206} \text{ mol Ca}^{2+} = \frac{1}{412} \text{ mol Ca}^{2+}$$

16. Given, initial strength of acetic acid = 0.06 N

Final strength = 0.042 N; Volume = 50 mL

∴ Initial millimoles of $\text{CH}_3\text{COOH} = 0.06 \times 50 = 3$

Final millimoles of $\text{CH}_3\text{COOH} = 0.042 \times 50 = 2.1$

∴ Millimoles of CH_3COOH adsorbed = $3 - 2.1 = 0.9$ mmol

$$= 0.9 \times 60 \text{ mg} = 54 \text{ mg}$$

$$17. \frac{n_{\text{O}_2}}{n_{\text{N}_2}} = \frac{\frac{(m_{\text{O}_2})}{(M_{\text{O}_2})}}{\frac{(m_{\text{N}_2})}{(M_{\text{N}_2})}}$$

where, m_{O_2} = given mass of O_2 , m_{N_2} = given mass of N_2 , M_{O_2} = molecular mass of O_2 , M_{N_2} = molecular mass of N_2 , n_{O_2} = number of moles of O_2 , n_{N_2} = number of moles of N_2

$$= \left[\frac{m_{\text{O}_2}}{m_{\text{N}_2}} \right] \frac{28}{32} = \frac{1}{4} \times \frac{28}{32} = \frac{7}{32}$$

18. From the formula, $M_f = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$

Given, $V_1 = 750 \text{ mL}$, $M_1 = 0.5 \text{ M}$

$V_2 = 250 \text{ mL}$, $M_2 = 2 \text{ M}$

$$= \frac{750 \times 0.5 + 250 \times 2}{750 + 250} = \frac{875}{1000} = 0.875 \text{ M}$$

19. Molarity = $\frac{\text{Moles of solute}}{\text{Volume of solution (L)}}$

$$\text{Moles of urea} = \frac{120}{60} = 2$$

Weight of solution = Weight of solvent + Weight of solute
= 1000 + 120 = 1120 g

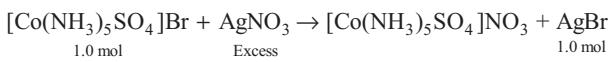
$$\Rightarrow \text{Volume} = \frac{1120 \text{ g}}{1.15 \text{ g/mL}} \times \frac{1}{1000 \text{ mL/L}} = 0.973 \text{ L}$$

$$\Rightarrow \text{Molarity} = \frac{2.000}{0.973} = 2.05 \text{ M}$$

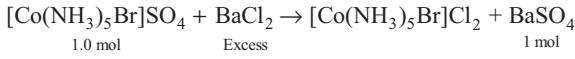
20. From the given relative abundance, the average weight of Fe can be calculated as

$$A = \frac{54 \times 5 + 56 \times 90 + 57 \times 5}{100} = 55.95$$

21. 1.0 L of mixture X contain 0.01 mole of each $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$. Also, with AgNO_3 , only $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ reacts to give AgBr precipitate as



With BaCl_2 , only $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ reacts giving BaSO_4 precipitate as



Hence, moles of Y and Z are 0.01 each.

22. Number of atoms = Number of moles

$$\times \text{Avogadro's number} (N_A)$$

$$\text{Number of atoms in 24 g C} = \frac{24}{12} \times N_A = 2N_A$$

$$\text{Number of atoms in } 56 \text{ g of Fe} = \frac{56}{56} N_A = N_A$$

$$\text{Number of atoms in } 27 \text{ g of Al} = \frac{27}{27} N_A = N_A$$

$$\text{Number of atoms in } 108 \text{ g of Ag} = \frac{108}{108} N_A = N_A$$

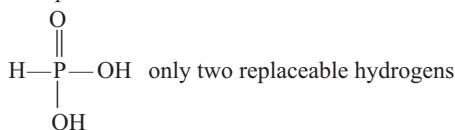
Hence, 24 g of carbon has the maximum number of atoms.

23. Mass of an electron = 9.108×10^{-31} kg

$$\therefore 9.108 \times 10^{-31} \text{ kg} = 1.0 \text{ electron}$$

$$\begin{aligned} \therefore 1 \text{ kg} &= \frac{1}{9.108 \times 10^{-31}} \text{ electrons} = \frac{10^{31}}{9.108} \times \frac{1}{6.023 \times 10^{23}} \\ &= \frac{1}{9.108 \times 6.023} \times 10^8 \text{ mole of electrons} \end{aligned}$$

24. Phosphorus acid is a dibasic acid as :



Therefore, normality = molarity \times basicity = $0.3 \times 2 = 0.60$

25. Molality is defined in terms of weight, hence independent of temperature. Remaining three concentration units are defined in terms of volume of solution, they depends on temperature.

26. Molality of a solution is defined as number of moles of solute present in 1.0 kg (1000 g) of solvent.

27. The balanced chemical reaction is



In this reaction, 3 moles of BaCl_2 combines with 2 moles of Na_3PO_4 . Hence, 0.5 mole of BaCl_2 require

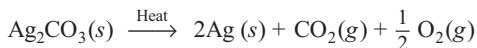
$$\frac{2}{3} \times 0.5 = 0.33 \text{ mole of } \text{Na}_3\text{PO}_4.$$

Since, available Na_3PO_4 (0.2 mole) is less than required mole (0.33), it is the limiting reactant and would determine the amount of product $\text{Ba}_3(\text{PO}_4)_2$.

\therefore 2 moles of Na_3PO_4 gives 1 mole $\text{Ba}_3(\text{PO}_4)_2$

$$\therefore 0.2 \text{ mole of } \text{Na}_3\text{PO}_4 \text{ would give } \frac{1}{2} \times 0.2 = 0.1 \text{ mole } \text{Ba}_3(\text{PO}_4)_2$$

28. Unlike other metal carbonates that usually decomposes into metal oxides liberating carbon dioxide, silver carbonate on heating decomposes into elemental silver liberating mixture of carbon dioxide and oxygen gas as :

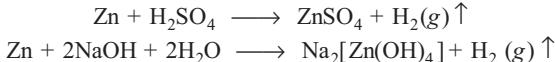


$$\text{MW} = 276 \text{ g} \quad 2 \times 108 = 216 \text{ g}$$

Hence, 2.76 g of Ag_2CO_3 on heating will give

$$\frac{216}{276} \times 2.76 = 2.16 \text{ g Ag as residue.}$$

29. The balanced chemical reaction of zinc with sulphuric acid and NaOH are



Since, one mole of $\text{H}_2(g)$ is produced per mole of zinc with both sulphuric acid and NaOH respectively, hydrogen gas is produced in the molar ratio of 1:1 in the above reactions.

30. Number of molecules present in 36 g of water

$$= \frac{36}{18} \times N_A = 2N_A$$

$$\text{Number of molecules present in } 28 \text{ g of CO} = \frac{28}{28} \times N_A = N_A$$

$$\text{Number of molecules present in } 46 \text{ g of C}_2\text{H}_5\text{OH} = \frac{46}{46} \times N_A = N_A$$

$$\text{Number of molecules present in } 54 \text{ g of N}_2\text{O}_5 = \frac{54}{108} \times N_A = 0.5 N_A$$

Here, N_A is Avogadro's number. Hence, 36 g of water contain the largest ($2N_A$) number of molecules.

31. In a neutral atom, atomic number represents the number of protons inside the nucleus and equal number of electrons around it. Therefore, the number of total electrons in molecule of CO_2 = electrons present in one carbon atom

$$+ 2 \times \text{electrons present in one oxygen atom} \\ = 6 + 2 \times 8 = 22.$$

32. $\frac{\text{Weight of a compound in gram (w)}}{\text{Molar mass (M)}} = \frac{\text{Number of moles (n)}}{\text{Avogadro number (N}_A)}$

$$\Rightarrow \frac{w(\text{O}_2)}{32} = \frac{N(\text{O}_2)}{N_A} \quad \dots(i)$$

$$\text{And } \frac{w(\text{N}_2)}{28} = \frac{N(\text{N}_2)}{N_A} \quad \dots(ii)$$

Dividing Eq. (i) by Eq. (ii) gives

$$\frac{N(\text{O}_2)}{N(\text{N}_2)} = \frac{w(\text{O}_2)}{w(\text{N}_2)} \times \frac{28}{32} = \frac{1}{4} \times \frac{28}{32} = \frac{7}{32}$$

33. Molar mass of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$.

(Atomic mass of Na = 23, C = 12, O = 16)

$$= 23 \times 2 + 12 + 48 + 18x$$

$$= 46 + 12 + 48 + 18x$$

$$= (106 + 18x)$$

Equivalent weight of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$

$$= \frac{\text{Molar mass}}{n \text{ factor}} = \frac{M}{2} = (53 + 9x)$$

[Here, m = molar mass and n factor = 2]

$$\text{Gram equivalent} = \frac{\text{Weight}}{\text{Equivalent weight}}$$

[Given, weight of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ = 1.43 g]

Hence, gram equivalent of

$$\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O} = \frac{1.43}{53 + 9x}$$

$$\text{Normality} = \frac{G_{\text{meq}}}{V_{\text{litre}}}$$

$$0.1 = \frac{1.43}{53 + 9x}$$

As, volume = 100 mL = 0.1 L

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$$\text{So, } 10^{-2} = \frac{1.43}{53 + 9x}$$

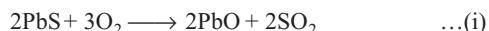
$$53 + 9x = 143$$

$$9x = 90$$

$$x = 10.00$$

- 34.** The equations of chemical reactions occurring during the process are

In the presence of oxygen



By self reduction



Thus 3 moles of O_2 produces 3 moles of Pb

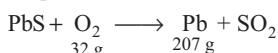
i.e. $32 \times 3 = 96$ g of O_2 produces $3 \times 207 = 621$ g of Pb

So 1000 g (1kg) of oxygen will produce

$$\begin{aligned} \frac{621}{96} \times 1000 &= 6468.75 \text{ g} \\ &= 6.4687 \text{ kg} \approx 6.47 \text{ kg} \end{aligned}$$

Alternative Method

From the direct equation,

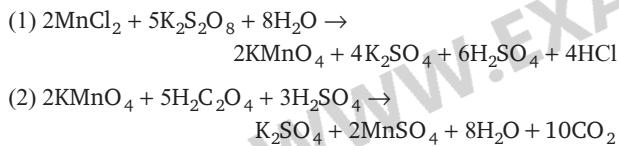


So, 32 g of O_2 gives 207 g of Pb

1 g of O_2 will give $\frac{207}{32}$ g of Pb

$$\begin{aligned} 1000 \text{ g of } \text{O}_2 &\text{ will give } \frac{207}{32} \times 1000 = 6468.75 \text{ g} \\ &= 6.46875 \text{ kg} \approx 6.47 \text{ kg} \end{aligned}$$

- 35.** The balanced equations are



Given, mass of oxalic acid added = 225 mg

$$\text{So, millimoles of oxalic acid added} = \frac{225}{90} = 2.5$$

Now from equation 2

Millimoles of KMnO_4 used to react with oxalic acid = 1 and
Millimoles of MnCl_2 required initially = 1

\therefore Mass of MnCl_2 required initially = $1 \times (55 + 71) = 126$ mg

Alternative Method

m moles of $\text{MnCl}_2 = m$ moles of $\text{KMnO}_4 = x$ (let)

and M_{eq} of $\text{KMnO}_4 = M_{\text{eq}}$ of oxalic acid

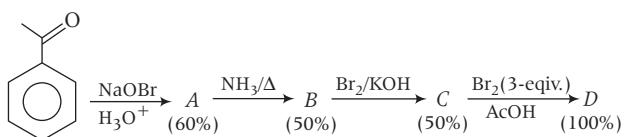
$$\text{So, } x \times 5 = \frac{225}{90} \times 2$$

Hence, $x = 1$

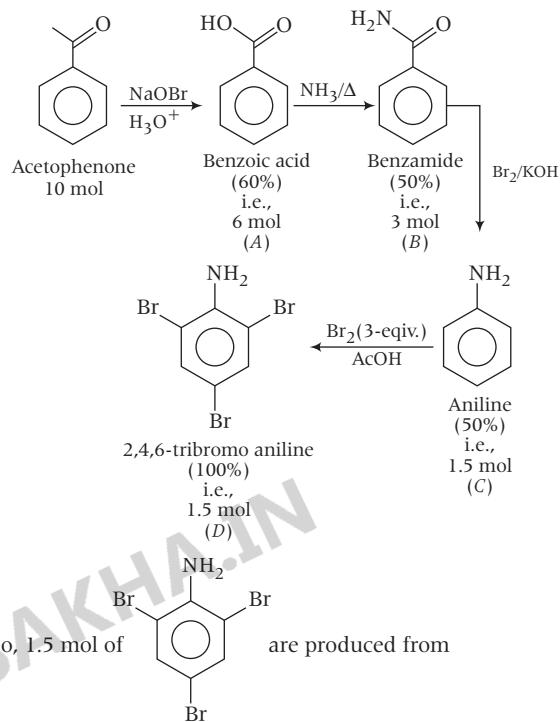
$\therefore m$ moles of $\text{MnCl}_2 = 1$

Hence mass of $\text{MnCl}_2 = (55 + 71) \times 1 = 126$ mg.

- 36.** Given,



The products formed are



$$\begin{array}{l} \text{Molar mass of} \\ \text{Br} \quad \text{Br} \\ \text{Br} \quad \text{Br} \\ = 240 + 14 + 4 + 72 = 330 \end{array}$$

$$\begin{array}{l} \text{Hence, amount of} \\ \text{Br} \quad \text{Br} \quad \text{NH}_2 \\ \text{Br} \quad \text{Br} \quad | \\ \text{Br} \quad \text{Br} \quad \text{NH}_2 \\ \text{produced is } 330 \times 1.5 = 495 \text{ g} \end{array}$$

- 37.** Molar mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$$\begin{aligned} &= 63.5 + 32 + 4 \times 16 + 5 \times 18 \\ &= 249.5 \text{ g} \end{aligned}$$

Also, molar mass represents mass of Avogadro number of molecules in gram unit, therefore

$\therefore 6.023 \times 10^{23}$ molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ weigh 249.5 g

$\therefore 10^{22}$ molecules will weigh $\frac{249.5}{6.023 \times 10^{23}} \times 10^{22} = 4.14 \text{ g}$

38. Molarity = $\frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$

$$= \frac{\text{Weight of solute}}{\text{Molar mass}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{3}{30} \times \frac{1000}{250} = 0.4 \text{ M}$$

39. Considering density of water to be 1.0 g/mL, 18 mL of water is 18 g (1.0 mol) of water and it contain Avogadro number of molecules. Also one molecule of water contain
 $2 \times (\text{one from each H-atom}) + 8 \times (\text{from oxygen atom}) = 10 \text{ electrons.}$
 $\Rightarrow 1.0 \text{ mole of H}_2\text{O contain} = 10 \times 6.023 \times 10^{23} = 6.023 \times 10^{24} \text{ electrons.}$

40. Carbon-12 isotope. According to modern atomic mass unit, one atomic mass unit (amu) is defined as one-twelfth of mass of an atom of C-12 isotope, i.e.

$$1 \text{ amu (u)} = \frac{1}{12} \times \text{weight of an atom of C-12 isotope.}$$

41. Moles of solute, $n_1 = \frac{w_1}{m_1}$; Moles of solvent, $n_2 = \frac{w_2}{m_2}$

$$\chi_1 \text{ (solute)} = 0.1 \text{ and } \chi_2 \text{ (solvent)} = 0.9$$

$$\therefore \frac{\chi_1}{\chi_2} = \frac{n_1}{n_2} = \frac{w_1}{m_1} \cdot \frac{m_2}{w_2} = \frac{1}{9}$$

$$\text{Molarity} = \frac{\text{Solute (moles)}}{\text{Volume (L)}} = \frac{w_1 \times 1000 \times 2}{m_1 (w_1 + w_2)}$$

$$\text{Note Volume} = \frac{\text{Total mass of solution}}{\text{Density}} = \left(\frac{w_1 + w_2}{2} \right) \text{ mL}$$

$$\text{Molality} = \frac{\text{Solute (moles)}}{\text{Solvent (kg)}} = \frac{w_1 \times 1000}{m_1 \times w_2}$$

Given, molarity = molality
 hence, $\frac{2000 w_1}{m_1 (w_1 + w_2)} = \frac{1000 w_1}{m_1 w_2}$

$$\therefore \frac{w_2}{w_1 + w_2} = \frac{1}{2} \Rightarrow w_1 = w_2 = 1$$

$$\therefore \frac{w_1 m_2}{m_1 w_2} = \frac{1}{9} \Rightarrow \frac{m_1 \text{ (solute)}}{m_2 \text{ (solvent)}} = 9$$

42. PLAN This problem can be solved by using concept of conversion of molarity into molality.

$$\text{Molarity} = 3.2 \text{ M}$$

Let volume of solution = 1000 mL = Volume of solvent

$$\text{Mass of solvent} = 1000 \times 0.4 = 400 \text{ g}$$

Since, molarity of solution is 3.2 molar

$$\therefore n_{\text{solute}} = 3.2 \text{ mol}$$

$$\text{Molality (m)} = \frac{3.2}{400 / 1000} = 8$$

Hence, correct integer is (8).

43. Mass of HCl in 1.0 mL stock solution

$$= 1.25 \times \frac{29.2}{100} = 0.365 \text{ g}$$

Mass of HCl required for 200 mL 0.4 M HCl

$$= \frac{200}{1000} \times 0.4 \times 36.5 = 0.08 \times 36.5 \text{ g}$$

$\therefore 0.365 \text{ g of HCl is present in 1.0 mL stock solution.}$

$$0.08 \times 36.5 \text{ g HCl will be present in} \frac{0.08 \times 36.5}{0.365} = 8.0 \text{ mL}$$

44. Partial pressure of $\text{N}_2 = 0.001 \text{ atm}$,

$$T = 298 \text{ K}, V = 2.46 \text{ dm}^3$$

From ideal gas law : $pV = nRT$

$$n(\text{N}_2) = \frac{pV}{RT} = \frac{0.001 \times 2.46}{0.082 \times 298} = 10^{-7}$$

$$\Rightarrow \text{Number of molecules of N}_2 = 6.023 \times 10^{23} \times 10^{-7} = 6.023 \times 10^{16}$$

Now, total surface sites available

$$= 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$$

$$\text{Surface sites used in adsorption} = \frac{20}{100} \times 6.023 \times 10^{17} = 2 \times 6.023 \times 10^{16}$$

\Rightarrow Sites occupied per molecules

$$= \frac{\text{Number of sites}}{\text{Number of molecules}} = \frac{2 \times 6.023 \times 10^{16}}{6.023 \times 10^{16}} = 2$$

45. Initial millimol of $\text{CH}_3\text{COOH} = 100 \times 0.5 = 50$

millimol of CH_3COOH remaining after adsorption

$$= 100 \times 0.49 = 49$$

\Rightarrow millimol of CH_3COOH adsorbed = $50 - 49 = 1$

\Rightarrow number of molecules of CH_3COOH adsorbed

$$= \frac{1}{1000} \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$$

$$\Rightarrow \text{Area covered up by one molecule} = \frac{3.01 \times 10^{-2}}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

46. Mass of 1.0 L water = 1000 g

$$\Rightarrow \text{Molarity} = \frac{1000}{18} = 55.56 \text{ mol L}^{-1}$$

47. Volume of one cylindrical plant virus = $\pi r^2 l$

$$= 3.14 (75 \times 10^{-8})^2 \times 5000 \times 10^{-8} \text{ cm}^3 = 8.83 \times 10^{-17} \text{ cm}^3$$

$$\Rightarrow \text{Mass of one virus} = \frac{\text{Volume of a virus}}{\text{Specific volume}}$$

$$= \frac{8.83 \times 10^{-17} \text{ cm}^3}{0.75 \text{ cm}^3 \text{ g}^{-1}} = 1.1773 \times 10^{-16} \text{ g}$$

\Rightarrow Molar mass of virus

= Mass of one virus \times Avogadro's number

$$= 1.1773 \times 10^{-16} \times 6.023 \times 10^{23} \text{ g}$$

$$= 70.91 \times 10^6 \text{ g}$$

48. Molar mass of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)

$$= 23 \times 2 + 32 + 64 + 10 \times 18 = 322 \text{ g}$$

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$$\Rightarrow \text{Mole of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \text{ in 1.0 L solution} = \frac{80.575}{322} = 0.25$$

$$\Rightarrow \text{Molarity of solution} = 0.25 \text{ M}$$

Also, weight of 1.0 L solution = 1077.2 g

weight of Na_2SO_4 in 1.0 L solution = $0.25 \times 142 = 35.5$ g

\Rightarrow Weight of water in 1.0 L solution = $1077.2 - 35.5 = 1041.7$ g

$$\Rightarrow \text{Molality} = \frac{0.25}{1041.7} \times 1000 = 0.24 \text{ m}$$

$$\begin{aligned} \text{Mole fraction of } \text{Na}_2\text{SO}_4 &= \frac{\text{Mole of } \text{Na}_2\text{SO}_4}{\text{Mole of } \text{Na}_2\text{SO}_4 + \text{Mole of water}} \\ &= \frac{0.25}{0.25 + \frac{1041.7}{18}} = 4.3 \times 10^{-3}. \end{aligned}$$

49. Compound *B* forms hydrated crystals with $\text{Al}_2(\text{SO}_4)_3$. Also, *B* is formed with univalent metal on heating with sulphur. Hence, compound *B* must have the molecular formula $M_2\text{SO}_4$ and compound *A* must be an oxide of *M* which reacts with sulphur to give metal sulphate as



$\therefore 0.321$ g sulphur gives 1.743 g of $M_2\text{SO}_4$

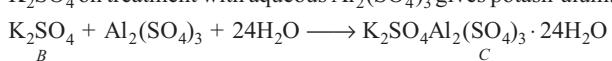
$\therefore 32.1$ g S (one mole) will give 174.3 g $M_2\text{SO}_4$

Therefore, molar mass of $M_2\text{SO}_4$ = 174.3 g

$\Rightarrow 174.3 = 2 \times \text{Atomic weight of } M + 32.1 + 64$

\Rightarrow Atomic weight of *M* = 39 , metal is potassium (K)

K_2SO_4 on treatment with aqueous $\text{Al}_2(\text{SO}_4)_3$ gives potash-alum.



If the metal oxide *A* has molecular formula MO_x , two moles of it combine with one mole of sulphur to give one mole of metal sulphate as



$\Rightarrow x = 2$, i.e. *A* is KO_2 .

50. The reaction involved is



millimol of $\text{Pb}(\text{NO}_3)_2$ taken = $45 \times 0.25 = 11.25$

millimol of $\text{Cr}_2(\text{SO}_4)_3$ taken = 2.5

Here, chromic sulphate is the limiting reagent, it will determine the amount of product.

$\therefore 1$ mole $\text{Cr}_2(\text{SO}_4)_3$ produces 3 moles PbSO_4 .

$\therefore 2.5$ millimol $\text{Cr}_2(\text{SO}_4)_3$ will produce 7.5 millimol PbSO_4 .

Hence, mole of PbSO_4 precipitate formed = 7.5×10^{-3}

Also, millimol of $\text{Pb}(\text{NO}_3)_2$ remaining unreacted

$$11.25 - 7.50 = 3.75$$

\Rightarrow Molarity of $\text{Pb}(\text{NO}_3)_2$ in final solution

$$= \frac{\text{millimol of } \text{Pb}(\text{NO}_3)_2}{\text{Total volume}} = \frac{3.75}{70} = 0.054 \text{ M}$$

Also, millimol of $\text{Cr}(\text{NO}_3)_3$ formed

$$= 2 \times \text{millimol of } \text{Cr}_2(\text{SO}_4)_3 \text{ reacted}$$

$$\Rightarrow \text{Molarity of } \text{Cr}(\text{NO}_3)_3 = \frac{5}{70} = 0.071 \text{ M}$$

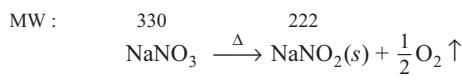
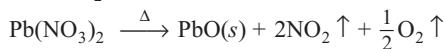
51. 93% H_2SO_4 solution weight by volume indicates that there is 93 g H_2SO_4 in 100 mL of solution.

If we consider 100 mL solution, weight of solution = 184 g

Weight of H_2O in 100 mL solution = $184 - 93 = 91$ g

$$\begin{aligned} \Rightarrow \text{Molality} &= \frac{\text{Moles of solute}}{\text{Weight of solvent (g)}} \times 1000 \\ &= \frac{93}{98} \times \frac{1000}{91} = 10.42 \end{aligned}$$

52. Heating below 600°C converts $\text{Pb}(\text{NO}_3)_2$ into PbO but to NaNO_3 into NaNO_2 as



$$\text{Weight loss} = 5 \times \frac{28}{100} = 1.4 \text{ g}$$

$$\Rightarrow \text{Weight of residue left} = 5 - 1.4 = 3.6 \text{ g}$$

Now, let the original mixture contain *x* g of $\text{Pb}(\text{NO}_3)_2$.

$\therefore 330$ g $\text{Pb}(\text{NO}_3)_2$ gives 222 g PbO

$$\therefore x \text{ g } \text{Pb}(\text{NO}_3)_2 \text{ will give } \frac{222x}{330} \text{ g } \text{PbO}$$

Similarly, 85 g NaNO_3 gives 69 g NaNO_2

$$\Rightarrow (5-x) \text{ g } \text{NaNO}_3 \text{ will give } \frac{69(5-x)}{85} \text{ g } \text{NaNO}_2$$

$$\Rightarrow \text{Residue : } \frac{222x}{330} + \frac{69(5-x)}{85} = 3.6 \text{ g}$$

Solving for *x* gives, $x = 3.3$ g $\text{Pb}(\text{NO}_3)_2 \Rightarrow \text{NaNO}_3 = 1.7$ g.

53. Reactions involved are



Actual yield of C_4H_{10} = 55 g which is 85% of theoretical yield.

$$\Rightarrow \text{Theoretical yield of } \text{C}_4\text{H}_{10} = \frac{55 \times 100}{85} = 64.70 \text{ g}$$

Also, 2 moles (218 g) $\text{C}_2\text{H}_5\text{Br}$ gives 58 g of butane.

$\Rightarrow 64.70$ g of butane would be obtained from

$$\frac{2}{58} \times 64.70 = 2.23 \text{ moles } \text{C}_2\text{H}_5\text{Br}$$

Also yield of bromination reaction is only 90%, in order to have 2.23 moles of $\text{C}_2\text{H}_5\text{Br}$, theoretically

$$\frac{2.23 \times 100}{90} = 2.48 \text{ moles of } \text{C}_2\text{H}_5\text{Br} \text{ required.}$$

Therefore, moles of C_2H_6 required = 2.48

\Rightarrow Volume of C_2H_6 (NTP) required = $2.48 \times 22.4 = 55.55$ L.

54. Moles of sugar = $\frac{34.2}{342} = 0.1$

Moles of water in syrup = $214.2 - 34.2 = 180$ g

Therefore, (i) Molality = $\frac{\text{Moles of solute}}{\text{Weight of Solvent (g)}} \times 1000$

$$= \frac{0.1}{180} \times 1000 = 0.55$$

(ii) Mole fraction of sugar = $\frac{\text{Mole of sugar}}{\text{Mole of sugar} + \text{Mole of water}}$

$$= \frac{0.1}{0.1 + 10} = 9.9 \times 10^{-3}$$

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- 55.** From the given elemental composition, empirical formula can be derived as :

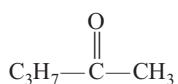
Element	C	H	O
Weight %	69.77	11.63	18.60
Mole %	5.81	11.63	1.1625 (obtained by dividing from M)
Simple ratio	5	10	1

Hence, empirical formula is $C_5H_{10}O$ and empirical formula weight is 86.

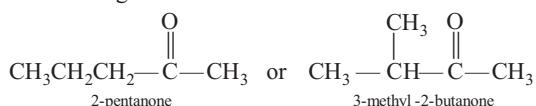
Since, empirical formula weight and molecular weight both are (86), empirical formula is the molecular formula also.

Also, the compound does not reduce Fehling's solution, therefore it is not an aldehyde, but it forms bisulphite, it must be a ketone.

Also, it gives positive iodoform test, it must be a methyl ketone.



Based on the above information, the compound may be one of the following :



- 56.** (a) Let us consider 1.0 L solution for all the calculation.

$$(i) \text{ Weight of 1 L solution} = 1250 \text{ g}$$

$$\text{Weight of Na}_2\text{S}_2\text{O}_3 = 3 \times 158 = 474 \text{ g}$$

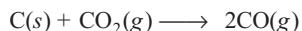
$$\Rightarrow \text{Weight percentage of Na}_2\text{S}_2\text{O}_3 = \frac{474}{1250} \times 100 = 37.92$$

$$(ii) \text{ Weight of H}_2\text{O in 1 L solution} = 1250 - 474 = 776 \text{ g}$$

$$\text{Mole fraction of Na}_2\text{S}_2\text{O}_3 = \frac{3}{3 + \frac{776}{18}} = 0.065$$

$$(iii) \text{ Molality of Na}^+ = \frac{3 \times 2}{776} \times 100 = 7.73 \text{ m}$$

- 57.** (a) After passing through red-hot charcoal, following reaction occurs



If the 1.0 L original mixture contain x litre of CO_2 , after passing from tube containing red-hot charcoal, the new volumes would be :

$$2x \text{ (volume of CO obtained from CO}_2) + 1 - x \text{ (original CO)} = 1 + x = 1.6 \text{ (given)}$$

$$\Rightarrow x = 0.6$$

Hence, original 1.0 L mixture has 0.4 L CO and 0.6 L of CO_2 , i.e. 40% CO and 60% CO_2 by volume.

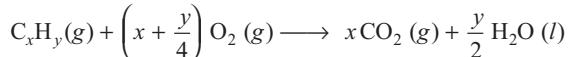
- (b) According to the given information, molecular formula of the compound is M_3N_2 . Also, 1.0 mole of compound has 28 g of nitrogen. If X is the molar mass of compound, then :

$$X \times \frac{28}{100} = 28$$

$$\Rightarrow X = 100 = 3 \times \text{Atomic weight of } M + 28$$

$$\Rightarrow \text{Atomic weight of } M = \frac{72}{3} = 24$$

- 58.** In the present case, $V \propto n$ (\because all the volumes are measured under identical conditions of temperature and pressure) Hence, the reaction stoichiometry can be solved using volumes as :



volume of $\text{CO}_2(g) + \text{O}_2(g)$ (remaining unreacted) = 25

\Rightarrow Volume of $\text{CO}_2(g)$ produced

$$= 10 \text{ mL (15 mL O}_2 \text{ remaining)}$$

$\therefore 1 \text{ mL C}_x\text{H}_y$ produces x mL of CO_2

$$\therefore 5 \text{ mL C}_x\text{H}_y \text{ will produce } 5x \text{ mL of CO}_2 = 10 \text{ mL} \Rightarrow x = 2$$

Also, 1 mL C_xH_y combines with $\left(x + \frac{y}{4}\right)$ mL of O_2

5 mL C_xH_y will combine with $5\left(x + \frac{y}{4}\right)$ mL of O_2

$$\Rightarrow 5\left(x + \frac{y}{4}\right) = 15 \text{ (15 mL of O}_2 \text{ out of 30 mL)}$$

(remaining unreacted)

$$\Rightarrow y = 4, \text{ hence hydrocarbon is C}_2\text{H}_4.$$

- 59.** Oxides of sodium and potassium are converted into chlorides according to following reactions :



Finally all the chlorides of NaCl and KCl are converted into AgCl , hence

moles of $(\text{NaCl} + \text{KCl})$ = moles of AgCl

(one mole of either NaCl or KCl gives one mole of AgCl)

Now, let the chloride mixture contain x g NaCl .

$$\Rightarrow \frac{x}{58.5} + \frac{0.118 - x}{74.5} = \frac{0.2451}{143.5}$$

Solving for x gives $x = 0.0338$ g (mass of NaCl)

$$\Rightarrow \text{Mass of KCl} = 0.118 - 0.0338 = 0.0842 \text{ g}$$

$$\text{Also, moles of Na}_2\text{O} = \frac{1}{2} \times \text{moles of NaCl}$$

$$\Rightarrow \text{Mass of Na}_2\text{O} = \frac{1}{2} \times \frac{0.0338}{58.5} \times 62 = 0.0179 \text{ g}$$

$$\text{Similarly, mass of K}_2\text{O} = \frac{1}{2} \times \frac{0.0842}{74.5} \times 94 = 0.053 \text{ g}$$

$$\Rightarrow \text{Mass \% of Na}_2\text{O} = \frac{0.0179}{0.5} \times 100 = 3.58\%$$

$$\text{Mass \% of K}_2\text{O} = \frac{0.053}{0.5} \times 100 = 10.6\%$$

- 60.** From the vapour density information

$$\text{Molar mass} = \text{Vapour density} \times 2 \text{ (}\because \text{ Molar mass of H}_2 = 2\text{)}$$

$$= 38.3 \times 2 = 76.6$$

Now, let us consider 1.0 mole of mixture and it contains x mole of NO_2 .

$$\Rightarrow 46x + 92(1-x) = 76.6 \Rightarrow x = 0.3348$$

$$\text{Also, in 100 g mixture, number of moles} = \frac{100}{76.6}$$

$$\Rightarrow \text{Moles of NO}_2 \text{ in mixture} = \frac{100}{76.6} \times 0.3348 = 0.437$$

16 Some Basic Concepts of Chemistry

61. Most of the elements found in nature exist as a mixture of isotopes whose atomic weights are different. The atomic weight of an element is the average of atomic weights of all its naturally occurring isotopes.

62. Average atomic weight

$$= \frac{\Sigma \text{Percentage of an isotope} \times \text{Atomic weight}}{100}$$

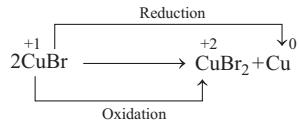
$$\Rightarrow 10.81 = \frac{10.01x + 11.01(100 - x)}{100} \Rightarrow x = 20\%$$

Therefore, natural boron contains 20% (10.01) isotope and 80% other isotope.

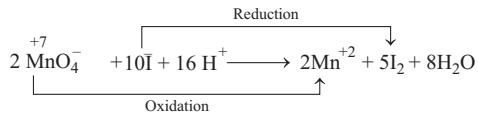
Topic 2 Equivalent Concept, Neutralisation and Redox Titration

1. In disproportionation reactions, same element undergoes oxidation as well as reduction.

e.g.



Here, CuBr get oxidised to CuBr₂ and also it get reduced to Cu. Other given reactions and their types are given below.



In the given reaction, MnO₄⁻ get oxidised to Mn²⁺ and I⁻ get reduced to I₂. It is an example of redox reaction. The reaction takes place in acidic medium.

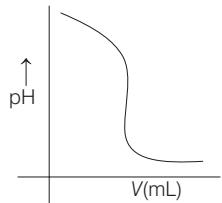


The given reaction is an example of decomposition reaction. Here, one compound split into two or more simpler compounds, atleast one of which must be in elemental form.

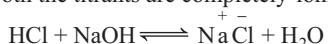


The given reaction is an example of displacement reaction. In this reaction, an atom (or ion) replaces the ion (or atom) of another element from a compound.

2. The graph that shows the correct change of pH of the titration mixture in the experiment is



In this case, both the titrants are completely ionised.



As H[⊕] is added to a basic solution, [OH[⊖]] decreases and [H⁺] increases. Therefore, pH goes on decreasing. As the equivalence point is reached, [OH[⊖]] is rapidly reduced. After this point [OH[⊖]] decreases rapidly and pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

The difference in the volume of NaOH solution between the end point and the equivalence point is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point. Most of them change their colour across this pH change.

3. 100 mL (cm³) of hexane contains 0.27 g of fatty acid.

In 10 mL solution, mass of the fatty acid,

$$m = \frac{0.27}{100} \times 10 = 0.027\text{ g}$$

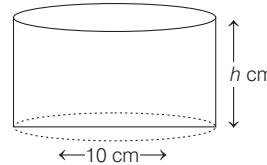
Density of fatty acid, $d = 0.9\text{ g cm}^{-3}$

∴ Volume of the fatty acid over the watch glass,

$$V = \frac{m}{d} = \frac{0.027}{0.9} = 0.03\text{ cm}^3$$

Let, height of the cylindrical monolayer = $h\text{ cm}$

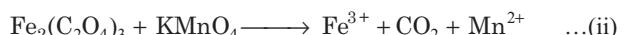
∴ Volume of the cylinder = Volume of fatty acid



$$\Rightarrow V = \pi r^2 \times h$$

$$\Rightarrow h = \frac{V}{\pi r^2} = \frac{0.03\text{ cm}^3}{3 \times (10)^2\text{ cm}^2} = 1 \times 10^{-4}\text{ cm} = 1 \times 10^{-6}\text{ m}$$

4. The oxidation of a mixture of one mole of each of FeC₂O₄, Fe₂(C₂O₄)₃, FeSO₄ and Fe₂(SO₄)₃ in acidic medium with KMnO₄ is as follows :



Change in oxidation number of Mn is 5. Change in oxidation number of Fe in (i), (ii) and (iii) are +3, +6, +1, respectively.

$$n_{\text{eq}} \text{KMnO}_4 = n_{\text{eq}} [\text{FeC}_2\text{O}_4 + \text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{FeSO}_4]$$

$$n \times 5 = 1 \times 3 + 1 \times 6 + 1 \times 1$$

$$\therefore n = 2$$

5. Given, $W_{\text{Ca}(\text{HCO}_3)_2} = 0.81\text{ g}$

$$W_{\text{Mg}(\text{HCO}_3)_2} = 0.73\text{ g}$$

$$M_{\text{Ca}(\text{HCO}_3)_2} = 162\text{ g mol}^{-1}$$

$$M_{\text{Mg}(\text{HCO}_3)_2} = 146\text{ mol}^{-1}$$

$$V_{\text{H}_2\text{O}} = 100\text{ mL}$$

$$\text{Now, } n_{\text{eq}} (\text{CaCO}_3) = n_{\text{eq}} [\text{Ca}(\text{HCO}_3)_2] + n_{\text{eq}} [\text{Mg}(\text{HCO}_3)_2]$$

$$\frac{W}{100} \times 2 = \frac{0.81}{162} \times 2 + \frac{0.73}{146} \times 2$$

$$\therefore \frac{W}{100} = 0.005 + 0.005$$

$$W = 0.01 \times 100 = 1$$

$$\text{Thus, hardness of water sample} = \frac{1}{100} \times 10^6 = 10,000\text{ ppm}$$

6. The reaction takes place as follows,



Now, 50 mL of 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ is needed to neutralize 25 mL of NaOH.

$$\therefore \text{Meq of } \text{H}_2\text{C}_2\text{O}_4 = \text{Meq of NaOH}$$

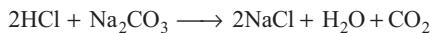
$$50 \times 0.5 \times 2 = 25 \times M_{\text{NaOH}} \times 1$$

$$M_{\text{NaOH}} = 2\text{M}$$

$$\begin{aligned} \text{Now, molarity} &= \frac{\text{Number of moles}}{\text{Volume of solution (in L)}} \\ &= \frac{\text{Weight / molecular mass}}{\text{Volume of solution (in L)}} \\ 2 &= \frac{w_{\text{NaOH}}}{40} \times \frac{1000}{50} \\ w_{\text{NaOH}} &= \frac{2 \times 40 \times 50}{1000} = 4\text{g} \end{aligned}$$

Thus, (*) none option is correct.

7. The reaction of HCl with Na_2CO_3 is as follows:



We know that, M_{eq} of HCl = M_{eq} of Na_2CO_3

$$\frac{25}{1000} \times 1 \times M_{\text{HCl}} = \frac{30}{1000} \times 0.1 \times 2$$

$$M_{\text{HCl}} = \frac{30 \times 0.2}{25} = \frac{6}{25}\text{M}$$

The reaction of HCl with NaOH is as follows:

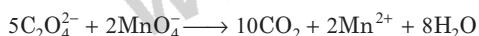


Also, M_{eq} of HCl = M_{eq} of NaOH

$$\frac{6}{25} \times 1 \times \frac{V}{1000} = \frac{30}{1000} \times 0.2 \times 1$$

$$V = 25\text{mL}$$

8. Reaction of oxalate with permanganate in acidic medium.



$$n\text{-factor : } (4 - 3) \times 2 = 2 \quad (7 - 2) = 5$$

$$\text{Number of mole} \quad 5 \quad 2 \quad 10$$

$\Rightarrow 5\text{C}_2\text{O}_4^{2-}$ ions transfer $10e^-$ to produce 10 molecules of CO_2 .

So, number of electrons involved in producing 10 molecules of CO_2 is 10. Thus, number of electrons involved in producing 1 molecule of CO_2 is 1.

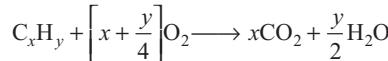
9. We can calculate the simplest whole number ratio of C and H from the data given, as

Element	Relative mass	Molar mass	Relative mole	Simplest whole number ratio
C	6	12	$\frac{6}{12} = 0.5$	$\frac{0.5}{0.5} = 1$
H	1	1	$\frac{1}{1} = 1$	$\frac{1}{0.5} = 2$

Alternatively this ratio can also be calculated directly in the terms of x and y as

$$\frac{12x}{y} = \frac{6}{1} \text{ (given and molar mass of C = 12, H = 1)}$$

Now, after calculating this ratio look for condition 2 given in the question i.e. quantity of oxygen is half of the quantity required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O . We can calculate number of oxygen atoms from this as consider the equation.



$$\text{Number of oxygen atoms required} = 2 \times \left[x + \frac{y}{4} \right] = \left[2x + \frac{y}{2} \right]$$

$$\text{Now given, } z = \frac{1}{2} \left[2x + \frac{y}{2} \right] = \left[x + \frac{y}{4} \right]$$

Here we consider x and y as simplest ratios for C and H so now putting the values of x and y in the above equation.

$$z = \left[x + \frac{y}{4} \right] = \left[1 + \frac{2}{4} \right] = 1.5$$

Thus, the simplest ratio figures for x , y and z are $x = 1$, $y = 2$ and $z = 1.5$

Now, put these values in the formula given i.e. $\text{C}_x\text{H}_y\text{O}_z = \text{C}_1\text{H}_2\text{O}_{1.5}$

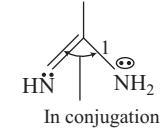
So, empirical formula will be $[\text{C}_1\text{H}_2\text{O}_{1.5}] \times 2 = \text{C}_2\text{H}_4\text{O}_3$

10. Methyl orange show Pinkish colour towards more acidic medium and yellow orange colour towards basic or less acidic media. Its working pH range is



Weak base have the pH range greater than 7. When methyl orange is added to this weak base solution it shows yellow orange colour.

Now when this solution is titrated against strong acid the pH move towards more acidic range and reaches to end point near 3.9 where yellow orange colour of methyl orange changes to Pinkish red resulting to similar change in colour of solution as well.

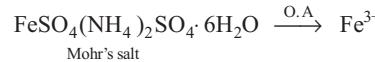


11. H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is -1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state -2.

H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax lined glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.

12. n -factor of dichromate is 6.

Also, n -factor of Mohr's salt is 1 as :



$\therefore 1$ mole of dichromate = 6 equivalent of dichromate.

$\therefore 6$ equivalent of Mohr's salt would be required.

Since, n -factor of Mohr's salt is 1, 6 equivalent of it would also be equal to 6 moles.

Hence, 1 mole of dichromate will oxidise 6 moles of Mohr's salt.

18 Some Basic Concepts of Chemistry

13. The following reaction occur between $S_2O_3^{2-}$ and $Cr_2O_7^{2-}$:



Change in oxidation number of $Cr_2O_7^{2-}$ per formula unit is 6 (it is always fixed for $Cr_2O_7^{2-}$).

$$\text{Hence, equivalent weight of } K_2Cr_2O_7 = \frac{\text{Molecular weight}}{6}$$

14. It is an example of disproportionation reaction because the same species (ClO^-) is being oxidised to ClO_3^- as well as reduced to Cl^- .

15. Oxalic acid dihydrate $H_2C_2O_4 \cdot 2H_2O$: mw = 126

It is a dibasic acid, hence equivalent weight = 63

$$\Rightarrow \text{Normality} = \frac{6.3}{63} \times \frac{1000}{250} = 0.4 \text{ N}$$

$$\Rightarrow N_1V_1 = N_2V_2$$

$$\Rightarrow 0.1 \times V_1 = 0.4 \times 10$$

$$\text{Hence, } V_1 = 40 \text{ mL}$$

16. In MnO_4^- , oxidation state of Mn is +7

In $Cr(CN)_6^{3-}$, oxidation state of Cr is +3

In NiF_6^{2-} , Ni is in + 4 oxidation state.

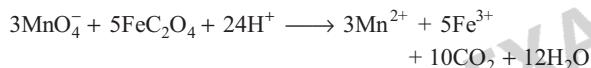
In CrO_2Cl_2 , oxidation state of Cr is +6.

17. In S_8 , oxidation number of S is 0, elemental state.

In S_2F_2 , F is in - 1 oxidation state, hence S is in + 1 oxidation state.

In H_2S , H is in +1 oxidation state, hence S is in - 2 oxidation state.

18. The balanced redox reaction is :



\therefore 5 moles of FeC_2O_4 require 3 moles of $KMnO_4$

\therefore 1 mole of FeC_2O_4 will require $\frac{3}{5}$ mole of $KMnO_4$.

19. The balanced chemical reaction is :



\therefore 5 moles SO_3^{2-} reacts with 2 moles of $KMnO_4$

\therefore 1 mole of SO_3^{2-} will react with $\frac{2}{5}$ mole $KMnO_4$.

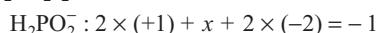
20. The balanced redox reaction is :



Hence, the coefficients of reactants in balanced reaction are 2, 5 and 16 respectively.

21. Volume strength of H_2O_2 = Normality $\times 5.6 = 1.5 \times 5.6 = 8.4 \text{ V}$

22. In $Ba(H_2PO_2)_2$, oxidation number of Ba is +2. Therefore,

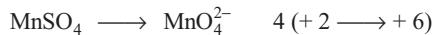
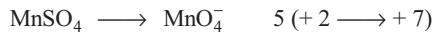
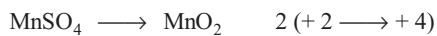
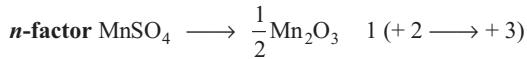


$$\Rightarrow x = +1$$

23. Equivalent weight in redox system is defined as :

$$E = \frac{\text{Molar mass}}{n\text{-factor}}$$

Here n -factor is the net change in oxidation number per formula unit of oxidising or reducing agent. In the present case, n -factor is 2 because equivalent weight is half of molecular weight. Also,



Therefore, $MnSO_4$ converts to MnO_2 .

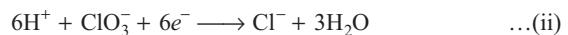
24. PLAN This problem includes concept of redox reaction. A redox reaction consists of oxidation half-cell reaction and reduction half-cell reaction. Write both half-cell reactions, i.e. oxidation half-cell reaction and reduction half-cell reaction. Then balance both the equations.

Now determine the correct value of stoichiometry of H_2SO_4 .



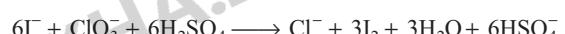
Here, I^- is converted into I_2 . Oxidation number of I is increasing from -1 to 0 hence, this is a type of oxidation reaction.

Reduction half-reaction



- Here, H_2O releases as a product. Hence, option (d) is correct.

Multiplying equation (i) by 3 and adding in equation (ii)



- Stoichiometric coefficient of HSO_4^- is 6.

Hence, option (a), (b) and (d) are correct.

25. Oxalic acid solution titrated with NaOH solution using phenolphthalein as an indicator.

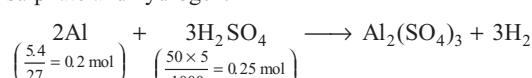


Equivalent of $H_2C_2O_4$ reacted = Equivalent of NaOH reacted

$$= \frac{5 \times 2 \times 0.1}{1000} = \frac{9 \times M_{(NaOH)} \times 1}{1000}$$

$$M_{(NaOH)} = \frac{1}{9} = 0.11$$

26. Aluminium reacts with sulphuric acid to form aluminium sulphate and hydrogen.



H_2SO_4 is limiting reagent and moles of $H_2(g)$ produced = 0.25 mol

Using ideal gas equation,

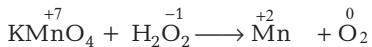
$$pV = nRT \\ \Rightarrow V = \frac{0.25 \times 0.082 \times 300}{1 \text{ atm}} = 6.15 \text{ L}$$

27. Given, volume of solution = 20.0 mL

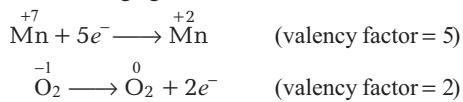
Impure sample of H_2O_2 = 0.2 g

Mass of $KMnO_4$ = 0.316 g

Impure H_2O_2 react with KMnO_4 (acidic)



KMnO_4 acts as an oxidising agent,



We have to compare both KMnO_4 and H_2O_2 .

$$(\text{Mass equivalent})_{\text{H}_2\text{O}_2} = (\text{Mass equivalent})_{\text{KMnO}_4}$$

$$\frac{\text{Weight}}{\text{molecular weight / valence factor}} \times 1000 = \frac{\text{weight}}{\text{molecular weight / valence factor}} \times 1000$$

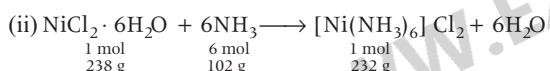
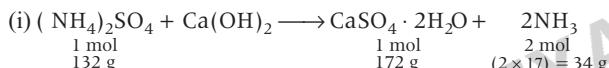
$$\frac{(\text{weight})_{\text{H}_2\text{O}_2}}{34/2} \times 1000 = \frac{0.316}{158/5} \times 1000$$

$$\begin{aligned} (\text{weight})_{\text{H}_2\text{O}_2} &= \frac{0.316}{158} \times 5 \times \frac{34}{2} \\ &= \frac{26.86}{158} \end{aligned}$$

$$(\text{weight})_{\text{H}_2\text{O}_2} = 0.17 \text{ g}$$

$$\begin{aligned} (\text{Purify})_{\text{H}_2\text{O}_2} &= \frac{(\text{Pure})_{\text{H}_2\text{O}_2}}{(\text{Impure})_{\text{H}_2\text{O}_2}} \times 100 \\ &= \frac{0.17}{0.2} \times 100 = 85\% \end{aligned}$$

28. Balanced equations of reactions used in the problem are as follows



Now, in Eq. (i)

if, 1584 g of ammonium sulphate is used.

$$\text{i.e., } 1584 \text{ g } (\text{NH}_4)_2\text{SO}_4 = \frac{1584}{132} = 12 \text{ mol}$$

So, according to the Eq. (i) given above 12 moles of $(\text{NH}_4)_2\text{SO}_4$ produces

(a) 12 moles of gypsum

(b) 24 moles of ammonia

Here, 12 moles of gypsum = $12 \times 172 = 2064 \text{ g}$

and 24 moles of $\text{NH}_3 = 24 \times 17 = 408 \text{ g}$

Further, as given in question,

24 moles of NH_3 produced in reaction (i) is completely utilised by 952g or 4 moles of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to produce 4 moles of $[\text{Ni}(\text{NH}_3)_6] \text{Cl}_2$.

So, 4 moles of $[\text{Ni}(\text{NH}_3)_6] \text{Cl}_2 = 4 \times 232 = 928 \text{ gms}$

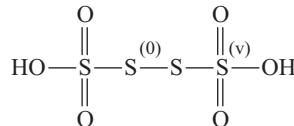
Hence, total mass of gypsum and nickel ammonia coordination compound $[\text{Ni}(\text{NH}_3)_6] \text{Cl}_2 = 2064 + 928 = 2992$

29. Both assertion and reason are factually true but the reason does not exactly explain the assertion. The correct explanation is, methyl orange and phenolphthalein changes their colour at different pH.

30. If x is the oxidation state of Cu then :

$$3 + 2 \times 2 + 3x + 7 \times (-2) = 0 \Rightarrow x = 7/3$$

31. $\text{Na}_2\text{S}_4\text{O}_6$ is a salt of $\text{H}_2\text{S}_4\text{O}_6$ which has the following structure



\Rightarrow Difference in oxidation number of two types of sulphur = 5

32. Only F and Na show only one non-zero oxidation state.

$$\text{O} = \text{O}^-, \text{O}^{2-}, \text{O}^{2+};$$

$$\text{Cl} = -1 \text{ to } +7$$

$$\text{N} = -3 \text{ to } +5$$

$$\text{P} = -3 \text{ to } +5$$

$$\text{Sn} = +2, +4$$

$$\text{Tl} = +1, +3 \text{ (rare but does exist)}$$

$$\text{Ti} = +2, +3, +4$$

33. Average titrate value is 25.15, but the number of significant figure cannot be greater than the same in either of them being manipulated.

34. The balanced reaction is



$$\text{Moles of P}_4\text{O}_{10} = \frac{852}{284} = 3$$

$$\text{Moles of CaO required} = 3 \times 6 = 18$$

$$\text{Mass of CaO required} = 18 \times 56 = 1008 \text{ g}$$

35. Meq of oxalate = $10 \times 0.2 \times 2 = 4$

Meq of MnO_2 formed = Meq of oxalate = 4

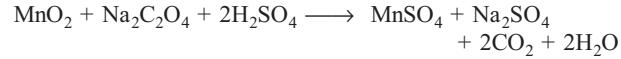
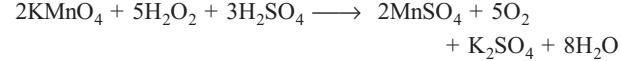
Meq of KMnO_4 in 20 mL = 4

\Rightarrow Normality of $\text{H}_2\text{O}_2 \times 20 = 4$

\Rightarrow Normality of $\text{H}_2\text{O}_2 = 0.20 \text{ N}$

$$\Rightarrow \text{Molarity of H}_2\text{O}_2 = \frac{0.20}{2} = 0.10 \text{ M}$$

The balanced reactions are



36. The balanced chemical reaction is



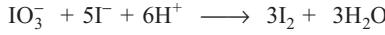
$$\text{millimol of CuCO}_3 = \frac{0.5 \times 1000}{123.5} = 4.048$$

\Rightarrow Millimol of H_2SO_4 required = 4.048

\therefore Millimol = Molarity × Volume (in mL)

$$\Rightarrow \text{Volume} = \frac{4.048}{0.50} = 8.096 \text{ mL}$$

37. The redox reaction involved are



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$$\text{millimol of KIO}_3 \text{ used} = \frac{0.1}{214} \times 1000 = 0.467$$

$$\Rightarrow \text{millimol of I}_2 \text{ formed} = 3 \times 0.467 = 1.4$$

$$\Rightarrow \text{millimol of Na}_2\text{S}_2\text{O}_3 \text{ consumed} = 2 \times 1.4 = 2.8$$

$$\Rightarrow \text{Molarity of Na}_2\text{S}_2\text{O}_3 = \frac{2.8}{45} = 0.062 \text{ M}$$

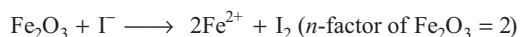
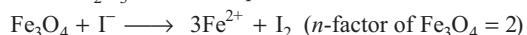
38. Meq of H₂O₂ = Meq of I₂ = Meq of Na₂S₂O₃

If N is normality of H₂O₂, then

$$N \times 25 = 0.3 \times 20 \Rightarrow N = 0.24$$

$$\Rightarrow \text{Volume strength} = N \times 5.6 = 1.334 \text{ V}$$

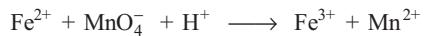
39. Let the original sample contains x millimol of Fe₃O₄ and y millimol of Fe₂O₃. In the first phase of reaction,



$$\Rightarrow \text{Meq of I}_2 \text{ formed} = \text{Meq} (\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3) \\ = \text{Meq of hypo required}$$

$$\Rightarrow 2x + 2y = 11 \times 0.5 \times 5 = 27.5 \quad \dots(\text{i})$$

Now, total millimol of Fe²⁺ formed = 3x + 2y. In the reaction



$$\text{n-factor of Fe}^{2+} = 1$$

$$\Rightarrow \text{Meq of MnO}_4^- = \text{Meq of Fe}^{2+}$$

$$\Rightarrow 3x + 2y = 12.8 \times 0.25 \times 5 \times 2 = 32 \quad \dots(\text{ii})$$

Solving Eqs. (i) and (ii), we get

$$x = 4.5$$

$$\text{and} \quad y = 9.25$$

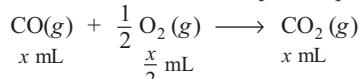
$$\Rightarrow \text{Mass of Fe}_3\text{O}_4 = \frac{4.5}{1000} \times 232 = 1.044 \text{ g}$$

$$\% \text{ mass of Fe}_3\text{O}_4 = \frac{1.044}{3} \times 100 = 34.80\%$$

$$\text{Mass of Fe}_2\text{O}_3 = \frac{9.25}{1000} \times 160 = 1.48 \text{ g}$$

$$\% \text{ mass of Fe}_2\text{O}_3 = \frac{1.48}{3} \times 100 = 49.33\%$$

40. The reaction involved in the explosion process is



The first step volume contraction can be calculated as :

$$\left(x + \frac{x}{2} + y + 2y \right) - (x + y) = 13$$

$$\Rightarrow x + 4y = 26 \quad \dots(\text{i})$$

The second volume contraction is due to absorption of CO₂.

$$\text{Hence,} \quad x + y = 14 \quad \dots(\text{ii})$$

Now, solving equations (i) and (ii),

$$x = 10 \text{ mL}, y = 4 \text{ mL} \text{ and volume of He} = 20 - 14 = 6 \text{ mL}$$

$$\Rightarrow \text{Vol \% of CO} = \frac{10}{20} \times 100 = 50\%$$

$$\text{Vol \% of CH}_4 = \frac{4}{20} \times 100 = 20\%$$

$$\text{Vol \% of He} = 30\%$$

41. The redox reaction involved is :



If M is molarity of H₂O₂ solution, then

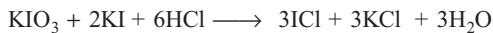
$$5M = \frac{0.508 \times 1000}{254} \quad (\because 1 \text{ mole H}_2\text{O}_2 \equiv 1 \text{ mole I}_2)$$

$$\Rightarrow M = 0.4$$

Also, n-factor of H₂O₂ is 2, therefore normality of H₂O₂ solution is 0.8 N.

$$\Rightarrow \text{Volume strength} = \text{Normality} \times 5.6 = 0.8 \times 5.6 = 4.48 \text{ V}$$

42. The reaction is



KIO₃ required for 20 mL original KI solution = 3 millimol.

$$\Rightarrow 7.5 \text{ millimol KIO}_3 \text{ would be required for original 50 mL KI.}$$

\Rightarrow Original 50 mL KI solution contain 15 millimol of KI.

After AgNO₃ treatment 5 millimol of KIO₃ is required, i.e. 10 millimol KI is remaining.

$$\Rightarrow 5 \text{ millimol KI reacted with 5 millimol of AgNO}_3.$$

$$\Rightarrow \text{Mass of AgNO}_3 = \frac{5}{1000} \times 170 = 0.85 \text{ g}$$

$$\Rightarrow \text{Mass percentage of AgNO}_3 = 85\%$$

43. CO₂ is evolved due to following reaction :



$$\text{Moles of CO}_2 \text{ produced} = \frac{pV}{RT} = \frac{750}{760} \times \frac{123.9}{1000} \times \frac{1}{0.082 \times 298} \\ = 5 \times 10^{-3}$$

$$\Rightarrow \text{Moles of NaHCO}_3 \text{ in 2 g sample} = 2 \times 5 \times 10^{-3} = 0.01$$

$$\Rightarrow \text{millimol of NaHCO}_3 \text{ in 1.5 g sample}$$

$$= \frac{0.01}{2} \times 1.5 \times 1000 = 7.5$$

Let the 1.5 g sample contain x millimol Na₂CO₃, then

$$2x + 7.5 = \text{millimol of HCl} = 15$$

$$\Rightarrow x = 3.75$$

$$\Rightarrow \text{Mass of NaHCO}_3 = \frac{7.5 \times 84}{1000} = 0.63 \text{ g}$$

$$\text{Mass of Na}_2\text{CO}_3 = \frac{3.75 \times 106}{1000} = 0.3975 \text{ g}$$

$$\Rightarrow \% \text{ mass of NaHCO}_3 = \frac{0.63}{1.50} \times 100 = 42 \%$$

$$\% \text{ mass of Na}_2\text{CO}_3 = \frac{0.3975}{1.5} \times 100 = 26.5\%$$

44. Mass of Fe₂O₃ = 0.552 g

$$\text{millimol of Fe}_2\text{O}_3 = \frac{0.552}{160} \times 1000 = 3.45$$

During treatment with Zn-dust, all Fe³⁺ is reduced to Fe²⁺, hence

millimol of Fe^{2+} (in 100 mL) = $3.45 \times 2 = 6.90$
 \Rightarrow In 25 mL aliquot, $\frac{6.90}{4} = 1.725$ millimol Fe^{2+} ion.

Finally Fe^{2+} is oxidised to Fe^{3+} , liberating one electron per Fe^{2+} ion. Therefore, total electrons taken up by oxidant.

$$= 1.725 \times 10^{-3} \times 6.023 \times 10^{23} \\ = 1.04 \times 10^{20}$$

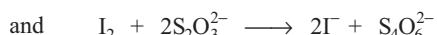
45. With KMnO_4 , oxalate ion is oxidised only as :



Let, in the given mass of compound, x millimol of $\text{C}_2\text{O}_4^{2-}$ ion is present, then

$$\text{Meq of } \text{C}_2\text{O}_4^{2-} = \text{Meq of } \text{MnO}_4^- \\ \Rightarrow 2x = 0.02 \times 5 \times 22.6 \Rightarrow x = 1.13$$

At the later stage, with I^- , Cu^{2+} is reduced as :



Let there be x millimol of Cu^{2+} .

$$\begin{aligned} \Rightarrow \text{Meq of } \text{Cu}^{2+} &= \text{Meq of } \text{I}_2 = \text{meq of hypo} \\ \Rightarrow x &= 11.3 \times 0.05 = 0.565 \\ \Rightarrow \text{Moles of } \text{Cu}^{2+} : \text{ moles of } \text{C}_2\text{O}_4^{2-} &= 0.565 : 1.13 = 1 : 2 \end{aligned}$$

46. Let us consider 10 mL of the stock solution contain x millimol oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ and y millimol of NaHC_2O_4 .

When titrated against NaOH , basicity of oxalic acid is 2 while that of NaHC_2O_4 is 1.

$$\Rightarrow 2x + y = 3 \times 0.1 = 0.3 \quad \dots (\text{i})$$

When titrated against acidic KMnO_4 , n -factors of both oxalic acid and NaHC_2O_4 would be 2.

$$\Rightarrow 2x + 2y = 4 \times 0.1 = 0.4 \quad \dots (\text{ii})$$

Solving equations (i) and (ii) gives

$$y = 0.1, x = 0.1$$

$$\Rightarrow \text{In 1.0 L solution, mole of } \text{H}_2\text{C}_2\text{O}_4 = \frac{0.1}{1000} \times 100 = 0.01$$

$$\text{Mole of } \text{NaHC}_2\text{O}_4 = \frac{0.1}{1000} \times 100 = 0.01$$

$$\Rightarrow \text{Mass of } \text{H}_2\text{C}_2\text{O}_4 = 90 \times 0.01 = 0.9 \text{ g}$$

$$\text{Mass of } \text{NaHC}_2\text{O}_4 = 112 \times 0.01 = 1.12 \text{ g}$$

47. Mass of chlorine in 1.0 g $X = \frac{35.5}{143.5} \times 2.9 = 0.717 \text{ g}$

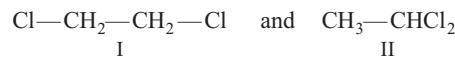
Now, the empirical formula can be derived as :

C	H	Cl
% wt :	24.24	4.04
Mole :	2	4
Simple ratio :	1	2

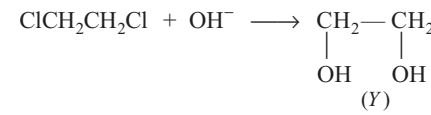
\Rightarrow Empirical formula = CH_2Cl .

Because X can be represented by two formulae of which one gives a dihydroxy compound with KOH indicates that X has two chlorine atoms per molecule.

$\Rightarrow X = \text{C}_2\text{H}_4\text{Cl}_2$ with two of its structural isomers.



On treatment with KOH, I will give ethane-1, 2-diol, hence it is Y . Z on treatment with KOH will give ethanal as



48. Let the n -factor of KMnO_4 in acid, neutral and alkaline media are N_1 , N_2 and N_3 respectively. Also, same volumes of reducing agent is used everytime, same number of equivalents of KMnO_4 would be required every time.

$$\Rightarrow 20N_1 = \frac{100}{3}N_2 = 100N_3 \Rightarrow N_1 = \frac{5}{3}N_2 = 5N_3$$

Also, n -factors are all integer and greater than or equal to one but less than six, N_3 must be 1.

$$\Rightarrow N_1 = 5, N_2 = 3$$



$$\Rightarrow \text{meq of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ required} = 100$$

$$\Rightarrow 100 = 1 \times 6 \times V \quad (n\text{-factor} = 6)$$

$$\Rightarrow V = 100/6 = 16.67 \text{ mL}$$

49. Meq of MnO_4^- required = $20 \times \frac{1}{50} \times 5 = 2$

$$\Rightarrow \text{Meq of } \text{Fe}^{2+} \text{ present in solution} = 2$$

$$\Rightarrow \text{millimol of } \text{Fe}^{2+} \text{ present in solution} = 2 \quad (n\text{-factor} = 1)$$

Also,

$\because 4$ millimol of Fe^{2+} are formed from 1 millimol N_2H_4

$$\therefore 2 \text{ millimol } \text{Fe}^{2+} \text{ from } \frac{1}{4} \times 2 = \frac{1}{2} \text{ millimol } \text{N}_2\text{H}_4$$

Therefore, molarity of hydrazine sulphate solution

$$= \frac{1}{2} \times \frac{1}{10} = \frac{1}{20}$$

\Rightarrow In 1 L solution $\frac{1}{20}$ mol $\text{N}_2\text{H}_4\text{SO}_4$ is present.

$$\Rightarrow \text{Amount of } \text{N}_2\text{H}_4\text{SO}_4 = \frac{1}{20} \times 130 = 6.5 \text{ gL}^{-1}$$

50. Molecular weight of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 286$

$$\Rightarrow \text{Molarity of carbonate solution} = \frac{1}{286} \times \frac{1000}{100} = 0.035$$

$$\Rightarrow \text{Normality of carbonate solution} = 2 \times 0.035 = 0.07 \text{ N}$$

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In acid solution : Normality of $\text{HNO}_3 = \frac{8 \times 5}{2000} = 0.02$

Normality of $\text{HCl} = \frac{5 \times 4.8}{2000} = 0.012$

Let normality of H_2SO_4 in final solution be N .

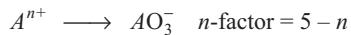
$$\Rightarrow (N + 0.02 + 0.012) \times 30 = 0.07 \times 42.9$$

$$\Rightarrow N = 0.0681$$

$$\Rightarrow \text{Gram equivalent of } \text{SO}_4^{2-} \text{ in 2 L solution} = 2 \times 0.0681 \\ = 0.1362$$

$$\Rightarrow \text{Mass of } \text{SO}_4^{2-} \text{ in solution} = 0.1362 \times \frac{96}{2} = 6.5376 \text{ g}$$

51. For the oxidation of A^{n+} as :



$$\Rightarrow \text{Gram equivalent of } A^{n+} = 2.68 \times 10^{-3} (5 - n)$$

Now equating the above gram equivalent with gram equivalent of KMnO_4 :

$$2.68 \times 10^{-3} (5 - n) = 1.61 \times 10^{-3} \times 5$$

$$\Rightarrow n = +2$$

52. During heating $M\text{CO}_3$ is converted into MO liberating CO_2 while BaO is remaining unreacted :



$\frac{\text{BaO}(s)}{4.08 \text{ g}}$	$\frac{\text{BaO}(s)}{3.64 \text{ g}}$
--	--

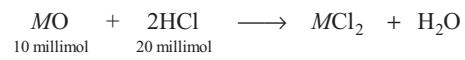
From the decomposition information, it can be deduced that the original mixture contained 0.01 mole of $M\text{CO}_3$ and the solid residue, obtained after heating, contain 0.01 mole (10 millimol) of MO .

Also, millimol of HCl taken initially = 100

millimol of NaOH used in back-titration = $16 \times 2.5 = 40$

\Rightarrow millimol of HCl reacted with oxide residue = 60

HCl reacts with oxides as :



$$60 - 20 = 40 \text{ millimol}$$

Therefore, the residue contain 20 millimol of BaO .

$$\begin{aligned} \text{Also,} \quad & \text{molar mass of BaO} = 138 + 16 \\ & = 154 \end{aligned}$$

$$\Rightarrow \text{Mass of BaO} = \frac{154 \times 20}{1000} = 3.08 \text{ g}$$

$$\Rightarrow \text{Mass of } M\text{CO}_3 = 4.08 - 3.08 = 1.0 \text{ g}$$

$$\therefore 0.01 \text{ mole of } M\text{CO}_3 \text{ weight } 1.0 \text{ g}$$

$$\therefore 1 \text{ mole of } M\text{CO}_3 = 100 \text{ g}$$

$$\Rightarrow 100 = (\text{Atomic weight of metal}) + (12 + 3 \times 16)$$

$$\Rightarrow \text{Atomic weight of metal} = 40, \text{ i.e. Ca}$$

2

Atomic Structure

Topic 1 Preliminary Developments and Bohr's Model

Objective Questions I (Only one correct option)

1. Which one of the following about an electron occupying the $1s$ -orbital in a hydrogen atom is incorrect? (The Bohr radius is represented by a_0) (2019 Main, 9 April II)

 - (a) The electron can be found at a distance $2a_0$ from the nucleus.
 - (b) The magnitude of the potential energy is double that of its kinetic energy on an average.
 - (c) The probability density of finding the electron is maximum at the nucleus.
 - (d) The total energy of the electron is maximum when it is at a distance a_0 from the nucleus.

2. If p is the momentum of the fastest electron ejected

(2019 Main, 8 April II)

- (a) $\frac{4}{9}\lambda$ (b) $\frac{3}{4}\lambda$
 (c) $\frac{2}{3}\lambda$ (d) $\frac{1}{2}\lambda$

3. What is the work function of the metal, if the light of wavelength 4000 \AA generates photoelectron of velocity $6 \times 10^5 \text{ ms}^{-1}$ from it?

(Mass of electron = 9×10^{-31} kg)

Velocity of light = 3×10^8 ms⁻¹

Planck's constant $\equiv 6.626 \times 10^{-34}$ Js

Charge of electron $\equiv 1.6 \times 10^{-19} \text{ eV}^{-1}$)

(2019 Main, 12 Jan I)

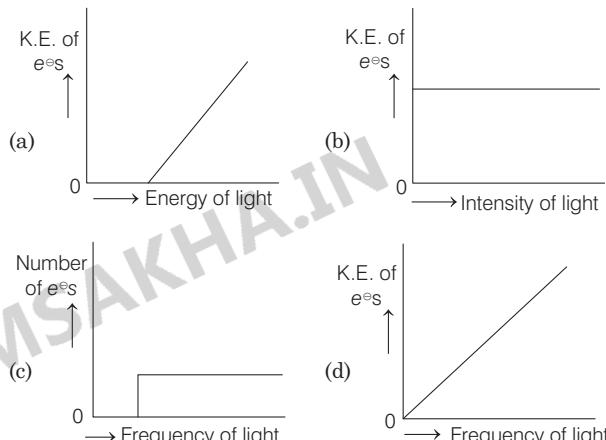
4. The ground state energy of hydrogen atom is -13.6 eV .
The energy of second excited state of He^+ ion in eV is
(2019 Main, 10 Jan II)

(2019 Main, 10 Jan II)

- (a) -54.4 (b) -3.4 (c) -6.04 (d) -27.2

5. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface? (2019 Main, 10 Jan I)

(2019 Main, 10 Jan I)



6. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of h/λ (where, λ is wavelength associated with electron wave) is given by (2016 Main)

- (a) 2 meV (b) $\sqrt{\text{meV}}$ (c) $\sqrt{2 \text{ meV}}$ (d) meV

7. Rutherford's experiment, which established the nuclear model of the atom, used a beam of (2002, 3M)

- (a) β -particles, which impinged on a metal foil and got absorbed
 (b) γ -rays, which impinged on a metal foil and got scattered

- (c) helium atoms, which impinged on a metal foil and got scattered

- (d) helium nuclei, which impinged on a metal foil and got scattered

- Rutherford's alpha particle scattering experiment eventually led to the conclusion that (198)

- (a) mass and energy are related
 - (b) electrons occupy space around the nucleus

- (c) neutrons are buried deep in the nucleus

- (d) the point of impact with matter can be pre-

24 Atomic Structure

9. The radius of an atomic nucleus is of the order of (1985, 1M)
 (a) 10^{-10} cm (b) 10^{-13} cm (c) 10^{-15} cm (d) 10^{-8} cm
10. Bohr's model can explain (1985, 1M)
 (a) the spectrum of hydrogen atom only
 (b) spectrum of an atom or ion containing one electron only
 (c) the spectrum of hydrogen molecule
 (d) the solar spectrum
11. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is (1984, 1M)
 (a) e, p, n, α (b) n, p, e, α
 (c) n, p, α, e (d) n, α, p, e
12. Rutherford's scattering experiment is related to the size of the (1983, 1M)
 (a) nucleus (b) atom (c) electron (d) neutron
13. Rutherford's experiment on scattering of α -particles showed for the first time that the atom has (1981, 1M)
 (a) electrons (b) protons
 (c) nucleus (d) neutrons

Objective Questions II

(One or more than one correct option)

14. The energy of an electron in the first Bohr orbit of H-atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) (1988)
 (a) -3.4 eV (b) -4.2 eV (c) -6.8 eV (d) $+6.8$ eV
15. The atomic nucleus contains (1988, 1M)
 (a) protons (b) neutrons (c) electrons (d) photons
16. The sum of the number of neutrons and proton in the isotope of hydrogen is (1986, 1M)
 (a) 6 (b) 5 (c) 4 (d) 3
17. When alpha particles are sent through a thin metal foil, most of them go straight through the foil, because (1984, 1M)
 (a) alpha particles are much heavier than electrons
 (b) alpha particles are positively charged
 (c) most part of the atom is empty space
 (d) alpha particles move with high velocity
18. Many elements have non-integral atomic masses, because (1984, 1M)
 (a) they have isotopes
 (b) their isotopes have non-integral masses
 (c) their isotopes have different masses
 (d) the constituents, neutrons, protons and electrons, combine to give fractional masses

Match the Columns

19. Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the n th orbit of the atom and List-II contains options showing how they depend on n .

	List-I	List-II
(I)	Radius of the n th orbit	(P) $\propto n^{-2}$
(II)	Angular momentum of the electron in the n th orbit	(Q) $\propto n^{-1}$
(III)	Kinetic energy of the electron in the n th orbit	(R) $\propto n^0$
(IV)	Potential energy of the electron in the n th orbit	(S) $\propto n^1$ (T) $\propto n^2$ (U) $\propto n^{1/2}$

Which of the following options has the correct combination considering List-I and List-II? (2019 Adv.)

- (a) (III), (P) (b) (III), (S)
 (c) (IV), (U) (d) (IV), (Q)

20. Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the n th orbit of the atom and List-II contains options showing how they depend on n .

	List-I	List-II
(I)	Radius of the n th orbit	(P) $\propto n^{-2}$
(II)	Angular momentum of the electron in the n th orbit	(Q) $\propto n^{-1}$
(III)	Kinetic energy of the electron in the n th orbit	(R) $\propto n^0$
(IV)	Potential energy of the electron in the n th orbit	(S) $\propto n^1$ (T) $\propto n^2$ (U) $\propto n^{1/2}$

Which of the following options has the correct combination considering List-I and List-II? (2019 Adv.)

- (a) (II), (R) (b) (I), (P)
 (c) (I), (T) (d) (II), (Q)

21. According to Bohr's theory,
 E_n = Total energy K_n = Kinetic energy
 V_n = Potential energy r^n = Radius of n th orbit
 Match the following : (2006, 6M)

	Column I	Column II
A.	$V_n/K_n = ?$	p. 0
B.	If radius of n th orbit $\propto E_n^x$, $x = ?$	q. -1
C.	Angular momentum in lowest orbital	r. -2
D.	$\frac{1}{r^n} \propto Z^y$, $y = ?$	s. 1

Fill in the Blanks

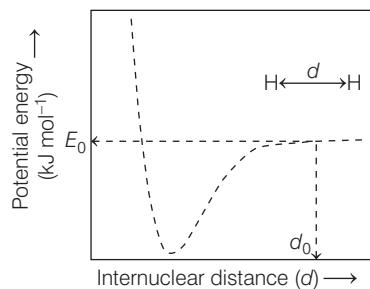
22. The light radiations with discrete quantities of energy are called (1993, 1M)

23. The mass of a hydrogen is kg. (1982, 1M)
24. Isotopes of an element differ in the number of in their nuclei. (1982, 1M)
25. Elements of the same mass number but of different atomic numbers are known as (1983, 1M)

Numerical Answer Type Questions

26. The figure below is the plot of potential energy *versus* internuclear distance (*d*) of H₂ molecule in the electronic ground state. What is the value of the net potential energy *E*₀ (as indicated in the figure) in kJ mol⁻¹, for *d* = *d*₀ at which the electron-electron repulsion and the nucleus-nucleus repulsion energies are absent? As reference, the potential energy of H atom is taken as zero when its electron and the nucleus are infinitely far apart.

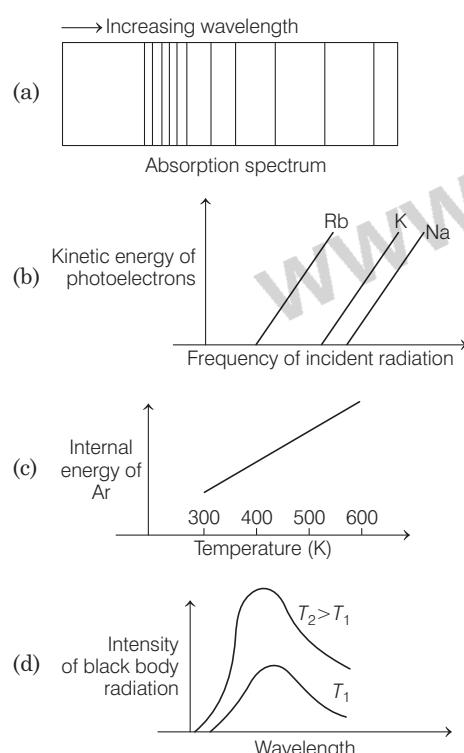
Use Avogadro constant as 6.023×10^{23} mol⁻¹. (2020 Adv.)



Topic 2 Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

Objective Questions I (Only one correct option)

1. The figure that is not a direct manifestation of the quantum nature of atoms is (2020 Main, 2 Sep I)



2. The number of orbitals associated with quantum numbers $n = 5, m_s = +\frac{1}{2}$ is (2020 Main, 7 Jan I)
- (a) 25 (b) 50 (c) 15 (d) 11

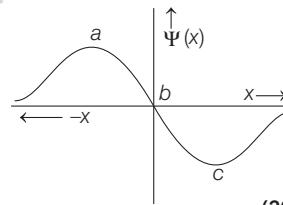
Subjective Questions

27. With what velocity should an α -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} m from the nucleus of the copper atom? (1997 (C), 3M)

3. Among the following, the energy of 2s-orbital is lowest in (2019 Main, 12 April II)

(a) K (b) H (c) Li (d) Na

4. The electrons are more likely to be found



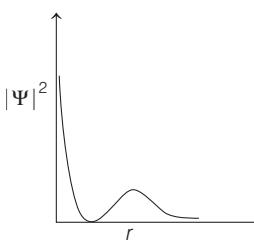
(2019 Main, 12 April I)

- (a) in the region *a* and *c* (b) in the region *a* and *b*
(c) only in the region *a* (d) only in the region *c*

5. The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are (2019 Main, 10 April II)

(a) Lyman and Paschen (b) Brackett and Pfund
(c) Paschen and Pfund (d) Balmer and Brackett

6. The graph between $|\Psi|^2$ and *r* (radial distance) is shown below. This represents (2019 Main, 10 April I)



- (a) 1s-orbital (b) 2p-orbital
(c) 3s-orbital (d) 2s-orbital

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7. For any given series of spectral lines of atomic hydrogen, let $\Delta\bar{v} = \bar{v}_{\text{max}} - \bar{v}_{\text{min}}$ be the difference in maximum and minimum frequencies in cm^{-1} . The ratio

$$\frac{\Delta\bar{v}_{\text{Lyman}}}{\Delta\bar{v}_{\text{Balmer}}} \text{ is} \quad (\text{2019 Main, 9 April I})$$

- (a) 27 : 5 (b) 5 : 4 (c) 9 : 4 (d) 4 : 1

8. The quantum number of four electrons are given below:

I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$

II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

IV. $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$

The correct order of their increasing energies will be
(2019 Main, 8 April I)

- (a) IV < III < II < I (b) I < II < III < IV
(c) IV < II < III < I (d) I < III < II < IV

9. If the de-Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to $1.5\pi a_0$ (a_0 is Bohr radius), then the value of n/Z is
(2019 Main, 12 Jan II)

- (a) 1.0 (b) 0.75 (c) 0.40 (d) 1.50

10. The de-Broglie wavelength (λ) associated with a photoelectron varies with the frequency (ν) of the incident radiation as, [ν_0 is threshold frequency]
(2019 Main, 11 Jan II)

(a) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$

(b) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$

(c) $\lambda \propto \frac{1}{(\nu - \nu_0)}$

(d) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$

11. Which of the following combination of statements is true regarding the interpretation of the atomic orbitals?
(2019 Main, 9 Jan II)

I. An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.

II. For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.

III. According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$.

IV. The plot of ψ vs r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

- (a) I, III (b) II, III (c) I, II (d) I, IV

12. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose? [$R_H = 1 \times 10^5 \text{ cm}^{-1}$, $h = 6.6 \times 10^{-34} \text{ Js}$, $c = 3 \times 10^8 \text{ ms}^{-1}$]
(2019 Main, 11 Jan I)

- (a) Paschen, $5 \rightarrow 3$ (b) Paschen, $\infty \rightarrow 3$
(c) Lyman, $\infty \rightarrow 1$ (d) Balmer, $\infty \rightarrow 2$

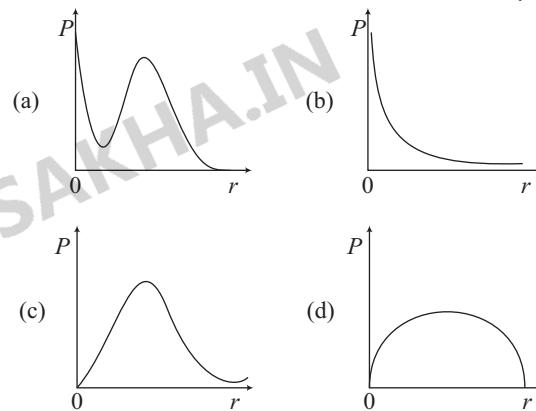
13. For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number (ν) against $\left(\frac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit)
(2019 Main, 9 Jan I)

- (a) non linear (b) linear with slope $-R_H$
(c) linear with slope R_H (d) linear with intercept $-R_H$

14. The radius of the second Bohr orbit for hydrogen atom is (Planck's constant (h) = $6.6262 \times 10^{-34} \text{ Js}$; mass of electron = $9.1091 \times 10^{-31} \text{ kg}$; charge of electron (e) = $1.60210 \times 10^{-19} \text{ C}$; permittivity of vacuum (ϵ_0) = $8.854185 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \text{ A}^2$)
(2017 Main)

- (a) 1.65 Å (b) 4.76 Å
(c) 0.529 Å (d) 2.12 Å

15. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr , at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is
(2016 Adv.)



16. Which of the following is the energy of a possible excited state of hydrogen?
(2015 Main)

- (a) + 13.6 eV (b) - 6.8 eV
(c) - 3.4 eV (d) + 6.8 eV

17. The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is
(2013 Main)

- (a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
(c) $5, 1, 1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

18. Energy of an electron is given by

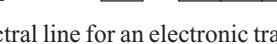
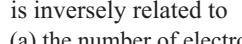
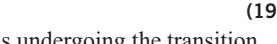
$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right) \quad (\text{2013 Main})$$

Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be ($h = 6.62 \times 10^{-34} \text{ Js}$ and $c = 3.0 \times 10^8 \text{ ms}^{-1}$)

- (a) $1.214 \times 10^{-7} \text{ m}$ (b) $2.816 \times 10^{-7} \text{ m}$
(c) $6.500 \times 10^{-7} \text{ m}$ (d) $8.500 \times 10^{-7} \text{ m}$

- 19.** The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] (2012)
 (a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$ (c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$
- 20.** The number of radial nodes in $3s$ and $2p$ respectively are
 (a) 2 and 0 (b) 0 and 2 (2005, 1M)
 (c) 1 and 2 (d) 2 and 1
- 21.** Which hydrogen like species will have same radius as that of Bohr orbit of hydrogen atom? (2004, 1M)
 (a) $n = 2$, Li^{2+} (b) $n = 2$, Be^{3+}
 (c) $n = 2$, He^+ (d) $n = 3$, Li^{2+}
- 22.** If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus, yet $1s^7$ is not observed, because it violates (2002, 3M)
 (a) Heisenberg uncertainty principle
 (b) Hund's rule
 (c) Pauli exclusion principle
 (d) Bohr postulate of stationary orbits
- 23.** The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for the electron spin represent (2001, 1M)
 (a) rotation of the electron in clockwise and anti-clockwise direction respectively
 (b) rotation of the electron in anti-clockwise and clockwise direction respectively
 (c) magnetic moment of the electron pointing up and down respectively
 (d) two quantum mechanical spin states which have no classical analogue
- 24.** The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order (2001, 1M)
 (a) 10^{-10} m (b) 10^{-20} m
 (c) 10^{-30} m (d) 10^{-40} m
- 25.** The number of nodal planes in a p_x orbital is (2001, 1M)
 (a) one (b) two (c) three (d) zero
- 26.** The electronic configuration of an element is $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$. This represents its (2000, 1M)
 (a) excited state (b) ground state
 (c) cationic form (d) anionic form
- 27.** The electrons, identified by quantum numbers n and l ,
 (i) $n = 4, l = 1$, (ii) $n = 4, l = 0$, (iii) $n = 3, l = 2$, (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as (1999, 2M)
 (a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
 (c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)
- 28.** The energy of an electron in the first Bohr orbit of H-atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) (1998, 2M)
 (a) -3.4 eV (b) -4.2 eV
 (c) -6.8 eV (d) $+6.8$ eV
- 29.** For a d -electron, the orbital angular momentum is (1997, 1M)
 (a) $\sqrt{6} \left(\frac{h}{2\pi} \right)$ (b) $\sqrt{2} \left(\frac{h}{2\pi} \right)$ (c) $\left(\frac{h}{2\pi} \right)$ (d) $2 \left(\frac{h}{2\pi} \right)$
- 30.** The first use of quantum theory to explain the structure of atom was made by (1997, 1M)
 (a) Heisenberg (b) Bohr
 (c) Planck (d) Einstein
- 31.** Which of the following has the maximum number of unpaired electrons? (1996, 1M)
 (a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+}
- 32.** The orbital angular momentum of an electron in $2s$ -orbital is (1996, 1M)
 (a) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (b) zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2} \cdot \frac{h}{2\pi}$
- 33.** Which of the following relates to photons both as wave motion and as a stream of particles? (1992, 1M)
 (a) Interference (b) $E = mc^2$
 (c) Diffraction (d) $E = h\nu$
- 34.** Which of the following does not characterise X-rays? (1992, 1M)
 (a) The radiation can ionise gases
 (b) It causes ZnS to fluoresce
 (c) Deflected by electric and magnetic fields
 (d) Have wavelengths shorter than ultraviolet rays
- 35.** The correct set of quantum numbers for the unpaired electron of chlorine atom is (1989, 1M)

n	l	m	n	l	m
(a) 2	1	0	(b) 2	1	1
(c) 3	1	1	(d) 3	0	0
- 36.** The correct ground state electronic configuration of chromium atom is (1989, 1M)
 (a) $[\text{Ar}] 3d^5 4s^1$ (b) $[\text{Ar}] 3d^4 4s^2$
 (c) $[\text{Ar}] 3d^6 4s^0$ (d) $[\text{Ar}] 4d^5 4s^1$
- 37.** The outermost electronic configuration of the most electronegative element is (1988, 90, 1M)
 (a) $ns^2 np^3$ (b) $ns^2 np^4$
 (c) $ns^2 np^5$ (d) $ns^2 np^6$
- 38.** The orbital diagram in which the Aufbau principle is violated (1988, 1M)

(a)		
(b)		
(c)		
(d)		
- 39.** The wavelength of a spectral line for an electronic transition is inversely related to (1988, 1M)
 (a) the number of electrons undergoing the transition
 (b) the nuclear charge of the atom
 (c) the difference in the energy of the energy levels involved in the transition
 (d) the velocity of the electron undergoing the transition

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40. The ratio of the energy of a photon of 200 \AA wavelength radiation to that of 4000 \AA radiation is (1986, 1M)

(a) $\frac{1}{4}$ (b) 4 (c) $\frac{1}{2}$ (d) 2.

41. Which one of the following sets of quantum numbers represents an impossible arrangement? (1986, 1M)

n	l	m	s
(a) 3	2	-2	$\frac{1}{2}$
(b) 4	0	0	$\frac{1}{2}$
(c) 3	2	-3	$\frac{1}{2}$
(d) 5	3	0	$-\frac{1}{2}$

42. Electromagnetic radiation with maximum wavelength is

(a) ultraviolet (b) radio wave (1985, 1M)
 (c) X-ray (d) infrared

43. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon? (1984, 1M)

(a) $3s$ (b) $2p$ (c) $2s$ (d) $1s$

44. Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($Z = 37$) is (1984, 1M)

(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
 (c) $5, 1, 1, +\frac{1}{2}$ (d) $6, 0, 0, +\frac{1}{2}$

45. The principal quantum number of an atom is related to the (a) size of the orbital (1983, 1M)

(b) spin angular momentum
 (c) orientation of the orbital in space
 (d) orbital angular momentum

46. Any p -orbital can accommodate upto (1983, 1M)

(a) four electrons
 (b) six electrons
 (c) two electrons with parallel spins
 (d) two electrons with opposite spins

Objective Questions II

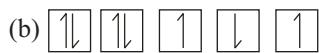
(One or more than one correct option)

47. The ground state energy of hydrogen atom is -13.6 eV . Consider an electronic state Ψ of He^+ whose energy, azimuthal quantum number and magnetic quantum number are -3.4 eV , 2 and 0, respectively.

Which of the following statement(s) is(are) true for the state Ψ ? (2019 Adv.)

- (a) It is a $4d$ state
 (b) The nuclear charge experienced by the electron in this state is less than $2e$, where e is the magnitude of the electronic charge
 (c) It has 2 angular nodes
 (d) It has 3 radial nodes

48. The ground state electronic configuration of nitrogen atom can be represented by (1999, 3M)

- (a) 
 (b) 
 (c) 
 (d) 

49. Which of the following statement (s) is (are) correct ?

(1998, 2M)

- (a) The electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ (atomic number of Cr = 24)
 (b) The magnetic quantum number may have a negative value
 (c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (atomic number of Ag = 47)
 (d) The oxidation state of nitrogen in HN_3 is -3

50. An isotope of $^{76}_{32}\text{Ge}$ is

(1984, 1M)

- (a) $^{77}_{32}\text{Ge}$ (b) $^{77}_{33}\text{As}$
 (c) $^{77}_{34}\text{Se}$ (d) $^{78}_{34}\text{Se}$

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Both Statement I and Statement II are correct; Statement II is the correct explanation of Statement I

- (b) Both Statement I and Statement II are correct; Statement II is not the correct explanation of Statement I

- (c) Statement I is correct; Statement II is incorrect

- (d) Statement I is incorrect; Statement II is correct

51. **Statement I** The first ionisation energy of Be is greater than that of B.

Statement II $2p$ -orbital is lower in energy than $2s$. (2000)

Passage Based Questions

The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2 . The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

52. The state S_1 is

(2010)

- (a) $1s$ (b) $2s$ (c) $2p$ (d) $3s$

53. Energy of the state S_1 in units of the hydrogen atom ground state energy is

(2010)

- (a) 0.75 (b) 1.50 (c) 2.25 (d) 4.50

54. The orbital angular momentum quantum number of the state S_2 is

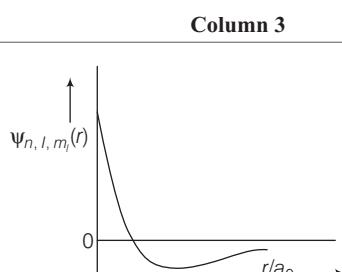
(2010)

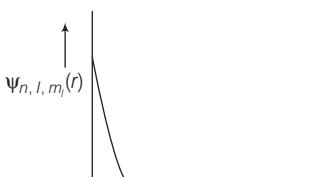
- (a) 0 (b) 1 (c) 2 (d) 3

Match the Columns

Answer Q. 55, Q. 55 and Q. 56 by appropriately matching the information given in the three columns of the following table.

The wave function, ψ_n, l, m_l is a mathematical function whose value depends upon spherical polar coordinates (r, θ, ϕ) of the electron and characterised by the quantum number n, l and m_l . Here r is distance from nucleus, θ is colatitude and ϕ is azimuth. In the mathematical functions given in the Table, Z is atomic number and a_0 is Bohr radius. (2017 Adv.)



Column 1	Column 2	Column 3
(I) 1s-orbital	(i) $\Psi_{n, l, m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\left(\frac{Zr}{a_0}\right)}$	(P) 
(II) 2s-orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto \frac{1}{a_0^3}$
(III) 2p _z -orbital	(iii) $\Psi_{n, l, m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\left(\frac{Zr}{a_0}\right)} \cos\theta$	(R) Probability density is maximum at nucleus
(IV) 3d _{z^2} -orbital	(iv) xy-plane is a nodal plane	(S) Energy needed to excite electron from $n = 2$ state to $n = 4$ state is $\frac{27}{32}$ times the energy needed to excite electron from $n = 2$ state to $n = 6$ state

Column I	Column II
A. Orbital angular momentum of the electron in a hydrogen-like atomic orbital.	p. Principal quantum number
B. A hydrogen-like one-electron wave function obeying Pauli's principle.	q. Azimuthal quantum number
C. Shape, size and orientation of hydrogen-like atomic orbitals.	r. Magnetic quantum number
D. Probability density of electron at the nucleus in hydrogen-like atom.	s. Electron spin quantum number

Fill in the Blanks

59. The outermost electronic configuration of Cr is (1994, 1M)

60. 8 g each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of (1989, 1M)

61. The uncertainty principle and the concept of wave nature of matter were proposed by and respectively. (1988, 1M)

62. Wave functions of electrons in atoms and molecules are called (1993, 1M)

63. The $2p_x$, $2p_y$ and $2p_z$ orbitals of atom have identical shapes but differ in their (1993, 1M)

64. When there are two electrons in the same orbital, they have spins. (1983, 1M)

True/False

- 65.** In a given electric field, β -particles are deflected more than α -particles in spite of α -particles having larger charge. (1993, 1M)

66. The electron density in the XY -plane in $3d_{x^2 - y^2}$ orbital is zero. (1986, 1M)

67. The energy of the electron in the $3d$ -orbital is less than that in the $4s$ -orbital in the hydrogen atom. (1983, 1M)

68. Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} to 10^{-5} cm. (1983, 1M)

69. The outer electronic configuration of the ground state chromium atom is $3d^4 4s^2$. (1982, 1M)

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Integer Answer Type Questions

70. Not considering the electronic spin, the degeneracy of the second excited state ($n = 3$) of H-atom is 9, while the degeneracy of the second excited state of H^- is (2015 Adv.)
 71. In an atom, the total number of electrons having quantum numbers (2014 Adv.)

$$n = 4, |m_l| = 1 \text{ and } m_s = -\frac{1}{2} \text{ is}$$

72. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de-Broglie wavelength of He gas at -73°C is ' M ' times that of the de-Broglie wavelength of Ne at 727°C . M is (2013 Adv.)

73. The work function (Φ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is (2011)

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
Φ (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

74. The maximum number of electrons that can have principal quantum number, $n = 3$ and spin quantum number, $m_s = -1/2$, is (2011)

Subjective Questions

75. (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given, $r = a_0$).
 (b) Find de-Broglie wavelength of the electron in first Bohr orbit.
 (c) Find the orbital angular momentum of $2p$ -orbital in terms of $h/2\pi$ units. (2005, 2M)

76. (a) The Schrodinger wave equation for hydrogen atom is

$$\Psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

where, a_0 is Bohr's radius. Let the radial node in $2s$ be at r_0 . Then, find r in terms of a_0 .

- (b) A base ball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of base ball. (2004, 2M)

77. The wavelength corresponding to maximum energy for hydrogen is 91.2 nm. Find the corresponding wavelength for He^+ ion. (2003, 2M)

78. Calculate the energy required to excite 1 L of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol⁻¹. (2000)

79. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å. (1997 (C), 2M)

80. Consider the hydrogen atom to be proton embedded in a cavity of radius a_0 (Bohr's radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the

work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. (1996, 2M)

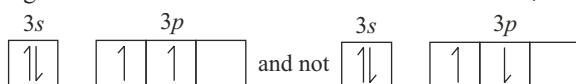
81. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. (1996, 1M)
 82. Iodine molecule dissociates into atoms after absorbing light to 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $\text{I}_2 = 240 \text{ kJ mol}^{-1}$) (1995, 2M)
 83. Find out the number of waves made by a Bohr's electron in one complete revolution in its 3rd orbit. (1994, 3M)
 84. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum? (1993, 3M)
 85. Estimate the difference in energy between 1st and 2nd Bohr's orbit for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8} \text{ m}$? Which hydrogen atom-like species does this atomic number correspond to? (1993, 5M)

86. According to Bohr's theory, the electronic energy of hydrogen atom in the n th Bohr's orbit is given by :

$$E_n = \frac{-21.7 \times 10^{-19}}{n^2} \text{ J}$$

Calculate the longest wavelength of electron from the third Bohr's orbit of the He^+ ion. (1990, 3M)

87. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2? (1985, 2M)
 88. Give reason why the ground state outermost electronic configuration of silicon is (1985, 2M)



89. The electron energy in hydrogen atom is given by $E_n = \frac{-21.7 \times 10^{-12}}{n^2}$ erg. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? (1984, 3M)

90. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in the Bohr's orbit, $n = 2$ returns to the orbit, $n = 1$ in the hydrogen atom. The ionisation potential of the ground state hydrogen atom is 2.17×10^{-11} erg per atom. (1982, 4M)

91. The energy of the electron in the second and third Bohr's orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted light when the electron drops from the third to the second orbit. (1981, 3M)

Answers

Topic 1

1. (d) 2. (a) 3. (b) 4. (c)
 5. (d) 6. (c) 7. (d) 8. (b)
 9. (b) 10. (b) 11. (d) 12. (a)
 13. (c) 14. (a) 15. (a,b) 16. (d)
 17. (a,c) 18. (a,c) 19. (a) 20. (c)
 21. A → r; B → q; C → p, D → s
 22. (photons) 23. $(1.66 \times 10^{-27} \text{ kg})$ 24. (neutrons)
 25. (isobars) 26. (-5242.41) 27. 6.3×10^6

Topic 2

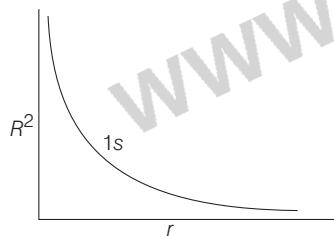
1. (c) 2. (a) 3. (a) 4. (a)
 5. (a) 6. (d) 7. (c) 8. (c)
 9. (b) 10. (d) 11. (d) 12. (b)
 13. (c) 14. (d) 15. (c) 16. (c)
 17. (a) 18. (a) 19. (c) 20. (a)
 21. (b) 22. (c) 23. (d) 24. (c)
 25. (a) 26. (b) 27. (a) 28. (a)
 29. (a) 30. (b) 31. (d) 32. (b)

33. (a) 34. (c) 35. (c) 36. (a)
 37. (c) 38. (b) 39. (c) 40. (d)
 41. (c) 42. (b) 43. (d) 44. (a)
 45. (a) 46. (d) 47. (a,c) 51. (c)
 48. (a,d) 49. (a,b,c) 50. (b,d) 55. (c)
 52. (b) 53. (c) 54. (b) 59. Cr = [Ar] $3d^5, 4s^1$
 56. (a) 57. (d) 58. A → q; B → p, q, r, s C → p, q, r D → p, q, r
 59. $Cr = [Ar] 3d^5, 4s^1$ 60. 1 : 16
 61. Heisenberg, de-Broglie. 62. orbital
 63. Orientation in space 64. opposite
 65. True 66. False 67. True 68. False
 69. False 70. (3) 71. (6) 72. (5)
 73. (4.14 eV) 74. (9) 77. (22.8 nm) 78. (98.44 kJ)
 79. (63.56 V) 81. $(2.725 \times 10^6 \text{ M}^{-1})$
 82. $(2.16 \times 10^{20} \text{ J/atom})$ 86. (471 nm) 87. (10)
 89. $(3.66 \times 10^{-5} \text{ cm})$ 90. (1220 Å) 91. (660 nm)

Hints & Solutions

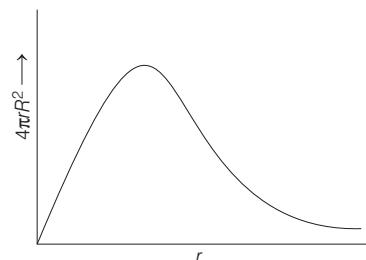
Topic 1 Preliminary Developments and Bohr's Model

1. Statement (d) is incorrect. For 1s-orbital radial probability density (R^2) against r is given as:



For 1s-orbital, probability density decreases sharply as we move away from the nucleus.

The radial distribution curves obtained by plotting radial probability functions vs r for 1s-orbital is



The graph initially increases and then decreases. It reaches a maximum at a distance very close to the nucleus and then

decreases. The maximum in the curve corresponds to the distance at which the probability of finding the electron is maximum.

2. The expression of kinetic energy of photo electrons,

$$KE = \frac{1}{2} mv^2 = E - E_0$$

When, $KE \gg E_0$, the equation becomes,

$$\begin{aligned} KE &= \frac{1}{2} mv^2 = E \\ \Rightarrow \frac{1}{2} mv^2 &= \frac{hc}{\lambda} \Rightarrow \frac{p^2}{2m^2} = \frac{hc}{\lambda} \\ \Rightarrow \lambda &= hc \times 2m^2 \times \frac{1}{p^2} \Rightarrow \lambda \propto \frac{1}{p^2} \\ E &= \frac{hc}{\lambda} = \text{energy of incident light.} \end{aligned}$$

E_0 = threshold energy or work functions,

$$\frac{1}{2} mv^2 = \frac{1}{2} \times \frac{(mv)^2}{m^2} = \frac{1}{2} \times \frac{p^2}{m^2}$$

$\because p = \text{momentum} = mv$

As per the given condition,

$$\begin{aligned} \frac{\lambda_2}{\lambda_1} &= \left(\frac{p_1}{p_2} \right)^2 \\ \Rightarrow \frac{\lambda_2}{\lambda} &= \left(\frac{p}{1.5 \times p} \right)^2 = \left(\frac{2}{3} \right)^2 = \frac{4}{9} \end{aligned}$$

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$$\Rightarrow \lambda_2 = \frac{4}{9} \lambda \quad \left[\because \lambda_1 = \lambda, P_1 = p \right]$$

3. Work function of metal (ϕ) = $h\nu_0$
where, ν_0 = threshold frequency

$$\text{Also, } \frac{1}{2} m_e \nu^2 = h\nu - h\nu_0$$

$$\text{or } \frac{1}{2} m_e \nu^2 = h\nu - \phi \quad \dots(\text{i})$$

$$\frac{1}{2} m_e \nu^2 = \frac{hc}{\lambda} - \phi \quad \dots(\text{ii})$$

Given : $\lambda = 4000 \text{ \AA} = 4000 \times 10^{-10} \text{ m}$

$$\nu = 6 \times 10^5 \text{ ms}^{-1},$$

$$m_e = 9 \times 10^{-31} \text{ kg}, c = 3 \times 10^8 \text{ ms}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

Thus, on substituting all the given values in Eq. (i), we get

$$\begin{aligned} \frac{1}{2} \times 9 \times 10^{-31} \text{ kg} \times (6 \times 10^5 \text{ ms}^{-1})^2 \\ = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{4000 \times 10^{-10} \text{ m}} - \phi \\ \therefore \phi = 1.62 \times 10^{-21} \text{ kg m}^2 \text{s}^{-2} - 4.96 \times 10^{-19} \text{ J} \\ = 3.36 \times 10^{-19} \text{ J} \quad [1 \text{ kg m}^2 \text{s}^{-2} = 1 \text{ J}] \\ = 2.1 \text{ eV} \end{aligned}$$

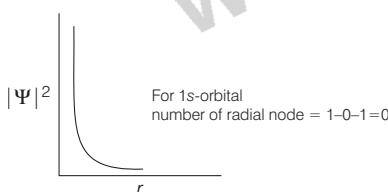
4. The ground state energy of H-atom is + 13.6 eV.

For second excited state, $n = 2 + 1 = 3$

$$\begin{aligned} \therefore E_3(\text{He}^+) &= -13.6 \times \frac{Z^2}{n^2} \text{ eV} \quad [\because \text{for He}^+, Z = 2] \\ &= -13.6 \times \frac{2^2}{3^2} \text{ eV} = -6.04 \text{ eV} \end{aligned}$$

5. For photoelectric effect,

$$(i) \quad KE = E - E_0$$



where,

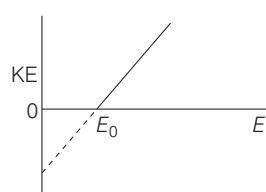
KE = Kinetic energy of ejected electrons.

E = Energy of incident light = $h\nu$

E_0 = Threshold energy = $h\nu_0$

ν = Frequency of incident light

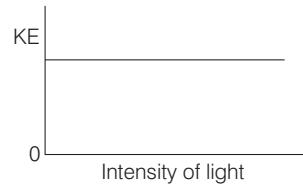
ν_0 = Threshold frequency



Slope = ± 1 , intercept = $-E_0$

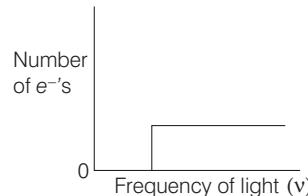
So, option (a) is correct.

- (ii) KE of ejected electrons does not depend on the intensity of incident light.



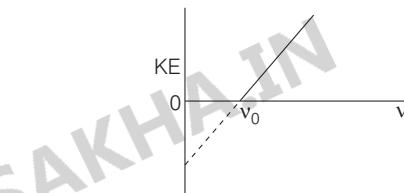
So, option (b) is correct.

- (iii) When, number of ejected electrons is plotted with frequency of light, we get



So, option (c) is also correct.

- (iv) $KE = h\nu - h\nu_0$



Slope = $+ h$, intercept = $-h\nu_0$. So, option (d) is not correct.

6. Plan As you can see in options, energy term is mentioned hence, we have to find out relation between h/λ and energy. For this, we shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron (λ) = $\frac{h}{p}$

$$\Rightarrow p = \frac{h}{\lambda} \quad \dots(\text{i})$$

Kinetic energy of an electron = eV

$$\text{As we know that, } KE = \frac{p^2}{2m}$$

$$\therefore eV = \frac{p^2}{2m} \quad \text{or} \quad p = \sqrt{2meV} \quad \dots(\text{ii})$$

From equations (i) and (ii), we get $\frac{h}{\lambda} = \sqrt{2meV}$

7. Rutherford used α -particle (He^{2+} nuclei) in his experiment.

8. According to Rutherford's model, there is a heavily positively charged nucleus and negatively charged electrons occupies space around it in order to maintain electro-neutrality.

9. Radius of a nucleus is in the order of 10^{-13} cm, a fact.

10. Bohr's model is applicable to one-electron system only.

11. Neutron has no charge, hence e/m is zero for neutron. Next, α -particle (He^{2+}) has very high mass compared to proton and electron, therefore very small e/m ratio. Proton and electron

have same charge (magnitude) but former is heavier, hence has smaller value of e/m .

$$\frac{e}{m} : n < \alpha < p < e$$

- 12. The negligibly small size of nucleus compared to the size of atom was first established in Rutherford's experiment.
- 13. The most important findings of Rutherford's experiment is discovery of nucleus.
- 14. Energy of electron in H-atom is determined by the expression:

$$E_n = -\frac{13.6}{n^2} \text{ eV} \quad \text{where, } n = 1, 2, 3, \dots$$

In excited states, $E_2 = -\frac{13.6}{4} = -3.4 \text{ eV}$

$$E_3 = -\frac{13.6}{9} = -1.51 \text{ eV etc.}$$

- 15. Nucleus is composed of neutrons and protons.
- 16. The isotopes of hydrogen are ${}_1\text{H}^2$ and ${}_1\text{H}^3$.
- 17. Alpha particles passes mostly undeflected when sent through thin metal foil mainly, because
 - (i) it is much heavier than electrons.
 - (ii) most part of atom is empty space.
- 18. Many elements have several isotopes. For such elements, atomic mass is average of the atomic masses of different isotopes, which is usually non-integral.
- 19. (III) Kinetic energy of the electron in n th orbit,

$$\text{K.E.} = +13.6 \times \frac{Z^2}{n^2}$$

$$\text{or} \quad \text{K.E.} \propto \frac{1}{n^2} \quad \text{or} \quad \text{K.E.} \propto n^{-2}$$

From list-II, correct match is (III P).

(IV) Potential energy of the electron in the n th orbit,

$$\text{P.E.} = -2 \times 13.6 \times \frac{Z^2}{n^2}$$

$$\text{P.E.} \propto \frac{1}{n^2}$$

$$\text{P.E.} \propto n^{-2}$$

From List II, correct match is (IV P).

Hence, correct matching from list-I and list-II on the basis of given option is (III, P).

- 20. (I) Radius of the n th orbit,

$$r = 0.529 \times \frac{n^2}{Z}$$

Here, $r \propto n^2$

From list-II, correct match is (I, T)

(II) Angular momentum of the electron,

$$mv r = \frac{nh}{2\pi} \quad \text{or} \quad mv r \propto n$$

From list-II, correct match (II, S)

Hence, correct matching from list-I and list-II on the basis of given option is (I, T).

$$21. \text{ A. } V_n = -\frac{1}{4\pi\epsilon_0} \left(\frac{Ze^2}{r} \right)$$

$$K_n = \frac{1}{8\pi\epsilon_0} \left(\frac{Ze^2}{r} \right)$$

$$\Rightarrow \frac{V_n}{K_n} = -2 \text{ — (r)}$$

$$\text{B. } E_n = -\frac{Ze^2}{8\pi\epsilon_0 r} \propto r^{-1}$$

$$\Rightarrow x = -1 \text{ — (q)}$$

$$\text{C. Angular momentum} = \sqrt{l(l+1)} \frac{h}{2\pi} = 0 \text{ in } 1s\text{-orbital} \text{ — (p)}$$

$$\text{D. } r_n = \frac{a_0 n^2}{Z} \Rightarrow \frac{1}{r_n} \propto Z \text{ — (s)}$$

- 22. Photons have quantised energy.

$$23. \text{ Mass of one H-atom} = \frac{10^{-3}}{6.023 \times 10^{23}} \text{ kg} = 1.66 \times 10^{-27} \text{ kg}$$

- 24. Isotopes have different number of neutrons.

- 25. Isobars have same mass number but different atomic numbers.

- 26. Given that, electrons and nucleus are at infinite distance, so potential energy of H-atom is taken as zero.

Therefore, according to Bohr's model, potential energy of a H-atom with electron in its ground state = -27.2 eV

At $d = d_0$, nucleus-nucleus and electron-electron repulsion is absent.

Hence, potential energy will be calculated for 2H atoms = $-2 \times 27.2 \text{ eV} = -54.4 \text{ eV}$

Potential energy of 1 mol H atoms in kJ

$$= \frac{54.4 \times 6.02 \times 10^{23} \times 1.6 \times 10^{-19}}{1000} = -5242.4192 \text{ kJ/mol}$$

- 27. When α -particle stop at 10^{-13} m from nucleus, kinetic energy is zero, i.e. whole of its kinetic energy at the starting point is now converted into potential energy.

Potential energy of this α -particle can be determined as

$$\boxed{\text{PE} = -\frac{Z_1 \times Z_2 e^2}{(4\pi\epsilon_0) r}}$$

$$(Z_1 = +2, Z_2 = +29, \epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ m}^{-1}, r = 10^{-13} \text{ m})$$

$$\Rightarrow |\text{PE}| = \frac{2 \times 29 \times (1.6 \times 10^{-19})^2}{4 \times 3.14 \times 8.85 \times 10^{-12} \times 10^{-13}} \text{ J}$$

$$= 1.33 \times 10^{-13} \text{ J}$$

= kinetic energy of α -particle at $t = 0$

$$\Rightarrow \text{KE} = \frac{1}{2} mv^2 = 1.33 \times 10^{-13}$$

$$\Rightarrow v = \sqrt{\frac{2 \times 1.33 \times 10^{-13}}{4 \times 1.66 \times 10^{-27}}} = 6.3 \times 10^6 \text{ ms}^{-1}$$

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Topic 2 Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

1. Quantum nature of atoms are associated with following phenomena or processes :

(i) Absorption spectrum (ii) Emission spectrum
(iii) Black body radiation (iv) Photo-electricity

Internal energy (U) of particles like atoms depends upon the thermodynamic variables (p, V, T) of the system. Thus, $U = f(p, T)$ or $U = f_1(T, V)$ or $U = f_2(p, V)$

So, quantum nature of atom is not associated with its internal energy.

Graph (c) is not a direct manifestation of the quantum nature of atoms.

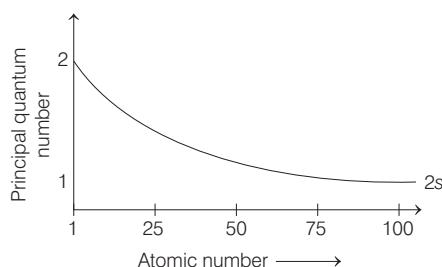
2. According to quantum mechanical atom model, for each value of n (principal quantum number), there are ' n ' different values of l (azimuthal quantum number), i.e. $l = 0, 1, 2, \dots, (n-1)$. And, for each value of l , there are $2l+1$ different values of m_l (magnetic quantum number), i.e. $m_l = 0, \pm 1, \pm 2 \dots \pm l$.

\therefore Total number of possible combinations of n, l and m_l , for a given value of n is n^2 , and each such combination is associated with an orbital. Each orbital can occupy a maximum of two electrons, having a different value of spin quantum number (m_s), which are $+\frac{1}{2}$ or $-\frac{1}{2}$.

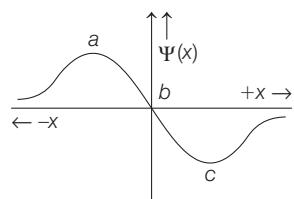
\therefore Number of orbitals associated with $n = 5$ is $n^2 = 25$. Each of those orbitals can be associated with $m_s = +\frac{1}{2}$ as well as $m_s = -\frac{1}{2}$.

\therefore Answer = 25

3. The energy of $2s$ -orbital is lowest in K(potassium). An orbital gets larger as the principal quantum number n increases. Correspondingly, the energy of the electron in such an orbital becomes less negative, meaning that the electron is less strongly bound and has less energy. The graph of principal quantum number with atomic number is



4. The electrons are more likely to be found in the region a and c . At b , wave function becomes zero and is called radial nodal surface or simply node.



The graph between wavefunction (ψ) and distance (r) from the nucleus helps in determining the shape of orbital.

5. According to Rydberg's equation,

$$\frac{1}{\lambda} = \frac{R_H}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{or} \quad \frac{1}{\lambda} \propto \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For shortest wavelength, i.e. highest energy spectral line, n_2 will be (∞).

For the given spectral series, ratio of the shortest wavelength of two spectral series can be calculated as follows :

$$(a) \frac{\lambda_L}{\lambda_P} = \frac{\frac{1}{3^2} - \frac{1}{\infty^2}}{\frac{1}{1^2} - \frac{1}{\infty^2}} = \frac{\frac{1}{9} - 0}{1 - 0} = \frac{1}{9}$$

$$(b) \frac{\lambda_{Bk}}{\lambda_{Pf}} = \frac{\frac{1}{5^2} - \frac{1}{\infty^2}}{\frac{1}{4^2} - \frac{1}{\infty^2}} = \frac{\frac{1}{25} - 0}{\frac{1}{16} - 0} = \frac{16}{25}$$

$$(c) \frac{\lambda_P}{\lambda_{Pf}} = \frac{\frac{1}{5^2} - \frac{1}{\infty^2}}{\frac{1}{3^2} - \frac{1}{\infty^2}} = \frac{\frac{1}{25} - 0}{\frac{1}{9} - 0} = \frac{9}{25}$$

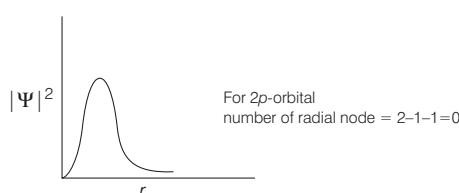
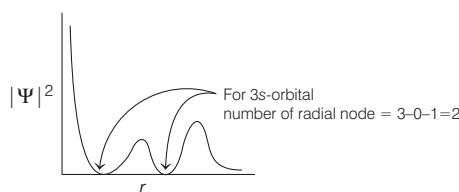
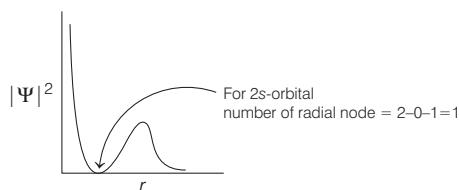
$$(d) \frac{\lambda_B}{\lambda_{Bk}} = \frac{\frac{1}{4^2} - \frac{1}{\infty^2}}{\frac{1}{2^2} - \frac{1}{\infty^2}} = \frac{\frac{1}{16} - 0}{\frac{1}{4} - 0} = \frac{4}{16} = \frac{1}{4}$$

Note Lyman = L ($n_1 = 1$), Balmer = B ($n_1 = 2$)

Paschen = P ($n_1 = 3$), Brackett = Bk ($n_1 = 4$)

Pfund = Pf ($n_1 = 5$)

6. The graphs between $|\Psi|^2$ and r are radial density plots having $(n-l-1)$ number of radial nodes. For 1s, 2s, 3s and 2 p-orbitals these are respectively.



Thus, the given graph between $|\Psi|^2$ and r represents 2s-orbital.

7. For any given series of spectral lines of atomic hydrogen.

Let $\Delta\bar{v} = \bar{v}_{\max} - \bar{v}_{\min}$ be the difference in maximum and minimum frequencies in cm^{-1} .

For Lyman series,

$$\Delta\bar{v} = \bar{v}_{\max} - \bar{v}_{\min}$$

General formula:

$$\bar{v} = 109,677 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

For Lyman $n_1 = 1, n_2 = 2, 3, \dots$

$$\begin{aligned}\bar{v}_{\max} &= 109,677 \left(\frac{1}{1} - \frac{1}{\infty} \right) = 109,677 \left(\frac{1}{1} - 0 \right) \\ &= 109,677\end{aligned}$$

$$\bar{v}_{\min} = 109,677 \left(\frac{1}{1} - \frac{1}{(2)^2} \right)$$

$$\begin{aligned}\Delta\bar{v}_{\text{Lyman}} &= \bar{v}_{\max} - \bar{v}_{\min} \\ &= 109,677 - \left[\frac{109,677 \times 3}{4} \right] = \frac{109,677}{4}\end{aligned}$$

For Balmer series,

$$\bar{v}_{\max} = 109,677 \left(\frac{1}{(2)^2} - \frac{1}{\infty} \right) \Rightarrow \frac{109,677}{4}$$

$$\bar{v}_{\min} = 109,677 \left(\frac{1}{(2)^2} - \frac{1}{(3)^2} \right) \Rightarrow \frac{109,677 \times 5}{36}$$

$$\Delta\bar{v} = \bar{v}_{\max} - \bar{v}_{\min} \\ \Delta\bar{v}_{\text{Balmer}} = \frac{109,677}{4} - \left[\frac{109,677 \times 5}{36} \right] = 109,677 \left(\frac{1}{9} \right)$$

$$\frac{\Delta\bar{v}_{\text{Lyman}}}{\Delta\bar{v}_{\text{Balmer}}} = \frac{109,677 / 4}{109,677 / 9}$$

$$\frac{\Delta\bar{v}_{\text{Lyman}}}{\Delta\bar{v}_{\text{Balmer}}} = \frac{9}{4}$$

\therefore The ratio of $\frac{\Delta\bar{v}_{\text{Lyman}}}{\Delta\bar{v}_{\text{Balmer}}}$ is 9 : 4.

8. Smaller the value of $(n + l)$, smaller the energy. If two or more sub-orbits have same values of $(n + l)$, sub-orbits with lower values of n has lower energy. The $(n + l)$ values of the given options are as follows :

I. $n = 4, l = 2 ; n + l = 6$

II. $n = 3, l = 2 ; n + l = 5$

III. $n = 4, l = 1, n + l = 5$

IV. $n = 3, l = 1, n + l = 4$

Among II and III, $n = 3$ has lower value of energy. Thus, the correct order of their increasing energies will be

$$\text{IV} < \text{II} < \text{III} < \text{I}$$

9. Number of waves = $\frac{\text{Circumference}}{\text{Wavelength}} \Rightarrow n = \frac{2\pi r}{\lambda}$

$$\therefore 2\pi r = n\lambda \quad \dots(\text{i})$$

Also, we know that radius (r) of an atom is given by

$$r = \frac{a_0 n^2}{Z}$$

Thus, Eq. (i) becomes

$$2\pi a_0 \frac{n^2}{Z} = n\lambda \quad \dots(\text{ii})$$

$$\therefore 2\pi a_0 \frac{n^2}{Z} = n(1.5 \pi a_0) [\text{Given, } \lambda = 1.5 \pi a_0] \\ \frac{n}{Z} = \frac{1.5 \pi a_0}{2\pi a_0} = \frac{1.5}{2} = 0.75$$

10. de-Broglie wavelength (λ) for electron is given by

$$\lambda = \frac{h}{\sqrt{2m \times \text{KE}}} \quad \dots(\text{i})$$

Also, according to photoelectric effect

$$\text{KE} = h\nu - h\nu_0$$

On substituting the value of KE in Eq (i), we get

$$\lambda = \frac{h}{\sqrt{2m \times (h\nu - h\nu_0)}}$$

$$\therefore \lambda \propto \frac{1}{(\nu - \nu_0)^{1/2}}$$

11. (I) Angular momentum, $mvr = \frac{nh}{2\pi}$

$$\Rightarrow mvr \propto n$$

\propto distance from the nucleus

- (II) This statement is incorrect as size of an orbit

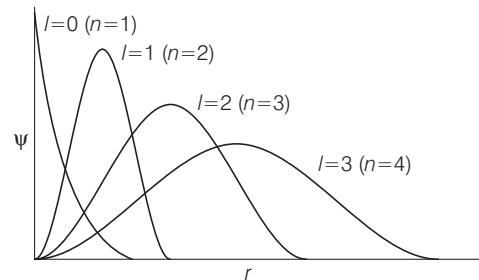
\propto Azimuthal quantum number (l)
($\because n = \text{constant}$)

- (III) This statement is incorrect as at ground state,
 $n = 1, l = 0$

\Rightarrow Orbital angular momentum (wave mechanics)

$$= \sqrt{l(l+1)} \frac{h}{2\pi} = 0 \quad [\because l = 0]$$

- (IV) The given plot is



$$12. \Delta E = hc \times \frac{1}{\lambda} = hc \times \left[R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \times Z^2 \right]$$

$$\Rightarrow \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{hc}{R_H \times \lambda \times Z^2 \times hc} \quad [\text{for H, atom } Z = 1]$$

$$= \frac{1}{R_H \times \lambda} = \frac{1}{(1 \times 10^7 \text{ m}^{-1})} \times \frac{1}{(900 \times 10^{-9} \text{ m})}$$

$$\Rightarrow \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{9}$$

$$\text{So, in option (b)} \frac{1}{3^2} - \frac{1}{\infty^2} = \frac{1}{9} - 0 = \frac{1}{9}$$

$$\left[\because n_1 = 3, n_2 = \infty \right]$$

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13. According to Rydberg's formula,

$$\text{wave number } (\bar{v}) = R_H Z^2 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

Given, $n_i = n$, $n_f = 8$ [∴ it is the case of emission]

$$\bar{v} = R_H \times (1)^2 \left[\frac{1}{n^2} - \frac{1}{8^2} \right]$$

$$\bar{v} = R_H \left[\frac{1}{n^2} - \frac{1}{64} \right] = \frac{R_H}{n^2} - \frac{R_H}{64}$$

On comparing with equation of straight line, $y = mx + c$, we get

$$\text{Slope} = R_H, \text{ intercept} = \frac{-R_H}{64}.$$

Thus, plot of wave number (\bar{v}) against $\frac{1}{n^2}$ will be linear with slope (+ R_H).

14. Bohr radius (r_n) = $\epsilon_0 n^2 h^2$

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 k Z}$$

$$k = \frac{1}{4\pi \epsilon_0}$$

$$\therefore r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 Z} = n^2 \frac{a_0}{Z}$$

where, m = mass of electron

e = charge of electron

h = Planck's constant

k = Coulomb constant

$$r_n = \frac{n^2 \times 0.53}{Z} \text{ Å}$$

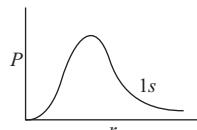
Radius of n^{th} Bohr orbit for H-atom

$$= 0.53 n^2 \text{ Å} \quad [\text{Z} = 1 \text{ for H-atom}]$$

∴ Radius of 2nd Bohr orbit for H-atom

$$= 0.53 \times (2)^2 = 2.12 \text{ Å}$$

15. This graph shows the probability of finding the electron within shell at various distances from the nucleus (radial probability). The curve shows the maximum, which means that the radial probability is greatest for a given distance from the nucleus. This distance is equal to Bohr's radius = a_0



- (a) It is for 2s-orbital.
- (b) It is radial wave function for 1s.
- (c) Correct
- (d) Probability cannot be zero at a certain distance from nucleus.

16. ∴ $E_n = -\frac{13.6}{n^2} \text{ eV}$ where, $n = 1, 2, 3 \dots$

$$\text{In excited states, } E_2 = -\frac{13.6}{4} = -3.4 \text{ eV}$$

17. Given, atomic number of Rb, $Z = 37$

Thus, its electronic configuration is [Kr]5s¹. Since, the last electron or valence electron enter in 5s subshell.

So, the quantum numbers are $n = 5, l = 0$, (for s-orbital) $m = 0$ (∴ $m = +l$ to $-l$), $s = +1/2$ or $-1/2$.

18. Given, in the question $E = -2.178 \times 10^{-18} \text{ J} \left[\frac{Z^2}{n^2} \right]$

For hydrogen $Z = 1$,

$$\text{So, } E_1 = -2.178 \times 10^{-18} \text{ J} \left[\frac{1}{1^2} \right]$$

$$E_2 = -2.178 \times 10^{-18} \text{ J} \left[\frac{1}{2^2} \right]$$

Now, $E_1 - E_2$

$$\text{i.e. } \Delta E = 2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{hc}{\lambda}$$

$$2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}$$

$$\therefore \lambda \approx 1.21 \times 10^{-7} \text{ m}$$

19. According to Bohr's model,

$$\begin{aligned} mv r &= \frac{nh}{2\pi} \Rightarrow (mv)^2 = \frac{n^2 h^2}{4\pi^2 r^2} \\ \Rightarrow KE &= \frac{1}{2} mv^2 = \frac{n^2 h^2}{8\pi^2 r^2 m} \end{aligned} \quad \dots(i)$$

Also, Bohr's radius for H-atom is, $r = n^2 a_0$

Substituting 'r' in Eq. (i) gives

$$KE = \frac{h^2}{8\pi^2 n^2 a_0^2 m} \text{ when } n = 2, KE = \frac{h^2}{32\pi^2 a_0^2 m}$$

20. The number of radial nodes is given by expression $(n - l - 1)$.

For 3s, number of nodes = $3 - 0 - 1 = 2$

For 2p, number of nodes = $2 - 1 - 1 = 0$

21. Expression for Bohr's orbit is, $r_n = \frac{a_0 n^2}{Z} = a_0$ when $n = 2, Z = 4$.

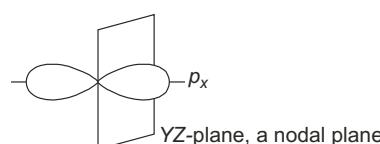
22. 1s⁷ violate Pauli exclusion principle, according to which an orbital cannot have more than two electrons.

23. $+\frac{1}{2}$ and $-\frac{1}{2}$ just represents two quantum mechanical spin states which have no classical analogue.

24. Using the de-Broglie's relationship :

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{0.2 \times \frac{5}{60 \times 60}} = 2.3 \times 10^{-30} \text{ m}$$

25. Nodal plane is an imaginary plane on which probability of finding an electron is minimum. Every p-orbital has one nodal plane :



26. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ is ground state electronic configuration of Cr.

27. (i) $n = 4, l = 1 \Rightarrow 4p$ -orbital
 (ii) $n = 4, l = 0 \Rightarrow 4s$ -orbital
 (iii) $n = 3, l = 2 \Rightarrow 3d$ -orbital
 (iv) $n = 3, l = 1 \Rightarrow 3d$ -orbital

According to Aufbau principle, energies of above mentioned orbitals are in the order of

$$(iv) 3p < (ii) 4s < (iii) 3d < (i) 4p$$

28. The energy of an electron in a Bohr atom is expressed as

$$E_n = -\frac{kZ^2}{n^2} \quad \text{where, } k = \text{Constant}, \\ Z = \text{Atomic number}, \\ n = \text{Orbit number}$$

$$= -13.6 \text{ eV for H (} n = 1 \text{)}$$

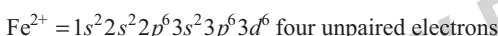
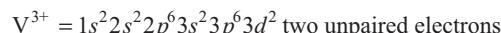
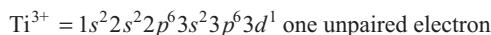
$$\text{when } n = 2, E_2 = \frac{-13.6}{2^2} \text{ eV} = -3.40 \text{ eV}$$

(n can have only integral value 1, 2, 3, ..., ∞)

29. The orbital angular momentum (L) = $\sqrt{l(l+1)} \frac{h}{2\pi}$
 $= \sqrt{6} \frac{h}{2\pi}$ ($l = 2$ for d -orbital)

30. Bohr first made use of quantum theory to explain the structure of atom and proposed that energy of electron in an atom is quantised.

31. $Mg^{2+} = 1s^2 2s^2 2p^6$ no unpaired electron



32. Expression for orbital angular momentum (L) is

$$L = \sqrt{l(l+1)} \frac{h}{2\pi} = 0 \quad \text{for } 2s\text{-electrons}$$

\therefore For s -orbital, $l = 0$.

33. Diffraction is property of wave, $E = mc^2$ determine energy of particle and $E = hv$ determine energy of photon. Interference phenomena is exhibited by both matter and waves.

34. X-rays is electrically neutral, not deflected in electric or magnetic fields.

35. $Cl(17) = 1s^2 2s^2 2p^6 3s^2 3p^5$

1	1	1
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The last, unpaired electron has, $n = 3, l = 1(p)$ and m can have any of the three value (-1, 0, +1).

36. $Cr(24) = \underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{Ar} 3d^5 4s^1$

The above configuration is exception to Aufbau's principle.

37. Fluorine, a halogen, is the most electronegative atom, has the electronic configuration $2s^2 2p^5$ (valence shell).

38. Option (b) is wrong representation according to aufbau principle. A high energy atomic orbital ($2p$) cannot be filled unless the low energy orbital ($2s$) is completely occupied.

$$39. \text{Transition energy } (\Delta E) = kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda}$$

$$\text{i.e.} \quad \Delta E \propto \frac{1}{\lambda}$$

$$40. E = \frac{hc}{\lambda} \Rightarrow \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = 2$$

$$41. \begin{array}{cccc} n & l & m & s \\ 3 & 2 & -3 & \frac{1}{2} \end{array}$$

This is the wrong set of quantum number because $|m|$ cannot be greater than l .

42. The wavelength order is

X-ray < ultraviolet < infrared < radio wave

43. When electron jumps to lower orbit photons are emitted while photons are absorbed when electron jumps to higher orbit. $1s$ -orbital is the lower most, electron in this orbital can absorb photons but cannot emit.

44. The valence shell configuration of Rubidium (Rb) is

$$[Kr] 5s^1 \quad n = 5, l = 0, m = 0, s = +\frac{1}{2} \quad \text{or} \quad -\frac{1}{2}$$

45. The principal quantum number ' n ' represents orbit number hence, determine the size of orbitals.

46. According to Pauli exclusion principle, an atomic orbital can accommodate at the most, two electrons, with opposite spins.

47. Given, ground state energy of hydrogen atom = -13.6 eV

$$\text{Energy of } He^+ = -3.4 \text{ eV}, Z = 2$$

$$\text{Energy of } He^+, E = -\frac{13.6 \times Z^2}{n^2} \text{ eV}$$

$$-3.4 \text{ eV} = \frac{-13.6 \times (2)^2}{n^2} \Rightarrow n = \sqrt{\frac{13.6 \times 4}{3.4}} \Rightarrow n = 4$$

Given, azimuthal quantum number (l) = 2 (d -subshell)

Magnetic quantum number (m) = 0

\therefore Angular nodes (l) = 2

Radial node = $n - l - 1 = 4 - 2 - 1 = 1$

$nl = 4d$ state

Hence, options (a), (c) are correct.

48. Both (a) and (d) are correct. The three electrons in the $2p$ -orbitals must have same spin, no matter up spin or down spin.

49. (a) $Cr = [Ar] 3d^5 4s^1$, an exception to aufbau principle.

- (b) For a given value of l, m can have any value from $(-l$ to $+l)$, so can have negative value.

- (c) Ag is in copper group with $d^{10} s^1$ configuration,
 i.e. 46 electrons are spin paired.

50. Isotones have same number of neutrons.

$^{32}Ge^{76}$, $^{33}As^{77}$ and $^{34}Se^{78}$ have same number (44) of neutrons, hence they are isotones.

38 Atomic Structure

51. Assertion is correct $\text{Be}(1s^2, 2s^2)$ has stable electronic configuration, removing an electron require more energy than the same for $\text{B}(2p^1)$. Reason is incorrect (Aufbau principle).

52. S_1 is spherically symmetrical state, i.e. it correspond to a s -orbital. Also, it has one radial node.

Number of radial nodes = $n - l - 1$

$$\Rightarrow n - 0 - 1 = 1 \Rightarrow n = 2 \text{ i.e. } S_1 = 2s\text{-orbital.}$$

53. Ground state energy of electron in H-atom (E_{H})

$$E_{\text{H}} = \frac{kZ^2}{n^2} = k \quad (Z = 1, n = 1)$$

For S_1 state of Li^{2+} ,

$$E = \frac{k(3)^2}{2^2} = \frac{9}{4} k \quad k = 2.25 k$$

54. In S_2 state, $E(\text{Li}^{2+}) = K$ (given)

$$K = \frac{qk}{n^2} \Rightarrow n = 3$$

Since, S_2 has one radial node.

$$3 - l - 1 = 1 \Rightarrow l = 1$$

55. In the wave function (ψ) expression for $1s$ -orbital of He^+ , there should be no angular part. Hence (iii) can't be true for ψ_{1s} of He^+ .

56. Correct : $2s$ orbital has one radial node.

No of radial node = $n - l - 1 = 2 - 0 - 1 = 1$

Also, when radial part of wave function (ψ) is plotted against ' r ', wave function changes its sign at node.

57. i is the correct expression of wave function for $1s$ -orbital of hydrogenic system.

58. A. Orbital angular momentum

$$(L) = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$$

i.e. L depends on azimuthal quantum number only.

- B. To describe a one electron wave function, three quantum numbers n, l and m are needed. Further to abide by Pauli exclusion principle, spin quantum number(s) is also needed.
- C. For shape, size and orientation, only n, l and m are needed.
- D. Probability density (ψ^2) can be determined if n, l and m are known.

59. $\text{Cr} = [\text{Ar}] 3d^5 4s^1$

60. 1 : 16

61. Heisenberg proposed uncertainty principle and de-Broglie proposed wave nature of electron.

62. orbital

63. $2p_x, 2p_y$ and $2p_z$ have different orientation in space.

64. Two electrons in same orbital must have opposite spin.

65. Very large mass of alpha particles than beta particles is responsible for less deflection in former case.

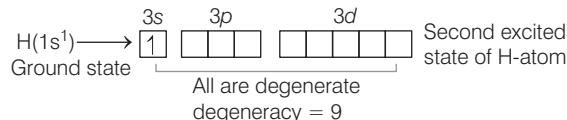
66. $3d_{x^2-y^2}$ orbital lies in XY -plane.

67. Aufbau principle.

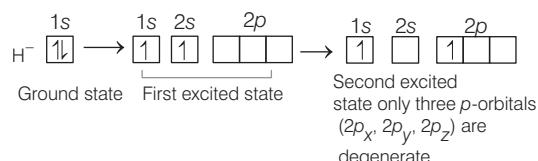
68. This is the wavelength of infrared radiation.

69. $\text{Cr} = 3d^5 4s^1$.

70. In an one electron (hydrogenic) system, all orbitals of a shell remains degenerate, hence in second excited state, the degeneracy of H-atom is nine



In case of many electrons system, different orbitals of a shell are non-degenerate. Hence,



71. **PLAN** This problem is based on concept of quantum number. Follow the following steps to solve this problem.
Write all possible orbitals having combination of same principal, azimuthal, magnetic and spin quantum number.

Then count the all possible electrons having given set of quantum numbers.

For $n = 4$, the total number of possible orbitals are

4s	4p	4d	4f
0	-1 0 +1	-2 -1 0 +1 +2	-3 -2 -1 0 +1 +2 +3

According to question $|m_l| = 1$, i.e. there are two possible values of m_l , i.e. +1 and -1 and one orbital can contain maximum two electrons one having $s = +\frac{1}{2}$ and other having $s = -\frac{1}{2}$.

So, total number of orbitals having $\{|m_l| = 1\} = 6$

Total number of electrons having

$$\{|m_l| = 1 \text{ and } m_s = -\frac{1}{2}\} = 6$$

72. **PLAN** $KE = \frac{1}{2}mv^2 = \frac{3}{2}RT$

$$\therefore m^2v^2 = 2mKE \quad \therefore mv = \sqrt{2mKE}$$

$$\lambda (\text{wavelength}) = \frac{h}{mv} = \frac{h}{\sqrt{2mKE}} \propto \frac{h}{\sqrt{2m(T)}}$$

where, $T = \text{Temperature in Kelvin}$

$$\lambda (\text{He at } -73^\circ\text{C} = 200 \text{ K}) = \frac{h}{\sqrt{2 \times 4 \times 200}}$$

$$\lambda (\text{Ne at } 727^\circ\text{C} = 1000 \text{ K}) = \frac{h}{\sqrt{2 \times 20 \times 1000}}$$

$$\therefore \frac{\lambda(\text{He})}{\lambda(\text{Ne})} = M = \sqrt{\frac{2 \times 20 \times 1000}{2 \times 4 \times 200}} = 5$$

Thus, $M = 5$

73. Energy of photon

$$= \frac{hc}{\lambda} J = \frac{hc}{e\lambda} eV = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.602 \times 10^{-19}} = 4.14 \text{ eV}$$

For photoelectric effect to occur, energy of incident photons must be greater than work function of metal. Hence, only Li, Na, K and Mg have work functions less than 4.14 V.

74. When $n = 3$, $l = 0, 1, 2$ i.e. there are $3s$, $3p$ and $3d$ -orbitals. If all these orbitals are completely occupied as



Total 18 electrons, 9 electrons with $s = +\frac{1}{2}$ and 9 with $s = -\frac{1}{2}$.

$$s = -\frac{1}{2}$$

Alternatively In any n th orbit, there can be a maximum of $2n^2$ electrons. Hence, when $n = 3$, number of maximum electrons = 18. Out of these 18 electrons, 9 can have spin $-\frac{1}{2}$ and remaining nine with spin $+\frac{1}{2}$.

75. (a) $mvr = \frac{nh}{2\pi}$

$$\Rightarrow v = \frac{nh}{2\pi mr} = \frac{6.625 \times 10^{-34}}{2 \times 3.14 \times 9.1 \times 10^{-31} \times 0.529 \times 10^{-10}} = 2.18 \times 10^6 \text{ ms}^{-1}$$

$$(b) \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6} = 0.33 \times 10^{-9} \text{ m}$$

(c) Orbital angular momentum

$$(L) = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{2} \left(\frac{h}{2\pi} \right)$$

[:: For p -orbital, $l = 1$]

76. (a) At radial node, ψ^2 must vanishes, i.e.

$$\psi_{2s}^2 = 0 = \left[\frac{1}{4\sqrt{2}\pi} \right]^2 \left(2 - \frac{r_0}{a_0} \right)^2 e^{-\frac{r_0}{a_0}}$$

$$\Rightarrow 2 - \frac{r_0}{a_0} = 0 \Rightarrow r_0 = 2a_0$$

$$(b) \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{100 \times 10^{-3} \times 100} = 6.625 \times 10^{-35} \text{ m}$$

$$= 6.625 \times 10^{-25} \text{ Å (negligibly small)}$$

77. The general Rydberg's equation is

$$\bar{v} = \frac{1}{\lambda} = R(Z)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} \propto Z^2$$

$$\Rightarrow \frac{\lambda(\text{He}^+)}{\lambda(\text{H})} = \frac{Z(\text{H})^2}{Z(\text{He}^+)^2} = \frac{1}{4}$$

$$\Rightarrow \lambda(\text{He}^+) = \frac{\lambda(\text{H})}{4} = \frac{91.2}{4} \text{ nm} = 22.8 \text{ nm}$$

78. Moles of $\text{H}_2 = \frac{pV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.0409$

$$\Rightarrow \text{Bond energy} = 0.0409 \times 436 = 17.84 \text{ kJ}$$

Number of H-atoms produced after dissociation

$$= 2 \times 0.0409 \times 6.023 \times 10^{23} = 4.93 \times 10^{22}$$

$$\text{Transition energy/atom} = 2.18 \times 10^{-18} \left(1 - \frac{1}{4} \right) \text{ J}$$

$$= \frac{3}{4} \times 2.18 \times 10^{-18} \text{ J}$$

\Rightarrow Total transition energy

$$= \frac{3}{4} \times 2.18 \times 10^{-18} \times 4.93 \times 10^{22} \text{ J}$$

$$= 80.60 \times 10^3 \text{ J} = 80.60 \text{ kJ}$$

Therefore, total energy required

$$= \text{dissociation energy} + \text{transition energy}$$

$$= (17.84 + 80.60) \text{ kJ} = 98.44 \text{ kJ}$$

79. If accelerated by potential difference of V volt, then

$$\frac{1}{2} mv^2 = eV$$

$$\Rightarrow \frac{p^2}{2m} = eV, \text{ here } p = \text{momentum } (mv)$$

$$\text{Using de-Broglie equation, } \lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}}$$

$$\Rightarrow 1.54 \times 10^{-10} = \frac{6.625 \times 10^{-34}}{(2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} V)^{1/2}}$$

Solving for V gives : $V = 63.56 \text{ V}$.

80. The work done in the given neutralisation process is

$$W = - \int_{a_0}^{\infty} F dr \text{ and } F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$\Rightarrow W = \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r} \right]_{a_0}^{\infty} = - \frac{e^2}{4\pi\epsilon_0 r} = \text{Total energy (E)}$$

Now, if ' V ' is magnitude of potential energy, then according to given information, kinetic energy (E_k) is $V/2$. Therefore,

$$E = -V + \frac{V}{2} \quad (\text{PE is always negative})$$

$$= -\frac{V}{2}$$

$$\Rightarrow V = -2E = \frac{-e^2}{2\pi\epsilon_0 r}$$

81. The Rydberg's equation for H-atom is

$$\frac{1}{\lambda} = \bar{v} \text{ (wave number)} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For Balmer series, $n_1 = 2$ and $n_2 = 3, 4, 5, \dots, \infty$

For shortest λ , n_2 has to be maximum, i.e. infinity. Then

$$\bar{v} = R_H \left(\frac{1}{4} - \frac{1}{\infty} \right) = \frac{R_H}{4} = \frac{1.09 \times 10^7}{4} = 2.725 \times 10^6 \text{ m}^{-1}$$

40 Atomic Structure

82. After breaking of the bond of I_2 molecule, the remaining energy would be distributed uniformly to iodine atoms as their kinetic energy, i.e.

$$E(\text{energy of photon}) = \text{Bond energy} + 2 \times \text{kinetic energy}$$

$$\Rightarrow \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}} = \frac{240 \times 10^3}{6.023 \times 10^{23}} + 2 \times E_k$$

$$\Rightarrow E_k = 2.16 \times 10^{20} \text{ J/atom}$$

83. The Bohr de-Broglie relationship is

$$2\pi r = n\lambda = \text{circumference of Bohr's orbit.}$$

i.e. number of complete waves formed in one complete revolution of electron in any Bohr orbit is equal to orbit number, hence three.

84. The expression for transition wavelength is given by Rydberg's equation :

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Equating the transition wavelengths of H-atom and He^+ ion,

$$R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_H \left(\frac{4}{2^2} - \frac{4}{4^2} \right)$$

Equating termwise on left to right of the above equation gives $n_1 = 1$ and $n_2 = 2$

85. For H-atom, the energy of a stationary orbit is determined as

$$E_n = -\frac{k}{n^2} \quad \text{where, } k = \text{constant } (2.18 \times 10^{-18} \text{ J})$$

$$\Rightarrow \Delta E (n=2 \text{ to } n=1) = k \left(1 - \frac{1}{4} \right) = \frac{3}{4} k$$

$$= 1.635 \times 10^{-18} \text{ J}$$

For a H-like species, energy of stationary orbit is determined as

$$E_n = -\frac{kZ^2}{n^2}$$

where, Z = atomic number

$$\Rightarrow \Delta E = kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{k}{hc} Z^2 \left(\frac{1}{1} - \frac{1}{4} \right) = R_H Z^2 \times \frac{3}{4}$$

$$\Rightarrow Z^2 = \frac{4}{3R_H \lambda} = \frac{4}{3 \times 1.097 \times 10^7 \times 3 \times 10^{-8}} = 4.05$$

$$\Rightarrow Z = 2 (\text{He}^+)$$

86. For H-like species, the energy of stationary orbit is expressed as

$$E(X) = Z^2 \times E(H)$$

$$\Rightarrow \text{For } He^+ (Z=2)$$

$$E = -\frac{4 \times 21.7 \times 10^{-19}}{n^2} \text{ J}$$

For longest wavelength transition from 3rd orbit, electron must jump to 4th orbit and the transition energy can be determined as

$$\Delta E = +4 \times 21.7 \times 10^{-19} \left(\frac{1}{9} - \frac{1}{16} \right) \text{ J} = 4.22 \times 10^{-19} \text{ J}$$

$$\text{Also, } \because \Delta E = \frac{hc}{\lambda}$$

$$\therefore \lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4.22 \times 10^{-19}} \text{ m}$$

$$= 471 \times 10^{-9} \text{ m} = 471 \text{ nm}$$

87. Ten, the given value of n and l correspond to $3d$ -orbital which has five fold degeneracy level.

88. The 2nd configuration is against Hund's rule of maximum multiplicity which states that the singly occupied degenerate atomic orbitals must have electrons of like spins.

89. The required transition is $n_1 = 2$ to $n_2 = \infty$ and corresponding transition energy is

$$\Delta E = 21.7 \times 10^{-12} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ erg}$$

$$= \frac{21.7}{4} \times 10^{-12} \text{ erg} = 5.425 \times 10^{-12} \text{ erg}$$

The longest wavelength that can cause above transition can be determined as :

$$\lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{5.425 \times 10^{-12} \times 10^{-7}}$$

$$= 3.66 \times 10^{-7} \text{ m} = 3.66 \times 10^{-5} \text{ cm}$$

90. Ionisation potential of H-like species

$$= E_1 = 2.17 \times 10^{-11} \text{ erg}$$

$$\Rightarrow \Delta E = 2.17 \times 10^{-11} \left(1 - \frac{1}{2^2} \right) \times 10^{-7} \text{ J}$$

$$= 1.6275 \times 10^{-18} \text{ J} \Rightarrow \lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{1.6275 \times 10^{-18}} \text{ m}$$

$$= 122 \times 10^{-9} \text{ m} = 1220 \text{ Å}$$

91. Transition energy $= [-2.41 - (-5.42)] \times 10^{-12} \text{ erg}$

$$= 3.01 \times 10^{-12} \text{ erg}$$

$$= 3.01 \times 10^{-19} \text{ J} \quad [\because 1 \text{ erg} = 10^{-7} \text{ J}]$$

$$\text{Also, } \Delta E = \frac{hc}{\lambda}$$

$$\Rightarrow \lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{3.01 \times 10^{-19}} \text{ m}$$

$$= 660 \times 10^{-9} \text{ m} = 660 \text{ nm}$$

3

Periodic Classification and Periodic Properties

Topic 1 History and Periodic Classification

Objective Questions I (Only one correct option)

- (c) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
 - (d) for transition elements the d -subshells are filled with electrons monotonically with increase in atomic number

Objective Question II

(One or more than one correct option)

4. The statements that is/are true for the long form of the periodic table is/are **(1988, 1M)**

 - (a) it reflects the sequence of filling the electrons in the order of sub-energy level s , p , d and f
 - (b) it helps to predict the stable valency states of the elements
 - (c) it reflects tends in physical and chemical properties of the elements
 - (d) it helps to predict the relative ionicity of the bond between any two elements

Topic 2 Periodic Properties

Objective Questions I (Only one correct option)

- 1.** The correct order of the ionic radii of O^{2-} , N^{3-} , F^- , Mg^{2+} , Na^+ and Al^{3+} is (2020 Main, 5 Sep II)

 - $N^{3-} < O^{2-} < F^- < Na^+ < Mg^{2+} < Al^{3+}$
 - $Al^{3+} < Na^+ < Mg^{2+} < O^{2-} < F^- < N^{3-}$
 - $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
 - $N^{3-} < F^- < O^{2-} < Mg^{2+} < Na^+ < Al^{3+}$

2. Within each pair of elements F and Cl, S and Se, and Li and Na, respectively, the elements that release more energy upon an electron gain are (2020 Main, 7 Jan II)

 - F, Se and Na
 - F, S and Li
 - Cl, S and Li
 - Cl, Se and Na

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- 6.** The correct order of the atomic radii of C, Cs, Al and S is
 (2019 Main, 11 Jan I)
 (a) C < S < Al < Cs (b) C < S < Cs < Al
 (c) S < C < Cs < Al (d) S < C < Al < Cs
- 7.** In general, the properties that decrease and increase down a group in the periodic table, respectively are
 (2019 Main, 9 Jan I)
 (a) electronegativity and atomic radius
 (b) electronegativity and electron gain enthalpy
 (c) electron gain enthalpy and electronegativity
 (d) atomic radius and electronegativity
- 8.** The ionic radii (in Å) of N³⁻, O²⁻ and F⁻ respectively are
 (2015 Main)
 (a) 1.36, 1.40 and 1.71 (b) 1.36, 1.71 and 1.40
 (c) 1.71, 1.40 and 1.36 (d) 1.71, 1.36 and 1.40
- 9.** Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?
 (a) CaSO₄ (b) BeSO₄ (2015 Main)
 (c) BaSO₄ (d) SrSO₄
- 10.** Which among the following is the most reactive?
 (a) Cl₂ (b) Br₂ (2015 Main)
 (c) I₂ (d) ICl
- 11.** Which one has the highest boiling point?
 (a) He (b) Ne (c) Kr (d) Xe
- 12.** The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na⁺ will be
 (2013 Main)
 (a) - 2.55 eV (b) - 5.1 eV
 (c) - 10.2 eV (d) + 2.55 eV
- 13.** Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar?
 (2013 Main)
 (a) Ca < S < Ba < Se < Ar (b) S < Se < Ca < Ba < Ar
 (c) Ba < Ca < Se < S < Ar (d) Ca < Ba < S < Se < Ar
- 14.** Identify the least stable ion amongst the following.
 (a) Li⁺ (b) Be⁻ (2002, 3M)
 (c) B⁻ (d) C⁻
- 15.** The set representing the correct order of first ionisation potential is
 (2001, 1M)
 (a) K > Na > Li (b) Be > Mg > Ca
 (c) B > C > N (d) Ge > Si > C
- 16.** The correct order of radii is
 (2000, 1M)
 (a) N < Be < B (b) F⁻ < O²⁻ < N³⁻
 (c) Na < Li < K (d) Fe³⁺ < Fe²⁺ < Fe⁴⁺
- 17.** The incorrect statement among the following. (1997(C), 1M)
 (a) The first ionisation potential of Al is less than the first ionisation potential of Mg
 (b) The second ionisation potential of Mg is greater than the second ionisation potential of Na
 (c) The first ionisation potential of Na is less than the first ionisation potential of Mg
 (d) The third ionisation potential of Mg is greater than third ionisation potential of Na
- 18.** Which of the following has the maximum number of unpaired electrons? (1996, 1M)
 (a) Mg²⁺ (b) Ti³⁺
 (c) V³⁺ (d) Fe²⁺
- 19.** Amongst the following elements (whose electronic configurations are given below), the one having the highest ionisation energy is (1990, 1M)
 (a) [Ne] 3s² 3p¹ (b) [Ne] 3s² 3p³
 (c) [Ne] 3s² 3p² (d) [Ar] 3d¹⁰ 4s² 4p³
- 20.** Which one of the following is the smallest in size? (1989, 1M)
 (a) N³⁻ (b) O²⁻
 (c) F⁻ (d) Na⁺
- 21.** The first ionisation potential of Na, Mg, Al and Si are in the order (1988, 1M)
 (a) Na < Mg > Al < Si (b) Na > Mg > Al > Si
 (c) Na < Mg < Al > Si (d) Na > Mg > Al < Si
- 22.** The electronegativity of the following elements increases in the order (1987, 1M)
 (a) C, N, Si, P (b) N, Si, C, P
 (c) Si, P, C, N (d) P, Si, N, C
- 23.** Atomic radii of fluorine and neon in Angstrom units are respectively given by (1987, 1M)
 (a) 0.72, 1.60 (b) 1.60, 1.60
 (c) 0.72, 0.72 (d) None of these
- 24.** The first ionisation potential in electron volts of nitrogen and oxygen atoms are respectively given by (1987, 1M)
 (a) 14.6, 13.6 (b) 13.6, 14.6
 (c) 13.6, 13.6 (d) 14.6, 14.6
- 25.** The hydration energy of Mg²⁺ is larger than that of (1984, 1M)
 (a) Al³⁺ (b) Na⁺
 (c) Be²⁺ (d) Mg³⁺
- 26.** The element with the highest first ionisation potential is (1982, 1M)
 (a) boron (b) carbon
 (c) nitrogen (d) oxygen
- 27.** The correct order of second ionisation potential of carbon, nitrogen, oxygen and fluorine is (1981, 1M)
 (a) C > N > O > F (b) O > N > F > C
 (c) O > F > N > C (d) F > O > N > C

Objective Questions II

(One or more than one correct option)

- 28.** The option(s) with only amphoteric oxides is(are) (2017 Adv.)
 (a) NO, B₂O₃, PbO, SnO₂ (b) Cr₂O₃, CrO, SnO, PbO
 (c) Cr₂O₃, BeO, SnO, SnO₂ (d) ZnO, Al₂O₃, PbO, PbO₂
- 29.** Ionic radii of (1999, 3M)
 (a) Ti⁴⁺ < Mn⁷⁺ (b) ³⁵Cl⁻ < ³⁷Cl⁻
 (c) K⁺ > Cl⁻ (d) P³⁺ > P⁵⁺

- 30.** The first ionisation potential of nitrogen and oxygen atoms are related as follows. (1989, 1M)
- The ionisation potential of oxygen is less than the ionisation potential of nitrogen
 - The ionisation potential of nitrogen is greater than the ionisation potential of oxygen
 - The two ionisation potential values are comparable
 - The difference between the two ionisation potential is too large
- 31.** Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because (1989, 1M)
- the hydration energy of sodium sulphate is more than its lattice energy
 - the lattice energy of barium sulphate is more than its hydration energy
 - the lattice energy has no role to play in solubility
 - the hydration energy of sodium sulphate is less than its lattice energy

Assertion and Reason

Read the following questions and answer as per the direction given below :

- Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
 - Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
 - Statement I is true; Statement II is false.
 - Statement I is false; Statement II is true.
- 32.** **Statement I** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
Statement II The reaction between nitrogen and oxygen requires high temperature. (2015 Main)
- 33.** **Statement I** Pb^{4+} compounds are stronger oxidising agents than Sn^{4+} compounds.
Statement II The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to ‘inert pair effect’. (2008, 3M)
- 34.** **Statement I** Band gap in germanium is small.
Statement II The energy spread of each germanium atomic energy level is infinitesimally small. (2007, 3M)
- 35.** **Statement I** The first ionisation energy of Be is greater than that of B.
Statement II 2p-orbital is lower in energy than 2s. (2000, (S), 1M)
- 36.** **Statement I** F-atom has a less negative electron affinity than Cl-atom.
Statement II Additional electrons are repelled more effectively by 3p-electrons in Cl-atom than by 2p-electrons in F-atom. (1998, 2M)

Numerical Answer Type Questions

- 37.** The 1st, 2nd and 3rd ionisation enthalpies, I_1 , I_2 , and I_3 , of four atoms with atomic numbers n , $n + 1$, $n + 2$, and $n + 3$, where $n < 10$, are tabulated below. What is the value of n ? (2020 Adv.)

Atomic number	Ionisation enthalpy (kJ/mol)		
	I_1	I_2	I_3
n	1681	3374	6050
$n + 1$	2081	3952	6122
$n + 2$	496	4562	6910
$n + 3$	738	1451	7733

Fill in the Blanks

- 38.** Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+} . The stability of the lower oxidation state is due to (1997, 1M)
- 39.** Ca^{2+} has a smaller ionic radius than K^+ because it has (1993, 1M)
- 40.** On Mulliken scale, the average of ionisation potential and electron affinity is known as (1985, 1M)
- 41.** The energy released when an electron is added to a neutral gaseous atom is called (1982, 1M)

True/False

- 42.** The basic nature of the hydroxides of group 13 (III B) decreases progressively down the group. (1993, 1M)
- 43.** The decreasing order of electron affinity of F, Cl, Br is $\text{F} > \text{Cl} > \text{Br}$. (1993, 1M)
- 44.** In group IA of alkali metals, the ionisation potential decreases down the group. Therefore, lithium is a poor reducing agent. (1987, 1M)
- 45.** The softness of group IA metals increases down the group with increasing atomic number. (1986, 1M)

Subjective Questions

- 46.** Arrange the following ions in order of their increasing radii Li^+ , Mg^{2+} , K^+ , Al^{3+} . (1997, 1M)
- 47.** Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation. (1996, 2M)
- 48.** Arrange the following as stated :
 “Increasing order of ionic size” N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+} (1991, 1M)
- 49.** Explain the following :
 “The first ionisation energy of carbon atom is greater than that of boron atom whereas, the reverse is true for the second ionisation energy.” (1989, 2M)
- 50.** Arrange the following in the order of their increasing size: Cl^- , S^{2-} , Ca^{2+} , Ar (1986, 1M)
- 51.** Arrange the following in order of their
 - decreasing ionic size Mg^{2+} , O^{2-} , Na^+ , F^-
 - increasing first ionisation energy Mg, Al, Si, Na
 - increasing bond length F_2 , N_2 , Cl_2 , O_2 (1985, 3M)

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Answers

Topic 1

1. (b) 2. (c) 3. (d) 4. (b,c,d)

Topic 2

1. (c) 2. (c) 3. (b) 4. (d)
5. (d) 6. (a) 7. (a) 8. (c)
9. (b) 10. (d) 11. (d) 12. (b)
13. (c) 14. (b) 15. (b) 16. (b)
17. (b) 18. (d) 19. (b) 20. (d)

21. (a) 22. (c) 23. (a) 24. (a)
25. (b) 26. (c) 27. (c) 28. (a,b)
29. (d) 30. (a,b,c) 31. (a,b) 32. (a)
33. (c) 34. (c) 35. (c) 36. (c)
37. (9) 38. (inert pair effect)
39. (higher effective nuclear charge)
40. (electronegativity) 41. (electron affinity)
42. F 43. F 44. F 45. T

Hints & Solutions

Topic 1 History and Periodic Classification

1. Atomic number (119) = $\begin{array}{ccc} 1 & 1 & 9 \\ \text{un} & \text{un} & \text{en} \end{array}$

So, symbol of the element = uue

Name of the element = ununennium

It is expected to be s-block element an alkali metal and the first element in eighth period. It is the lightest element that has not yet been synthesised.

2. The element with $Z = 120$ will be an alkaline earth metal. Recently, oganesson (Og) with atomic number 118 is named by IUPAC is a noble gas and placed just two place before 120. So, the general electronic configuration is represented as [noble gas] ns^2 and element with $Z = 120$ exist as an alkaline earth metal.

3. (a) **Correct statement** According to Moseley's law, the properties of elements are the periodic function of their atomic numbers.
(b) **Correct statement** The whole s-block, d-block, f-block and heavier p-block elements are metal.
(c) **Correct statement** Trend is not regular, Be has higher first ionisation energy than B, nitrogen has higher first ionisation energy than oxygen.
(d) **Incorrect statement** d-subshells are not filled monotonically, regularity break at chromium and copper.
4. (a) **Incorrect** Electrons are not filled in sub-energy levels s, p, d and f in the same sequence.
(b) **Correct** Number of valence shell electrons usually determine the stable valency state of an element.
(c) **Correct** Physical and chemical properties of elements are periodic function of atomic number which is the basis of modern, long form of periodic table.
(d) **Correct** Relative ionicity of the bond between any two elements is function of electronegativity difference of the bonded atoms which in turn has periodic trend in long form of periodic table.

Topic 2 Periodic Properties

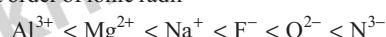
1. Size of species $\propto \frac{1}{\text{Nuclear charge}}$

Iso-electronic species are those atoms or ions which has the same number of electrons.

Size of species decreases with increasing protons.

More is effective nuclear charge (Z_{eff}) lesser will be ionic size.

Correct order of ionic radii



2. The first electron gain enthalpy is exothermic (or negative). Generally, electron gain enthalpy becomes less exothermic (or less negative) when comparing elements of a group from top to bottom.

Therefore, electron gain enthalpy of S > Se and Li > Na.

But there are some exceptions to this.

One of them is the case of a group 17 elements where electron gain is most negative for Cl instead of F, due to extra small size of fluorine.

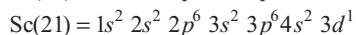
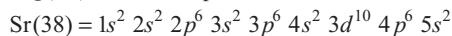
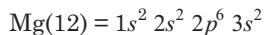
∴ Upon an electron gain, energy releases in the order :



3. The group number, number of valence electrons and valency of an element with atomic number 15 are 15, 5 and 3 respectively. Modern periodic table is based on the atomic number. Number of valence electrons present in an atom decides the group number. Electronic configuration of element having atomic number 15 = $1s^2 2s^2 2p^6 3s^2 \underbrace{3p^3}_{\text{Valence electrons}}$

As five electrons are present in valence shell, its group number is 15. Valency of element having atomic number 15 is +3 ($8 - 5 = 3$).

4. The electronic configuration of given elements are as follows :
 $\text{K}(19) = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$



First ionisation enthalpy (IE) of K is lowest among the given options. Here, the energy required to remove an electron from $4s^1$ is least as only one electron is present in the outermost shell. IE (I) is comparatively high for Mg and Sr and two electrons (fully-filled) are placed in s -orbital. Second ionisation enthalpy of K is highest among the given options.

Now, removal of an electron occur from p^6 (fully-filled). So, high energy is required to remove the electron. From the above discussion, it can be concluded that $(\text{IE}_2 - \text{IE}_1)$ value is maximum for K (potassium).

5. The electronegativity values of given elements on the Pauling scale can be shown as follows:

Period No.	Group 13	Group 14	Group 15	Group 16
3	Al (1.5)	Si (1.8)	P (2.1)	S (2.5)
4	Ga (1.6)	Ge (1.8)		Se (2.4)
5				Te (2.01)

On moving from left to right across a period, i.e. from Ga to Se, the effective nuclear charge increases and size decreases.

As a result, the value of electronegativity increases due to increase in the attraction between the outer electrons and the nucleus. Whereas on moving down the group, (i.e. from Se to Te), the atomic size increases.

As a result, the force of attraction between the outer electron and the nucleus decreases. Hence, the electronegativity decreases.

6. Element	Period No.	Group No.
C	2nd	14
{ Al	3rd	13 } Along the period atomic radius
S	3rd	16 } decreases, so, radii : Al > S.
Cs	6th	1

With the addition of a new shell, period number as well as atomic radius increases. It is because of the successive addition of one extra shell of electrons. So, the order of the atomic radii of the given elements will be: C < S < Al < Cs

7. The summary of variation of periodic properties is given in table below:

S.No.	Periodic property	Variation	
		Along a period	Along a group
1.	Atomic radius	Decreases	Increases
2.	Electron gain enthalpy	Increases	Decreases
3.	Electronegativity	Increases	Decreases

Thus, electronegativity decreases and atomic radius increases down a group in the periodic table.

8. Number of electrons in $\text{N}^{3-} = 7 + 3 = 10$

Number of electrons in $\text{O}^{2-} = 8 + 2 = 10$

Number of electrons in $\text{F}^- = 9 + 1 = 10$

Since, all the three species have each 10 electrons, hence they are isoelectronic species.

It is considered that, in case of isoelectronic species as the negative charge increases, ionic radii increases and therefore the value of ionic radii

$$\text{N}^{3-} = 1.71 \quad (\text{highest among the three})$$

$$\text{O}^{2-} = 1.40 \quad \text{F}^- = 1.36 \quad (\text{lowest among the three})$$

Time Saving Technique There is no need to mug up the radius values for different ions. This particular question can be solved through following time saving.

Trick The charges on the ions indicate the size as $\text{N}^{3-} > \text{O}^{2-} > \text{F}^-$. Thus, you have to look for the option in which the above trend is followed. Option(c) is the only one in which this trend is followed. Hence, it is the correct answer.

9. As we move down the group, size of metal increases. Be has lower size while SO_4^{2-} has bigger size, that's why BeSO_4 breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases.

On the other hand, rest of the metals, i.e Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time Saving Technique In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy. Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence, BeSO_4 is the right response.

10. Cl_2 , Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive, whereas, I and Cl have different electronegativities and bond between them are polarised and reactive. Therefore, interhalogen compounds are more reactive.

Time Saving Technique In this type of question of halogen, only go through the polarity of the molecules. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

11. As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe.

Therefore, more amount of energy is required to break these forces, thus boiling point also increases from He and Xe.

12. $\text{Na} \longrightarrow \text{Na}^+ + e^-$ First IE
 $\text{Na}^+ + e^- \longrightarrow \text{Na}$

Electron gain enthalpy of Na^+ is reverse of (IE)
 Because reaction is reverse so $\Delta H(\text{eq}) = -5.1 \text{ eV}$

13. Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the periodic table is as

Group No. 2	16	18
Ca	S	Ar
Ba	Se	

Thus, the order of increasing ΔH_{IE_1} is $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$

14. Be^- is the least stable ion, $\text{Be} (1s^2 2s^2)$ has stable electronic configuration, addition of electron decreases stability.

15. In a group, ionisation energy decreases down the group

$$\text{Be} > \text{Mg} > \text{Ca}$$

16. Among isoelectronic species, greater the negative charge, greater the ionic size, hence $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$.

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17. (a) **Correct statement** In a period, element of 2nd group has higher first ionisation potential than element of group 13.
 (b) **Incorrect statement** Mg^+ require less energy for further ionisation than Na^+ because of noble gas configuration of Na^+ .
 (c) **Correct statement** Ionisation energy increases from left to right in a period.

18. $Mg^{2+} = 1s^2 2s^2 2p^6$ = no unpaired electron
 $Ti^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ = one unpaired electron
 $V^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ = two unpaired electrons
 $Fe^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ = four unpaired electrons

19. $[Ne] 3s^2 3p^3$ has highest ionisation energy, periodic trend.

20. Among isoelectronic species, the relation in size is cation < neutral < anion
 Hence, Na^+ has smallest size.

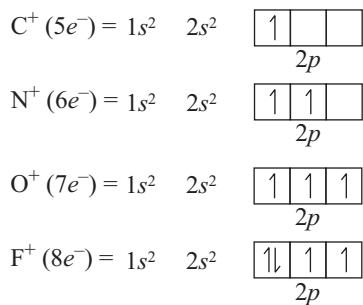
21. Ionisation energy increases from left to right in a period. However, exception occur between group 2 and group 13 elements on account of stability of electronic configuration of valence shell.



\Rightarrow The desired order is $Na < Mg > Al < Si$

22. Electronegativity increases from left to right in a period and decreases from top to bottom in a group. Variation is more rapid in group than in a period, hence the desired order is
 Electronegativity : $Si < P < C < N$

23. Atomic radius of noble gases are greater than halogens of same period, hence (a) is the correct answer.
24. First ionisation energy of oxygen is less than that of nitrogen on the ground of stability of valence shell configuration, hence (a) is the correct answer.
25. Hydration energy depends on charge of ion and ionic radius. Higher the charge, greater the hydration energy. On the other hand, smaller the size, greater the hydration energy. Charge is considered first for comparison. Hence, Mg^{2+} has higher hydration energy than Na^+ .
26. Nitrogen has highest ionisation potential due to exceptional stability of its valence shell configuration mentioned in question 21.
27. For second ionisation potential, electron will have to be removed from valence shell of the following ions:



In general, ionisation energy increases from left to right in a period. However, exception occur between adjacent atoms in a period, greater amount energy is required for removal of electron from completely half-filled or completely filled orbital than the same for adjacent atom with either less than completely half-filled or less than completely filled orbital. Therefore, ionisation potential of O^+ is greater than that of F^+ . Also ionisation potential of N^+ is greater than C^+ but less than both O^+ and F^+ (periodic trend). Hence, overall order is 2nd IP : $O > F > N > C$.

28. (c) is incorrect because NO is neutral oxide.
 (d) is incorrect because CrO is basic oxide.
29. (a) $Ti^{4+} > Mn^{7+}$ is the correct order of size due to lower positive charge on Ti^{4+} .
 (b) $^{37}Cl^- = ^{37}Cl^{3-}$: Isotopes with same charge have same size because isotopes differ in compositions of nuclei which do not affect the atomic/ionic radius.
 (c) $K^+ < Cl^-$ is the correct order. Among isoelectronic species, anion has greater size than cation.
 (d) $P^{3+} > P^{5+}$ is the correct order. For the same elements, lower the positive charge, larger the ions.
30. (a) and (b) are infact the same statements and both are correct. N has slightly greater ionisation energy than oxygen which is against periodic trend. This exception is due to completely half-filled ($2p^3$) orbital in nitrogen that makes ionisation slightly difficult than oxygen.
 (c) Also correct : Although N has greater first ionisation potential than oxygen, two values of ionisation potentials are comparable since they are adjacent in a period, i.e. electrons are removed from same orbit during ionisation.
 (d) Incorrect – opposite to (c). of the bonded atoms which in turn has periodic trend in long form of periodic table.
31. (a) **Correct** For greater solubility, hydration energy must be greater than lattice energy.
 (b) **Correct** Greater lattice energy discourage dissolution of a salt.
 (c) **Incorrect** When a salt dissolve, energy is required to break the lattice, which comes from hydration process.
 (d) **Incorrect** Explained in (A).
32. Statement I and II are true and Statement II is the correct explanation of statement I.
33. Statement I is true. Stronger oxidising agent is one which itself can easily be reduced. Pb^{4+} is unstable, due to inert pair effect, can easily be reduced to stable Pb^{2+} , hence a stronger oxidising agent than Sn^{4+} .
 Statement II is false. Due to inert pair effect, the higher oxidation states of group 14 elements becomes less stable for heavier member.
34. Both statements I and II are true and Statement II is the correct explanation of statement I.
35. Statement I is true Be has higher first ionisation energy than B which is against periodic trend.
 Statement II is false 2s-orbital is lower in energy than 2p, Aufbau's principle.

- 36.** Statement I is true; Statement II is false.

F atom has slightly lower affinity for the electron than chlorine. It is due to the reason that additional electrons are repelled more effectively by $2p$ -electrons in F than by $3p$ -electrons in Cl-atom.

- 37.** By observing the values of different ionisation energies, I_1 , I_2 and I_3 for atomic number ($n + 2$), it is observed that there is very large difference between the second ionisation energy and first ionisation energy ($I_2 \gg I_1$).

This indicates that number of valence shell electrons is 1 and atomic number ($n + 2$) should be an alkali metal.

Also for atomic number ($n + 3$), $I_3 \gg I_2$.

This indicates that it will be an alkaline earth metal which suggests that atomic number ($n + 1$) should be a noble gas and atomic number (n) should belong to halogen family. Since, $n < 10$; hence, $n = 9$ (F atom)

- 38.** Inert pair effect-favours lower oxidation state.

- 39.** Higher effective nuclear charge due to greater p/e ratio.

40. Electronegativity = $\frac{IP + EA}{2}$ (Mulliken formula)

- 41.** Electron affinity-definition.

- 42.** Basic nature of hydroxides increases down a group.

- 43.** Cl has maximum electron affinity, hence the correct order is Cl > F > Br

- 44.** Ionisation potential decreases down the group but this is not the only criteria of reducing power.

- 45.** In a group, size increases from top to bottom.

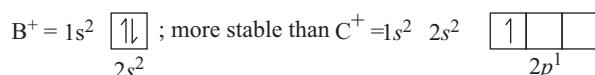
- 46.** $Li^+ < Al^{3+} < Mg^{2+} < K^+$. Size decreases from left to right in a period and it increases from top to bottom in a group. Variation is more pronounced in group than in period.

- 47.** $Zn = 3d^{10}4s^2$, $Cu = 3d^{10}4s^1$

The first ionisation energy is greater for Zn but reverse is true for 2nd ionisation energy.

- 48.** Ionic size $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

- 49.** The first ionisation energy of carbon is greater than the same of boron as predicted from periodic trend. However, for 2nd



ionisation trend is reversed due to stability of completely filled $2s$ -orbital of B^+ :

- 50.** Size $Ca^{2+} < Ar < Cl^- < S^{2-}$.

- 51.** (i) Mg^{2+} , O^{2-} , Na^+ and F^- are all isoelectronic, has 10 electrons each. Among isoelectronic species, the order of size is cation < neutral < anion.

Also, between cations, higher the charge, smaller the size and between anions, greater the negative charge, larger the size. Therefore, the decreasing order of ionic radii : $O^{2-} > F^- > Na^+ > Mg^{2+}$

- (ii) First ionisation energy increases from left to right in a period. However, exception occur between group 2 and 13 and group 15 and 16 where trend is reversed on the grounds of stability of completely filled and completely half-filled orbitals. Therefore, Ionisation energy (1st) : $Na < Al < Mg < Si$

- (iii) If the atoms are from same period, bond length is inversely proportional to bond order. In a group, bond length is related directly to atomic radius.

Therefore,

bond length $N_2 < O_2 < F_2 < Cl_2$

4

Chemical Bonding

Topic 1 Preliminary Concepts of Electrovalent and Covalent Bonding

Objective Questions I (Only one correct option)

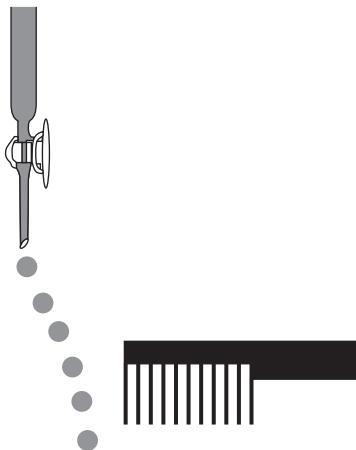
1. The isoelectronic set of ions is (2019 Main, 10 April I)
(a) F^- , Li^+ , Na^+ and Mg^{2+}
(b) N^{3-} , Li^+ , Mg^{2+} and O^{2-}
(c) Li^+ , Na^+ , O^{2-} and F^-
(d) N^{3-} , O^{2-} , F^- and Na^+
2. Which of the following compounds contain(s) no covalent bond(s)?
KCl, PH_3 , O_2 , B_2H_6 , H_2SO_4 (2018 Main)
(a) KCl, B_2H_6 , PH_3 (b) KCl, H_2SO_4
(c) KCl (d) KCl, B_2H_6
3. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is (2015 Main)
(a) ion-ion interaction (b) ion-dipole interaction
(c) London force (d) hydrogen bond
4. The nodal plane in the π -bond of ethene is located in
(a) the molecular plane (2002, 3M)
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon σ -bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ -bond
5. Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is (2000, 1M)
(a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight
6. Arrange the following compounds in order of increasing dipole moment, toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV) (1996, 1M)
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III

7. The number and type of bonds between two carbon atoms in CaC_2 are (1996, 1M)
(a) one sigma (σ) and one pi (π) bonds
(b) one sigma (σ) and two pi (π) bonds
(c) one sigma (σ) and one half pi (π) bonds
(d) one sigma (σ) bond
8. The molecule which has zero dipole moment is (1989, 1M)
(a) CH_2Cl_2 (b) BF_3 (c) NF_3 (d) ClO_2
9. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be (1980, 1M)
(a) X^+Y^- (b) X^-Y^+ (c) $X — Y$ (d) $X \rightarrow Y$
10. Which of the following compound is covalent? (1980, 1M)
(a) H_2 (b) CaO
(c) KCl (d) Na_2S
11. The total number of electrons that take part in forming the bonds in N_2 is (1980, 1M)
(a) 2 (b) 4 (c) 6 (d) 10
12. The compound which contains both ionic and covalent bonds is (1979, 1M)
(a) CH_4 (b) H_2 (c) KCN (d) KCl
- ### Objective Questions II
- (One or more than one correct option)
13. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature.
(a) SO_2 , $\text{C}_6\text{H}_5\text{Cl}$, H_2Se , BrF_5 (2019 Adv.)
(b) BeCl_2 , CO_2 , BCl_3 , CHCl_3
(c) NO_2 , NH_3 , POCl_3 , CH_3Cl
(d) BF_3 , O_3 , SF_6 , XeF_6
14. Dipole moment is shown by (1986, 1M)
(a) 1, 4-dichlorobenzene (b) *cis*-1, 2-dichloroethene
(c) *trans*-1, 2-dichloroethene (d) *trans*-1, 2-dichloro-2-pentene

Numerical Answer Type Questions

15. Consider the following compounds in the liquid form : O₂, HF, H₂O, NH₃, H₂O₂, CCl₄, CHCl₃, C₆H₆, C₆H₅Cl

When a charged comb is brought near their flowing stream, how many of them show deflection as per the following figure? (2020 Adv.)



16. Among the species given below, the total number of diamagnetic species is _____

H atom, NO₂ monomer, O₂⁻ (superoxide), dimeric sulphur in vapour phase, Mn₃O₄, (NH₄)₂[FeCl₄], (NH₄)₂[NiCl₄], K₂MnO₄, K₂CrO₄ (2018 Adv.)

Assertion and Reason

Read the following questions and answer as per the direction given below:

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
- (c) Statement I is correct; Statement II is incorrect
- (d) Statement I is incorrect; Statement II is correct

17. Statement I LiCl is predominantly a covalent compound.

Statement II Electronegativity difference between Li and Cl is too small. (1998, 2M)

Fill in the Blank

18. There are π -bonds in a nitrogen molecule. (1982, 1M)

True/False

19. All molecules with polar bonds have dipole moment. (1985, 1/2 M)

20. Linear overlapping of two atomic *p*-orbitals leads to a sigma bond. (1983, 1M)

Subjective Questions

21. Arrange the following ions in order of their increasing radii: Li⁺, Mg²⁺, K⁺, Al³⁺. (1997, 1M)

22. Between Na⁺ and Ag⁺, which is stronger Lewis acid and why? (1997, 3M)

23. In the reaction, $\Gamma^- + I_2 \longrightarrow I_3^-$, which is the Lewis acid? (1997, 1M)

24. Explain the difference in the nature of bonding in LiF and LiI. (1996, 2M)

25. The dipole moment of KCl is 3.336×10^{-29} C-m which indicates that it is a highly polar molecule. The interatomic distance between K⁺ and Cl⁻ in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. (1993, 2M)

26. Give reasons in two or three sentences only for the following : "Hydrogen peroxide acts as an oxidising as well as a reducing agent." (1992, 1M)

27. State four major physical properties that can be used to distinguish between covalent and ionic compounds. Mention the distinguishing features in each case. (1978, 2M)

Topic 2 VBT, Hybridisation and VSEPR Theory

Objective Questions I (Only one correct option)

1. The correct statements among I to III are :

- I. Valence bond theory cannot explain the color exhibited by transition metal complexes.
 - II. Valence bond theory can predict quantitatively the magnetic properties of transition metal complexes.
 - III. Valence bond theory cannot distinguish ligands as weak and strong field ones. (2019 Main, 9 April II)
- (a) II and III only
 - (b) I, II and III
 - (c) I and II only
 - (d) I and III only

2. The correct statement about ICl₅ and ICl₄⁻ is

(2019 Main, 8 April II)

- (a) ICl₅ is square pyramidal and ICl₄⁻ is tetrahedral
- (b) ICl₅ is square pyramidal and ICl₄⁻ is square planar
- (c) Both are isostructural
- (d) ICl₅ is trigonal bipyramidal and ICl₄⁻ is tetrahedral

3. The ion that has $sp^3 d^2$ -hybridisation for the central atom, is

(2019 Main, 8 April II)

- (a) [ICl₂]⁻
- (b) [BrF₂]⁻
- (c) [ICl₄]⁻
- (d) [IF₆]⁻

50 Chemical Bonding

4. The size of the iso-electronic species Cl^- , Ar and Ca^{2+} is affected by (2019 Main, 8 April I)
- azimuthal quantum number of valence shell
 - electron-electron interaction in the outer orbitals
 - principal quantum number of valence shell
 - nuclear charge
5. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? (2019 Main, 9 Jan II)
- $\text{O}_2 \rightarrow \text{O}_2^+$
 - $\text{N}_2 \rightarrow \text{N}_2^+$
 - $\text{O}_2 \rightarrow \text{O}_2^{2-}$
 - $\text{NO} \rightarrow \text{NO}^+$
6. Total number of lone pair of electron in I_3^- ion is (2018 Main)
- 3
 - 6
 - 9
 - 12
7. The group having isoelectronic species is (2017 Main)
- O^{2-} , F^- , Na^+ , Mg^{2+}
 - O^- , F^- , Na , Mg^+
 - O^{2-} , F^- , Na , Mg^{2+}
 - O^- , F^- , Na^+ , Mg^{2+}
8. The correct statement for the molecule, CsI_3 is (2014 Main)
- it is a covalent molecule
 - it contains Cs^+ and I_3^- ions
 - it contains Cs^{3+} and I^- ions
 - it contains Cs^+ , I^- and lattice I_2 molecule
9. The species having pyramidal shape is (2010)
- SO_3
 - BrF_3
 - SiO_3^{2-}
 - OSF_2
10. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is (2010)
- 1 and diamagnetic
 - 0 and diamagnetic
 - 1 and paramagnetic
 - 0 and paramagnetic
11. The species having bond order different from that in CO is (2007, 3M)
- NO^-
 - NO^+
 - CN^-
 - N_2
12. Among the following, the paramagnetic compound is (2007, 3M)
- Na_2O_2
 - O_3
 - N_2O
 - KO_2
13. Which of the following contains maximum number of lone pairs on the central atom? (2005, 1M)
- ClO_3^-
 - XeF_4
 - SF_4
 - I_3^-
14. Number of lone pair(s) in XeOF_4 is/are (2004, 1M)
- 0
 - 1
 - 2
 - 3
15. Which of the following are isoelectronic and isostructural ? NO_3^- , CO_3^{2-} , ClO_3^- , SO_3 (2003, 1M)
- NO_3^- , CO_3^{2-}
 - SO_3 , NO_3^-
 - ClO_3^- , CO_3^{2-}
 - CO_3^{2-} , SO_3
16. Among the following, the molecule with the highest dipole moment is (2003, 1M)
- CH_3Cl
 - CH_2Cl_2
 - CHCl_3
 - CCl_4
17. Which of the following molecular species has unpaired electron (s)? (2002, 3M)
- N_2
 - F_2
 - O_2^-
 - O_2^{2-}
18. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 . (2002, 3M)
- N : tetrahedral, sp^3 ; B: tetrahedral, sp^3
 - N : pyramidal, sp^3 ; B: pyramidal, sp^3
 - N: pyramidal, sp^3 ; B: planar, sp^2
 - N: pyramidal, sp^3 ; B: tetrahedral, sp^3
19. The correct order of hybridisation of the central atom in the following species NH_3 , $[\text{PtCl}_4]^{2-}$, PCl_5 and BCl_3 is (2001, 1M)
- dsp^2 , dsp^3 , sp^2 and sp^3
 - sp^3 , dsp^2 , sp^3 and sp^2
 - dsp^2 , sp^3 and dsp^3
 - dsp^2 , sp^3 , sp^2 and dsp^3
20. The common features among the species CN^- , CO and NO^+ are (2001, 1M)
- bond order three and isoelectronic
 - bond order three and weak field ligands
 - bond order two and acceptors
 - isoelectronic and weak field ligands
21. The hybridisation of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are (2000, 1M)
- sp , sp^3 and sp^2 respectively
 - sp , sp^2 and sp^3 respectively
 - sp^2 , sp and sp^3 respectively
 - sp^2 , sp^3 and sp respectively
22. In the compound $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$, the C_2-C_3 bonds is of (1999, 2M)
- $sp-sp^2$
 - sp^3-sp^3
 - $sp-sp^3$
 - sp^2-sp^3
23. The geometry of H_2S and its dipole moment are (1999, 2M)
- angular and non-zero
 - angular and zero
 - linear and non-zero
 - linear and zero
24. The geometry and the type of hybrid orbital present about the central atom in BF_3 is (1998, 2M)
- linear, sp
 - trigonal planar, sp^2
 - tetrahedral, sp^3
 - pyramidal, sp^3
25. Which one of the following compounds has sp^2 - hybridisation? (1997, 1M)
- CO_2
 - SO_2
 - N_2O
 - CO
26. Among KO_2 , AlO_2^- , BaO_2 and NO_2^+ , unpaired electron is present in (1997 C, 1M)
- NO_2^+ and BaO_2
 - KO_2 and AlO_2^-
 - Only KO_2
 - Only BaO_2
27. The cyanide ion CN^- and N_2 are isoelectronic, but in contrast to CN^- , N_2 is chemically inert because of (1997 C, 1M)
- low bond energy
 - absence of bond polarity
 - unsymmetrical electron distribution
 - presence of more number of electron in bonding orbitals

28. Among the following species, identify the isostructural pairs.

NF_3 , NO_3^- , BF_3 , H_3O^+ , N_3H (1996, 1M)

- (a) $[\text{NF}_3, \text{NO}_3^-]$ and $[\text{BF}_3, \text{H}_3\text{O}^+]$
- (b) $[\text{NF}_3, \text{N}_3\text{H}]$ and $[\text{NO}_3^-, \text{BF}_3]$
- (c) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{NO}_3^-, \text{BF}_3]$
- (d) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{N}_3\text{H}, \text{BF}_3]$

29. Which one of the following molecules is planar? (1996, 1M)

- (a) NF_3
- (b) NCl_3
- (c) PH_3
- (d) BF_3

30. The maximum possible number of hydrogen bonds a water molecule can form is (1992, 1M)

- (a) 2
- (b) 4
- (c) 3
- (d) 1

31. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is (1992, 1M)

- (a) sp^3
- (b) sp^2
- (c) sp
- (d) None of these

32. The molecule which has pyramidal shape is (1989, 1M)

- (a) PCl_3
- (b) SO_3
- (c) CO_3^{2-}
- (d) NO_3^-

33. Which of the following is paramagnetic? (1989, 1M)

- (a) O_2^-
- (b) CN^-
- (c) CO
- (d) NO^+

34. The Cl—C—Cl angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane respectively will be about (1988, 1M)

- (a) 120° and 109.5°
- (b) 90° and 109.5°
- (c) 109° and 90°
- (d) 109.5° and 120°

35. The molecule that has linear structure is (1988, 1M)

- (a) CO_2
- (b) NO_2
- (c) SO_2
- (d) SiO_2

36. The species in which the central atom uses sp^2 -hybrid orbitals in its bonding is (1988, 1M)

- (a) PH_3
- (b) NH_3
- (c) CH_3^+
- (d) SbH_3

37. Of the following compounds, which will have a zero dipole moment? (1987, 1M)

- (a) 1, 1-dichloroethylene
- (b) *cis*-1, 2-dichloroethylene
- (c) *trans*-1, 2-dichloroethylene
- (d) None of the above

38. The hybridisation of sulphur in sulphur dioxide is (1986, 1M)

- (a) sp
- (b) sp^3
- (c) sp^2
- (d) dsp^2

39. The bond between two identical non-metal atoms has a pair of electrons (1986, 1M)

- (a) unequally shared between the two
- (b) transferred fully from one atom to another
- (c) with identical spins
- (d) equally shared between them

40. On hybridisation of one s and one p -orbital we get

- (a) two mutually perpendicular orbitals (1984, 1M)
- (b) two orbitals at 180°
- (c) four orbitals directed tetrahedrally
- (d) three orbitals in a plane

41. Carbon tetrachloride has no net dipole moment because of

- (a) its planar structure (1983, 1M)
- (b) its regular tetrahedral structure
- (c) similar sizes of carbon and chlorine atoms
- (d) similar electron affinities of carbon and chlorine

42. The ion that is isoelectronic with CO is (1982, 1M)

- (a) CN^-
- (b) O_2^+
- (c) O_2^-
- (d) N_2^+

43. Among the following, the linear molecule is (1982, 1M)

- (a) CO_2
- (b) NO_2
- (c) SO_2
- (d) ClO_2

44. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are

- (a) pure p (1981, 1M)
- (b) sp -hybridised
- (c) sp^2 -hybridised
- (d) sp^3 -hybridised

Objective Questions II

(One or more than one correct option)

45. The molecules that will have dipole moment are (1992, 1M)

- (a) 2, 2-dimethyl propane
- (b) *trans*-2-pentene
- (c) *cis*-3-hexene
- (d) 2,2,3,3-tetramethyl butane

46. Which of the following have identical bond order?

- (a) CN^-
- (b) O_2^- (1992, 1M)
- (c) NO^+
- (d) CN^+

47. The linear structure assumed by (1991, 1M)

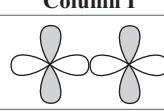
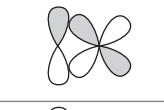
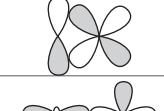
- (a) SnCl_2
- (b) CS_2
- (c) NO_2^+
- (d) NCO^-

48. CO_2 is isostructural with (1986, 1M)

- (a) HgCl_2
- (b) C_2H_2
- (c) SnCl_2
- (d) NO_2

Match the Columns

49. Match the orbital overlap figures shown in Column I with the description given in Column II and select the correct answer using the codes given below the Columns. (2014 Adv.)

	Column I	Column II
A.		1. p - d π antibonding
B.		2. d - d σ bonding
C.		3. p - d π bonding
D.		4. d - d π antibonding

52 Chemical Bonding

Codes

	A	B	C	D		A	B	C	D
(a)	4	3	2	1	(b)	1	2	3	4
(c)	2	3	1	4	(d)	4	1	2	3

50. Match each of the diatomic molecules in Column I with its property/properties in Column II. (2009)

Column I	Column II
A. B_2	p. Paramagnetic
B. N_2	q. Undergoes oxidation
C. O_2^-	r. Undergoes reduction
D. O_2	s. Bond order ≥ 2
	t. Mixing of 's' and 'p' orbitals

Codes

	A	B	C	D
(a)	q, r, s	p, r, t, s	q, r, t	p, q, t
(b)	p, q, r, t	q, r, s, t	p, q, r, t	p, r, s, t
(c)	q, r, s, t	p, q, r	r, s, t	p, q, r, t
(d)	p, q, s, t	p, q, s	p, t	q, r, t

Fill in the Blanks

51. Among N_2O , SO_2 , I_3^+ and I_3^- , the linear species are and (1997 C, 1M)
52. When N_2 goes to N_2^+ , the N—N bond distance ... , and when O_2 goes to O_2^+ the O—O bond distance (1996, 1M)
53. The two types of bonds present in B_2H_6 are covalent and (1994, 1M)
54. The kind of delocalisation involving sigma bond orbitals is called..... (1994, 1M)
55. The valence atomic orbitals on C in silver acetylide is hybridised. (1990, 1M)
56. The shape of CH_3^+ is (1990, 1M)
57. hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. (1982, 1M)
58. Pair of molecules which forms strongest intermolecular hydrogen bonds is (SiH_4 and SiF_4 , acetone and CHCl_3 , formic acid and acetic acid) (1981, 1M)
59. The angle between two covalent bonds is maximum in (CH_4 , H_2O , CO_2) (1981, 1M)

True/False

60. The dipole moment of CH_3F is greater than that of CH_3Cl . (1993, 1M)
61. H_2O molecule is linear. (1993, 1M)
62. The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. (1990, 1M)
63. sp^3 hybrid orbitals have equal s and p character. (1987, 1M)

64. In benzene, carbon uses all the three p-orbitals for hybridisation. (1987, 1M)

65. SnCl_2 is a non-linear molecule. (1985, $\frac{1}{2}$ M)

Integer Answer Type Questions

66. The sum of the number of lone pairs of electrons on each central atom in the following species is $[\text{TeBr}_6]^{2-}$, $[\text{BrF}_2]^+$, SNF_3 and $[\text{XeF}_3]^-$ (Atomic numbers : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54) (2017 Adv.)

67. Among the triatomic molecules/ions BeCl_2 , N_3^- , N_2O , NO_3^+ , O_3 , SCl_2 , ICl_2^- , I_3^- and XeF_2 , the total number of linear molecules(s)/ion(s) where the hybridisation of the central atom does not have contribution from the d-orbital(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe = 54] (2015 adv.)

68. A list of species having the formula XZ_4 is given below (2014 Adv.)

XeF_4 , SF_4 , SiF_4 , BF_4^- , BrF_4^- , $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{FeCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

69. The total number of lone-pair of electrons in melamine is (2013 Adv.)

70. Based on VSEPR theory, the number of 90° F—Br—F angles in BrF_5 is (2010)

Subjective Questions

71. Predict whether the following molecules are isostructural or not. Justify your answer.

(i) NMe_3 (ii) $\text{N}(\text{SiMe}_3)_3$ (2005, 2M)

72. On the basis of ground state electronic configuration, arrange the following molecules in increasing O—O bond length order. KO_2 , O_2 , $\text{O}_2[\text{AsF}_6]$ (2004, 2M)

73. Draw the shape of XeF_4 and OSF_4 according to VSEPR theory. Show the lone pair of electrons on the central atom. (2004, Main, 2M)

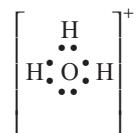
74. Using VSEPR theory, draw the shape of PCl_5 and BrF_5 . (2003, 2M)

75. Draw the molecular structures of XeF_2 , XeF_4 and XeO_2F_2 , indicating the location of lone pair(s) of electrons. (2000, 3M)

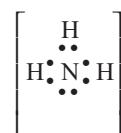
76. Interpret the non-linear shape of H_2S molecule and non-planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. (Atomic number : H = 1, P = 15, S = 16, Cl = 17) (1998, 4M)

77. Using the VSEPR theory, identify the type of hybridisation and draw the structure of OF_2 . What are the oxidation states of O and F ? (1997, 3M)

78. Write the Lewis dot structural formula for each of the following. Give also, the formula of a neutral molecule, which has the same geometry and the same arrangement of the bonding electrons as in each of the following. An example is given below in the case of H_3O^+ and NH_3 .



Lewis dot structure



Neutral molecule

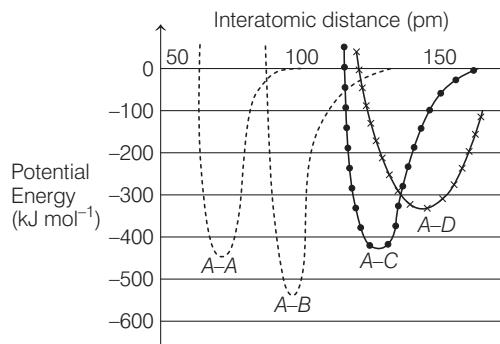
(1983, 4M)

- (i) O_2^{2-} (ii) CO_3^{2-} (iii) CN^- (iv) NCS^-

Topic 3 Resonance, LCAO, MOT, Other Bonding Types

Objective Questions I (Only one correct option)

1. The intermolecular potential energy for the molecules A , B , C and D given below suggests that: (2020 Main, 4 Sep I)



- (a) $A\text{-}B$ has the stiffest bond
 (b) D is more electronegative than other atoms
 (c) $A\text{-}A$ has the largest bond enthalpy
 (d) $A\text{-}D$ has the shortest bond length
2. During the change of O_2 to O_2^- , the incoming electron goes to the orbital. (2019 Main, 10 April I)
 (a) $\pi 2p_x$ (b) $\pi^* 2p_x$ (c) $\pi 2p_y$ (d) $\sigma^* 2p_z$
3. HF has highest boiling point among hydrogen halides, because it has (2019 Main, 9 April II)
 (a) lowest ionic character
 (b) strongest van der Waals' interactions
 (c) strongest hydrogen bonding
 (d) lowest dissociation enthalpy
4. Among the following species, the diamagnetic molecule is (2019 Main, 9 April II)
 (a) CO (b) B_2 (c) NO (d) O_2
5. Among the following, the molecule expected to be stabilised by anion formation is C_2 , O_2 , NO , F_2 . (2019 Main, 9 April I)
 (a) C_2 (b) F_2
 (c) NO (d) O_2
6. Among the following molecules/ions, C_2^{2-} , N_2^{2-} , O_2^{2-} , O_2
 Which one is diamagnetic and has the shortest bond length? (2019 Main, 8 April II)
 (a) C_2^{2-} (b) O_2 (c) O_2^{2-} (d) N_2^{2-}
7. Two pi and half sigma bonds are present in (2019 Main, 10 Jan I)
 (a) O_2^+ (b) N_2 (c) N_2^+ (d) O_2
8. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ? (2019 Main, 9 Jan I)
 (a) Both are unstable
 (b) Li_2^+ is unstable and Li_2^- is stable
 (c) Both are stable
 (d) Li_2^+ is stable and Li_2^- is unstable
9. According to molecular orbital theory, which of the following will not be a viable molecule? (2018 Main)
 (a) He_2^{2+} (b) He_2^+
 (c) H_2^- (d) H_2^{2-}
10. Which of the following species is not paramagnetic? (2017 Main)
 (a) NO (b) CO
 (c) O_2 (d) B_2
11. Assuming $2s$ - $2p$ mixing is not operative, the paramagnetic species among the following is (2014 Adv.)
 (a) Be_2 (b) B_2
 (c) C_2 (d) N_2
12. Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of (2013 Main)
 (a) $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$ (b) $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$
 (c) $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$ (d) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$
13. In which of the following pairs of molecules/ions both the species are not likely to exist? (2013 Main)
 (a) $\text{H}_2^+, \text{He}_2^{2-}$ (b) $\text{H}_2^-, \text{He}_2^{2-}$
 (c) $\text{H}_2^{2+}, \text{He}_2$ (d) $\text{H}_2^-, \text{He}_2^{2+}$
14. Hyperconjugation involves overlap of which of the following orbitals? (2008, 3M)
 (a) $\sigma - \sigma$ (b) $\sigma - p$
 (c) $p - p$ (d) $\pi - \pi$
15. According to MO theory, (2004, 1M)
 (a) O_2^+ is paramagnetic and bond order greater than O_2
 (b) O_2^+ is paramagnetic and bond order less than O_2
 (c) O_2^+ is diamagnetic and bond order is less than O_2
 (d) O_2^+ is diamagnetic and bond order is more than O_2

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16. Molecular shape of SF_4 , CF_4 and XeF_4 are (2000, 1M)
 (a) the same, with 2, 0 and 1 lone pair of electrons respectively
 (b) the same, with 1, 1 and 1 lone pair of electrons respectively
 (c) different, with 0, 1 and 2 lone pair of electrons respectively
 (d) different, with 1, 0 and 2 lone pair of electrons respectively
17. In compounds of type $E\text{Cl}_3$, where $E = \text{B}, \text{P}, \text{As}$ or Bi , the angles $\text{Cl}—E—\text{Cl}$ is in order (1999, 2M)
 (a) $\text{B} > \text{P} = \text{As} = \text{Bi}$ (b) $\text{B} > \text{P} > \text{As} > \text{Bi}$
 (c) $\text{B} < \text{P} = \text{As} = \text{Bi}$ (d) $\text{B} < \text{P} < \text{As} < \text{Bi}$
18. The correct order of increasing $\text{C}—\text{O}$ bond length of $\text{CO}, \text{CO}_3^{2-}, \text{CO}_2$ is (1999, 2M)
 (a) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$ (b) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
 (c) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$ (d) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$
19. Which contains both polar and non-polar bonds? (1997, 1M)
 (a) NH_4Cl (b) HCN
 (c) H_2O_2 (d) CH_4
20. Which one among the following does not have the hydrogen bond? (1983, 1M)
 (a) Phenol (b) Liquid NH_3
 (c) Water (d) HCl

Objective Questions II

(One or more than one correct option)

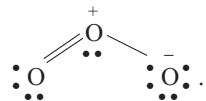
21. According to molecular orbital theory, which of the following statements is(are) correct? (2016 adv.)
 (a) C_2^{2-} is expected to be diamagnetic
 (b) O_2^{2+} is expected to have a longer bond length than O_2^-
 (c) N_2^+ and N_2^- have the same bond order
 (d) He_2^+ has the same energy as two isolated He atoms
22. Hydrogen bonding plays a central role in which of the following phenomena? (2014 Adv.)
 (a) Ice floats in water
 (b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
 (c) Formic acid is more acidic than acetic acid
 (d) Dimerisation of acetic acid in benzene
23. Which one of the following molecules is expected to exhibit diamagnetic behaviour? (2013 Main)
 (a) C_2 (b) N_2 (c) O_2 (d) S_2

Assertion and Reason

Read the following questions and answer as per the direction given below:

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
 (c) Statement I is correct; Statement II is incorrect.
 (d) Statement I is incorrect; Statement II is correct.

24. Statement I The electronic structure of O_3 is



Statement II structure is not allowed because octet around O cannot be expanded. (1998, 2M)

Match the Columns

25. Match the reactions in Column I with nature of the reactions/type of the products in Column II. (2007, 6M)

Column I	Column II
A. $\text{O}_2^- \longrightarrow \text{O}_2 + \text{O}_2^{2-}$	1. Redox reaction
B. $\text{CrO}_4^{2-} + \text{H}^+ \longrightarrow$	2. One of the products has trigonal planar structure
C. $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \longrightarrow$	3. Dimeric bridged tetrahedral metal ion
D. $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \longrightarrow$	4. Disproportionation

Codes				A B C D			
(a) 2	1, 4	3	4	(b) 1, 4	3	1, 2	1
(c) 2	3	1	4	(d) 3	4	2, 3	1

Integer Answer Type Questions

26. Chlorine reacts with hot and concentrated NaOH and produces compounds (X) and (Y). Compound (X) gives white precipitate with silver nitrate solution. The average bond order between Cl and O atoms in (Y) is (2020 Main, 7 Jan I)
27. Among $\text{H}_2, \text{He}_2^+, \text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2, \text{O}_2^-$ and F_2 , the number of diamagnetic species is (Atomic numbers : H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9) (2017 Adv.)

Subjective Questions

28. Write the MO electron distribution of O_2 . Specify its bond order and magnetic property. (2000, 3M)
29. Arrange the following as stated.
 "Increasing strength of hydrogen bonding ($X—\text{H}—X$)."
 $\text{O}, \text{S}, \text{F}, \text{Cl}, \text{N}$ (1991, 1M)
30. What effect should the following resonance of vinyl chloride have on its dipole moment? (1987, 1M)
- $$\text{CH}_2=\text{CH}-\text{Cl} \longleftrightarrow \text{CH}_2^--\text{C}^+\text{HCl}$$

Answers

Topic 1

1. (d) 2. (c) 3. (b) 4. (a)
 5. (a) 6. (b) 7. (b) 8. (b)
 9. (a) 10. (a) 11. (c) 12. (c)
 13. (a, c) 14. (a) 15. (6) 16. (1)
 17. (c) 18. (2) 19. F 20. T
 25. (80.2%)

Topic 2

1. (d) 2. (b) 3. (c) 4. (d)
 5. (d) 6. (c) 7. (a) 8. (d)
 9. (d) 10. (a) 11. (a) 12. (d)
 13. (d) 14. (b) 15. (a) 16. (a)
 17. (c) 18. (a) 19. (b) 20. (a)
 21. (b) 22. (d) 23. (a) 24. (b)
 25. (b) 26. (c) 27. (b) 28. (c)
 29. (d) 30. (b) 31. (a) 32. (a)
 33. (a) 34. (a) 35. (a) 36. (c)
 37. (c) 38. (c) 39. (d) 40. (b)
 41. (b) 42. (a) 43. (a) 44. (c)
 45. (b, c) 46. (a, c) 47. (b, c, d) 48. (a, b)

49. (c) A → 2; B → 3; C → 1; D → 4
 50. (b) A → p, q, r, t; B → q, r, s, t; C → p, q, r, t; D → p, r, s, t
 51. N₂O, I₃⁻ 52. increases, decreases
 53. three centre bond-two electrons
 54. hyperconjugation
 55. sp 56. Triangular planar 57. sp³
 58. HCOOH and CH₃COOH 59. CO₂ 60. F

Topic 3

61. F 62. F 63. F 64. F
 65. T 66. (6) 68. (4) 69. (6)
 1. (a) 2. (b) 3. (c) 4. (a)
 5. (a) 6. (a) 7. (c) 8. (d)
 9. (d) 10. (b) 11. (c) 12. (b)
 13. (c) 14. (b) 15. (a) 16. (d)
 17. (b) 18. (a) 19. (c) 20. (d)
 21. (a, c) 22. (a, b, d) 23. (a, b) 24. (a)
 25. (b) A → 1, 4; B → 3; C → 1, 2; D → 1 26. (1.67)
 27. (6) 28. (2)

Hints & Solutions

Topic 1 Preliminary Concepts of Electrovalent and Covalent Bonding

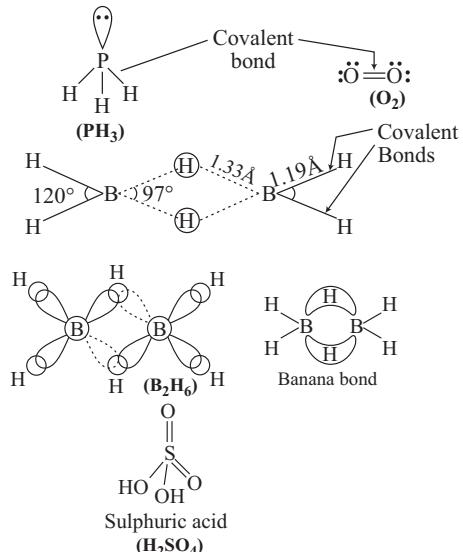
1. **Key Idea** Isoelectronic species contains same number of electrons.

The species with its atomic number and number of electrons are as follows :

Species (ions)	At. no. (Z)	No. of electrons
N ³⁻	7	7 + 3 = 10
O ²⁻	8	8 + 2 = 10
F ⁻	9	9 + 1 = 10
Na ⁺	11	11 - 1 = 10
Li ⁺	3	3 - 1 = 2
Mg ²⁺	12	12 - 2 = 10

Thus, option (d) contains isoelectronic set of ions.

2. KCl is the only ionic compound. The structure of PH₃, O₂, B₂H₆ and H₂SO₄ are given below



All bond between S and O atom are covalent bonds.

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3. Ion-ion interaction is dependent on the square of distance, i.e.
 ion-ion interaction $\propto \frac{1}{r^2}$

Similarly, ion-dipole interaction $\propto \frac{1}{r^3}$

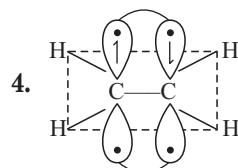
London force $\propto \frac{1}{r^6}$ and dipole-dipole interaction $\propto \frac{1}{r^3}$

Superficially it seems as both ion-dipole interaction and hydrogen bonding vary with the inverse cube of distance between the molecules but when we look at the exact expressions of field (force) created in two situations, it comes as

$$|E| \text{ or } |F| = \frac{2|P|}{4\pi \epsilon_0 r^3} \quad (\text{In case of ion-dipole interaction})$$

$$\text{and } F = \frac{2q^2 r - 4q^2 a}{4\pi \epsilon_0 r^3} \quad (\text{In case of dipole-dipole interaction})$$

From the above, it is clear that the ion-dipole interaction is the better answer as compared to dipole-dipole interaction, i.e. hydrogen bonding.

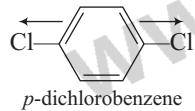


Pi bond is formed by the p -orbitals whose lobes have minima in the plane of molecule, hence molecular plane is the nodal plane of pi-bond.

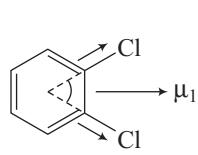
5. H-bond is the strongest intermolecular force.

All are different with 1, 0 and 2 lone pairs of electrons at central atom.

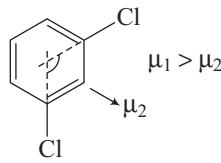
6. *p*-dichlorobenzene is non-polar.



The two dipole vectors cancelling each other giving zero resultant dipole moment. *o*-dichlorobenzene has greater dipole moment than *meta*-isomer.



(o-dichlorobenzene)
dipole vectors are at 60° angle



(m-dichlorobenzene)
dipole vectors are at 120° angle

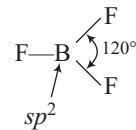
Toluene is less polar than both *ortho* and *para* dichlorobenzene. Therefore, the increasing order of dipole moment is

p-dichlorobenzene (IV) < toluene (I) < *m*-dichlorobenzene (II) < *o*-dichlorobenzene (III)

7. The carbide (C_2^{2-}) ion has the following bonding pattern:

$\bar{C} \equiv \bar{C}$: one sigma and two pi-bonds.

8. BF_3 has triangular planar arrangement.



Three identical vectors acting in outward direction at equal angles in a plane cancel each other giving zero resultant, hence non-polar.

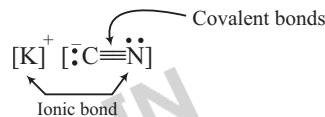
9. Strongly electropositive, univalent X will form an 1 : 1 ionic compound with strongly electronegative, univalent Y .



10. H_2 is a covalent, diatomic molecule with a sigma covalent bond between two hydrogen atoms.

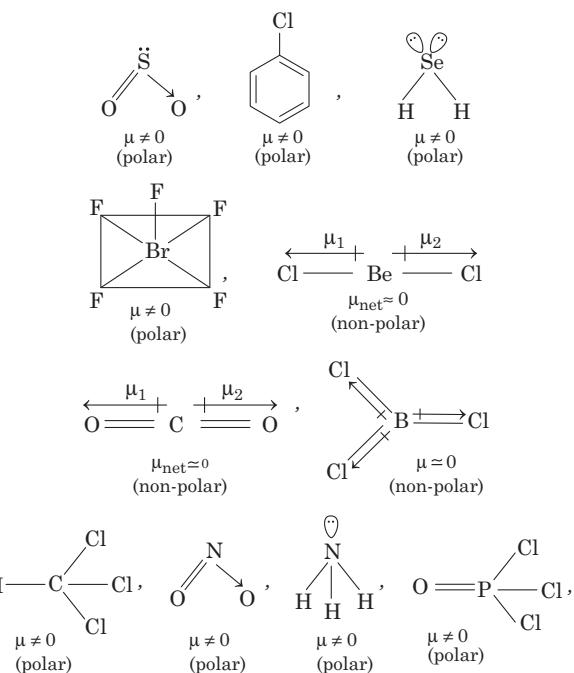
11. N_2 has triple bond and each covalent bond is associated with one pair of electrons, therefore, six electrons are involved in forming bonds in N_2 .

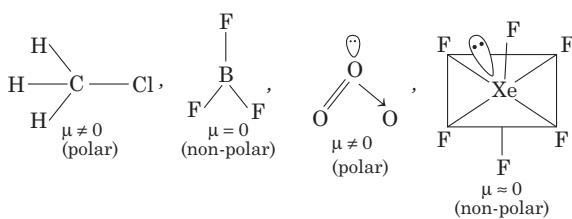
12. In KCN , the bonding between potassium ion and cyanide ion is ionic while carbon and nitrogen are covalently bonded in cyanide ion as:



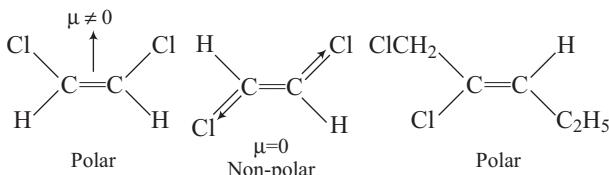
13. **Key Idea** Dipole moment of a bond depends on the difference in the electronegativities of bonded atoms. More is the difference in the electronegativities, greater will be the dipole moment. Also,
 For symmetrical molecule, $\mu = 0$
 For unsymmetrical molecule, $\mu \neq 0$

The molecules which gives permanent dipole moment are polar in nature.

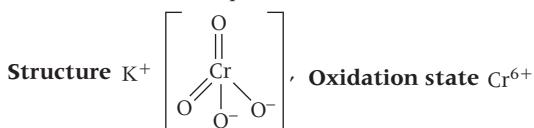




14. 1,4-dichlorobenzene is non-polar, individual dipole vectors cancel each other.



15. Only polar liquid will be attracted towards charged comb due to the formation of electrically charged droplets in the polar liquid stream, induced by a nearby charged object. Hence, liquid showing deflection are HF, H₂O, NH₃, H₂O₂, CHCl₃, C₆H₅Cl.
16. Among the given species only K₂CrO₄ is diamagnetic as central metal atom Cr in it has [Ar]3d⁰ electronic configuration i.e., all paired electrons. The structure and oxidation state of central metal atom of this compound are as follows



Rest all the compounds are **paramagnetic**. Reasons for their paramagnetism are given below

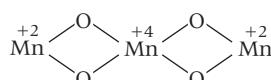
- (i) H-atom have 1s¹ electronic configuration, i.e. 1 unpaired electron.



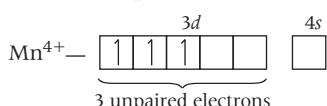
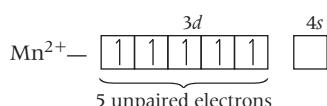
- (iii) O₂⁻ (Superoxide) has one unpaired electron in π^* molecular orbital.

- (iv) S₂ in vapour phase has O₂ like electronic configuration i.e., have 2 unpaired electrons in π^* molecular orbitals.

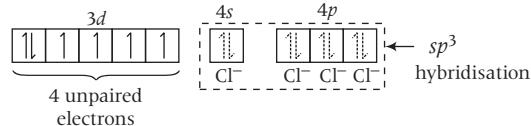
- (v) Mn₃O₄ has following structure



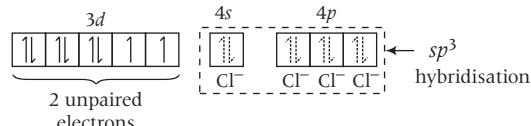
Thus, Mn is showing +2 and +4 oxidation states. The outermost electronic configuration of elemental Mn is 3d⁵4s². Hence, in both the above oxidation states it has unpaired electrons as



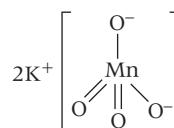
- (vi) (NH₄)₂FeCl₄ has Fe as central metal atom with +2 oxidation state. The electronic configuration of Fe²⁺ in the complex is



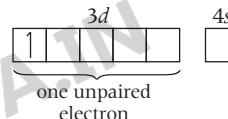
- (vii) (NH₄)₂NiCl₄ has Ni as central metal atom with +2 oxidation state. The electronic configuration of Ni²⁺ in the complex is



- (viii) In K₂MnO₄ central metal atom Mn has +6 oxidation state with following structure



Electronic configuration of Mn⁶⁺ is



17. Statement I is correct but Statement II is incorrect. The covalency in LiCl is due to small size of Li⁺ ion which brings about large amount of polarisation in bond.

18. These are 2 π -bonds in a nitrogen molecule.

19. The resultant of individual bond dipoles may or may not be non-zero.

20. Linear overlapping of p-orbitals form sigma bond while sidewise overlapping of two p-orbitals forms a pi bond.

21. Li⁺ < Al³⁺ < Mg²⁺ < K⁺

22. Ag⁺ is stronger Lewis acid because it can easily accommodate lone pair of electrons from Lewis base. On the other hand, Na⁺ has noble gas configuration, cannot accept lone pair of electron, not at all a Lewis acid.

23. I₂ is Lewis acid because I⁻ coordinate its one lone pair to I₂.

24. Both LiF and LiI are expected to be ionic compounds. However, LiI is predominantly covalent because of small size of Li⁺ and large size of iodide ion. A smaller cation and a larger anion introduces covalency in ionic compound.

25. Dipole moment is calculated theoretically as

$$\mu = q \cdot d$$

Here, $q = 1.6 \times 10^{-19}$ C and $d = 2.6 \times 10^{-10}$ m

$$\mu_{\text{Theo}} = 1.6 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.16 \times 10^{-29} \text{ cm}$$

$$\% \text{ ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{Theo}}} \times 100 = \frac{3.336 \times 10^{-29}}{4.16 \times 10^{-29}} \times 100$$

$$= 80.2\%$$

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- 26.** In hydrogen peroxide (H_2O_2), oxygen is in -1 oxidation state, can be oxidised to O_2 (zero oxidation state) or can be reduced to H_2O (-2 oxidation state of oxygen).

Hence, H_2O_2 can act as both oxidising agent and reducing agent. With strong oxidising agent like KMnO_4 , H_2O_2 acts as a reducing agent while with strong reducing agent like $\text{H}_2\text{C}_2\text{O}_4$, it acts as an oxidising agent.

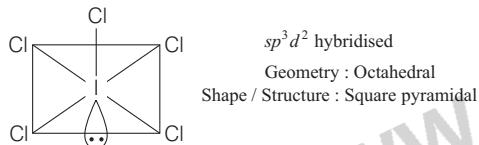
- 27.** (i) **Melting points** Ionic compounds have higher melting points than covalent compounds.
 (ii) **Boiling points** Ionic compounds have higher boiling points than covalent compounds.
 (iii) **Solubility** Ionic compounds have greater solubility in water than a covalent compound.
 (iv) **Conductivity in aqueous solution** Ionic compounds have greater electrical conductivity in aqueous solution while covalent compounds are usually non-conducting.

Topic 2 VBT, Hybridisation and VSEPR Theory

- 1.** Among the given statements, correct statements are I and III only. Valence bond theory (VBT) cannot explain the colour exhibited by transition metal complexes. This theory cannot distinguish ligands as weak and strong field ones.

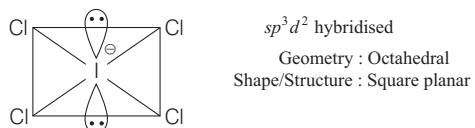
- 2.** For ICl_5

$$H = \frac{1}{2}(7 + 5 - 0 + 0) = 6 (\text{sp}^3\text{d}^2)$$



For ICl_4^-

$$H = \frac{1}{2}(7 + 4 - 0 + 1) = 6 (\text{sp}^3\text{d}^2)$$



So, ICl_5 and ICl_4^- are isolobal but not isostructural.

- 3.** **Key Idea** The hybridisation for a central atom in a species can be calculated using formula

$$H = \frac{1}{2}(V + M - C + A)$$

where, H = No. of hybridised orbitals used by central atoms.

V = No. of valence electrons of the central atom.

M = No. of mono-valent atoms (bonded).

C = No. of cationic (positive) charge.

A = No. of anionic (negative) charge.

The hybridisation of given species are as follows :

- For $[\text{ICl}_2^-]$ and $[\text{BrF}_2^-]$

$$H = \frac{1}{2}(7 + 2 - 0 + 1) = 5 (\text{sp}^3\text{d})$$

- For $[\text{ICl}_4^-]$,

$$H = \frac{1}{2}(7 + 4 - 0 + 1) = 6 (\text{sp}^3\text{d}^2)$$

- For $[\text{IF}_6^-]$,

$$H = \frac{1}{2}(7 + 6 - 0 + 1) = 7 (\text{sp}^3\text{d}^3)$$

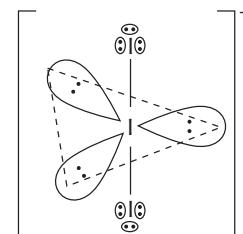
- 4.** The radius of isoelectronic species is inversely proportional to their nuclear charge or atomic number (Z). Thus, greater the value of Z , lesser the radii of isoelectronic species.

5.

Species	Valence MOs	Bond Order $\left(\frac{N_b - N_a}{2}\right)$	Paramagnetic/ Diamagnetic Nature
$\text{NO}(15e^-)$ $\searrow e^-$	$[8e^-] \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi * 2p_x^1 = \pi * 2p_y^0 \sigma * 2p_z^0$	$\frac{6 - 1}{2} = 2.5$	Paramagnetic
	$[8e^-] \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi * 2p_x^0 = \pi * 2p_y^0 \sigma * 2p_z^0$	$\frac{6 - 0}{2} = 3$	Diamagnetic
$\text{NO}^+(14e^-)$ $\nearrow N_2^+(13e^-)$ $\nearrow +2e^-$	$[8e^-] \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi * 2p_x^0 = \pi * 2p_y^0 \sigma * 2p_z^0$	$\frac{6 - 0}{2} = 3$	Diamagnetic
	$[8e^-] \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^1$ $\pi * 2p_x^0 = \pi * 2p_y^0 \sigma * 2p_z^0$	$\frac{5 - 0}{2} = 2.5$	Paramagnetic
$\text{O}_2(16e^-)$ $\nearrow O_2^+(15e^-)$ $\nearrow +2e^-$	$[8e^-] \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^1 = \pi * 2p_y^1 \sigma * 2p_z^0$ $[8e^-] \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^1 = \pi * 2p_y^0 \sigma * 2p_z^0$ $[8e^-] \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^2 = \pi * 2p_y^2 \sigma * 2p_z^0$	$\frac{6 - 2}{2} = 2$ $\frac{5 - 1}{2} = 2.5$ $\frac{6 - 4}{2} = 1$	Paramagnetic Paramagnetic Diamagnetic
	$[8e^-] \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^2 = \pi * 2p_y^2 \sigma * 2p_z^0$	$\frac{6 - 4}{2} = 1$	Diamagnetic

So, only in the conversion of $\text{NO} \rightarrow \text{NO}^+$, the bond order has increased ($2.5 \rightarrow 3$) and paramagnetic character has changed to diamagnetic.

- 6.** The structure of I_3^- ion is



Hence, 9 is the correct answer.

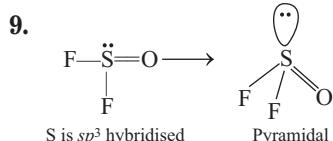
7. Isoelectronic species are those which contains same number of electrons.

Species	Atomic number	Number of electrons
O ²⁻	8	10
F ⁻	9	10
Na ⁺	11	10
Mg ²⁺	12	10
O ⁻	8	9
Na	11	11
Mg ⁺	12	11

∴ Option (a) is correct which contains isoelectronic species O²⁻, F⁻, Na⁺, Mg²⁺.

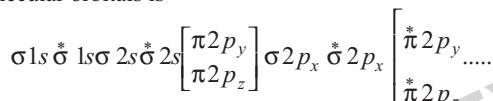
8. I₃⁻ is an ion made up of I₂ and I⁻ which has linear shape.

While Cs⁺ is an alkali metal cation.

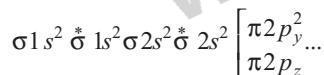


SO₃ is planar (S is sp^2 hybridised), BrF₃ is T-shaped and SiO₃²⁻ is planar (Si is sp^2 hybridised).

10. For molecules lighter than O₂, the increasing order of energies of molecular orbitals is



where, $\pi 2p_y$ and $\pi 2p_z$ are degenerate molecular orbitals, first singly occupied and then pairing starts if Hund's rule is obeyed. If Hund's rule is violated in B₂, electronic arrangement would be



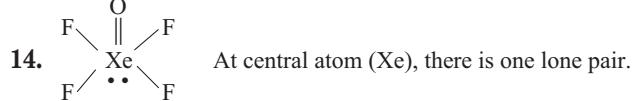
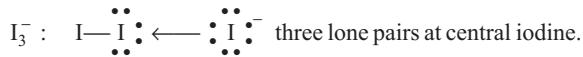
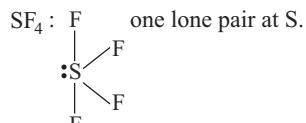
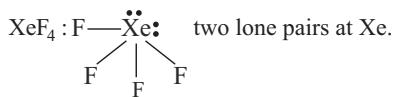
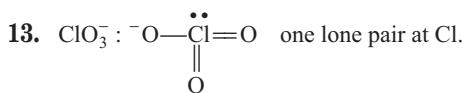
No unpaired electron-diamagnetic.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2}$$

$$= \frac{6 - 4}{2} = 1$$

11. The bond order of CO = 3. NO⁺, CN⁻ and N₂ are isoelectronic with CO, have the same bond order as CO. NO⁻ (16e⁻) has bond order of 2.

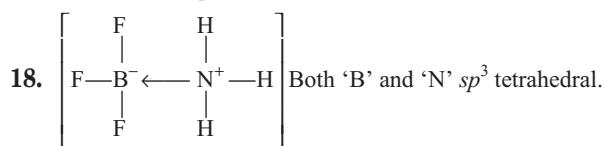
12. O₂⁻ in KO₂ has 17 electrons, species with odd electrons are always paramagnetic.



15. NO₃⁻ and CO₃²⁻ both have 32 electrons, central atom sp^2 hybridised, triangular planar.

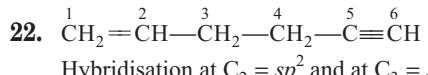
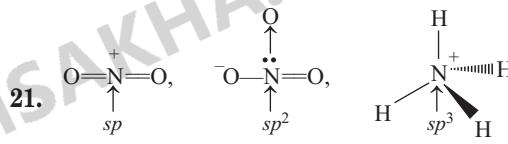
16. CH₃Cl has the highest dipole moment.

17. O₂⁻ has odd number(17) of electrons, therefore it must contain at least one unpaired electron.

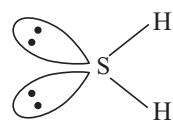


19. NH₃ = sp^3 , [PtCl₄]²⁻ = dsp^2 , PCl₅ = sp^3d , BCl₃ = sp^2

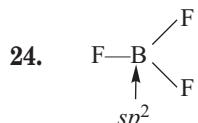
20. All three have 14 electrons (iso electronic) with bond order of three.



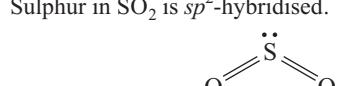
23. H₂S has sp^3 hybridised sulphur, therefore, angular in shape with non-zero dipole moment.



(Non-linear, polar molecule)



25. Sulphur in SO₂ is sp^2 -hybridised.



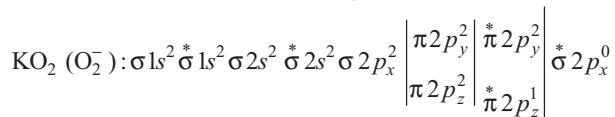
Electron pair = 2 (σ -bonds) + 1 (lone pair) = 3

Hybridisation = sp^2

Carbon in CO₂ is sp -hybridised, N in N₂O is sp -hybridised, carbon in CO is sp -hybridised.

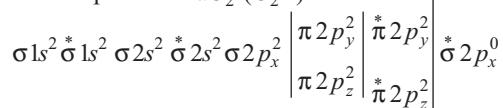
60 Chemical Bonding

26. Molecular orbital electronic configuration are



Has one unpaired electron in $\pi^* 2p_z$ orbital.

AlO_2^- has both oxygen in O^{2-} state, therefore, no unpaired electron is present. $\text{BaO}_2 (\text{O}_2^{2-})$

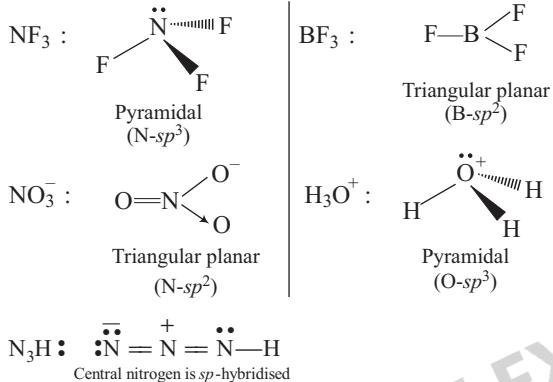


Has no unpaired electron.

NO_2^+ has $[\text{O}=\text{N}=\text{O}]$ bonding, hence no unpaired electron.

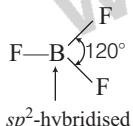
27. N_2 is a neutral, non-polar, inert molecule while CN^- is a highly polar, highly active ion.

- 28.



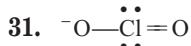
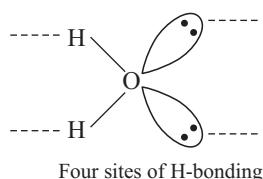
Therefore, $\text{NF}_3, \text{H}_3\text{O}^+$ and $\text{BF}_3, \text{NO}_3^-$ pairs have same shape.

29. BF_3 has triangular planar arrangement.



There identical vectors acting in outward direction, at equal angles in a plane, cancel each other giving zero resultant, hence non-polar.

30. A water molecule can form at the most four H-bonds.

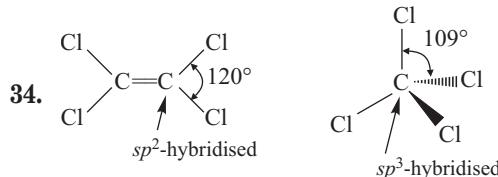


electron pairs at Cl = 2 (σ -bonds) + 2 (lone-pairs) = 4

Hybridisation at Cl = sp^3

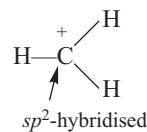
32. PCl_3 has sp^3 -hybridised phosphorus, with one lone pair. Therefore, molecule has pyramidal shape like ammonia.

33. O_2^- has odd number of electrons, hence it is paramagnetic.



35. CO_2 is linear because carbon is sp -hybridised.

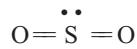
36. In CH_3^+ , there are only three electron pairs around carbon atom giving sp^2 -hybridisation state.



37. Dipole vectors in *trans*-1, 2-dichloroethylene are at 180° and directed in opposite direction, cancelling each other.



38. In SO_2 , the Lewis-dot structure is



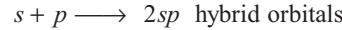
Electron pairs at S = 2 (σ -bonds) + 1 (lone-pair) = 3
 sp^2 hybridised.

NOTE

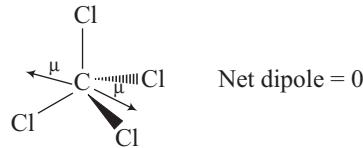
π -bonded electrons are not present in hybrid orbitals, therefore not counted in electron pairs. Rather π bonds are formed by lateral overlapping of pure p -orbitals.

39. Bonds between identical non-metal is purely covalent due to same electronegativities of the bonded atoms. Hence, the bonded atoms have equal holds on the shared pair of electrons.

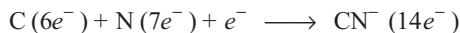
40. Hybridisation of one ‘s’ and one ‘p’ orbitals gives two sp hybrid orbitals oriented linearly at 180° .



41. CCl_4 has a regular tetrahedral shape.

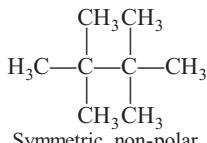
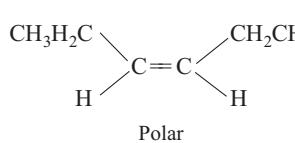
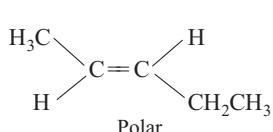
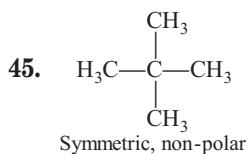


42. CO has a total of 14 electrons and CN^- also has 14 electrons.

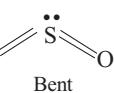
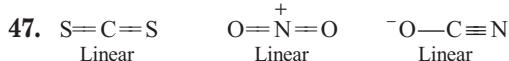


43. CO_2 is a linear molecule because of sp -hybridisation around carbon atom.

44. For non-polar MX_3 , it must have triangular planar arrangement, i.e. there should be sp^2 -hybridisation around M.

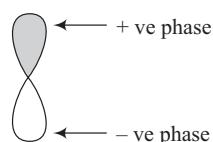


46. CN^- and NO^+ are isoelectronic, have the same bond order of 3.

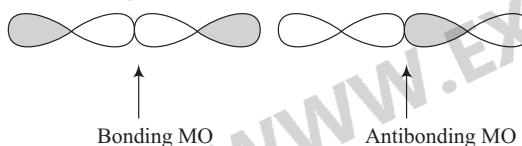


48. CO_2 , HgCl_2 , C_2H_2 are all linear.

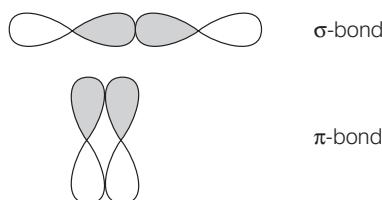
49. **PLAN** This problem includes basic concept of bonding. It can be solved by using the concept of molecular orbital theory.



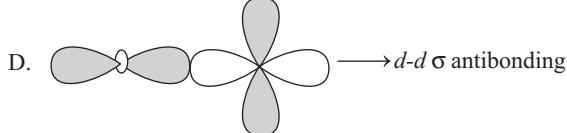
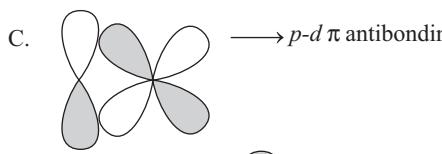
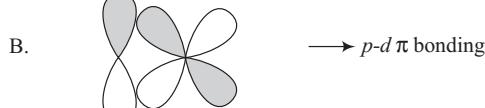
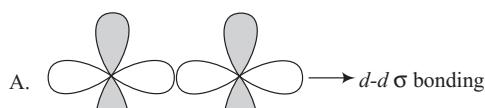
Any orbital has two phase +ve and -ve. In the following diagram, +ve phase is shown by darkening the lobes and -ve by without darkening the lobes.



When two same phase overlap with each other, it forms bonding molecular orbital otherwise antibonding.

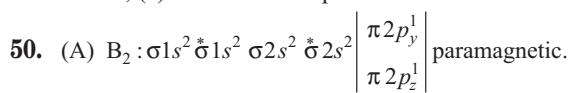


On the basis of above two concepts, correct matching can be done as shown below:



$$\therefore \text{A} \rightarrow 2, \text{B} \rightarrow 3, \text{C} \rightarrow 1, \text{D} \rightarrow 4$$

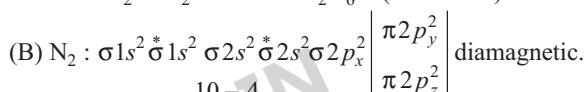
Hence, (c) is the correct option.



$$\text{Bond order} = \frac{6-4}{2} = 1$$

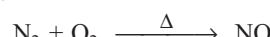
Bond is formed by mixing of *s* and *p* orbitals.

B_2 undergoes both oxidation and reduction as

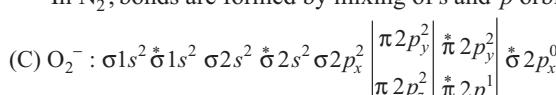


$$\text{Bond order} = \frac{10-4}{2} = 3 > 2$$

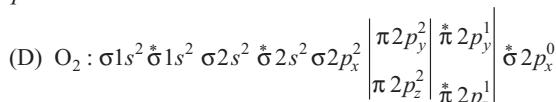
N_2 undergoes both oxidation and reduction as



In N_2 , bonds are formed by mixing of *s* and *p* orbitals.



Paramagnetic with bond order = 1.5. O_2^- undergoes both oxidation and reduction and bond involves mixing of *s* and *p*-orbitals.



Paramagnetic with bond order = 2.

O_2 undergoes reduction and the bond involves mixing of *s* and *p*-orbitals.

51. N_2O and I_3^- are linear species.

52. Bond order in N_2 is 3 while same in N_2^+ is 2.5, hence bond distance increases as N_2 goes to N_2^+ .

Bond order in O_2 is 2 while same in O_2^+ is 2.5, hence bond distance decreases as O_2 goes to O_2^+ .

53. Three centred-2 electrons.

54. Hyperconjugation involves delocalisation of σ -electrons.

55. *sp*-hybridised.

56. Triangular planar. Carbon in CH_3^+ is sp^2 hybridised.

62 Chemical Bonding

57. sp^3 -hybrid orbital holding the lone pair is involved in formation of ammonium ion.



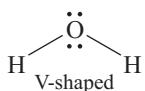
58. $\text{H}-\text{C}-\text{OH}$ and $\text{CH}_3-\text{C}-\text{OH}$. Both are capable of forming H-bonds.

59. CO_2 , it is 180° .

60. Dipole moment (μ) = $q.d$

Since electronegativity of F and Cl are very close, it is the internuclear distance (d) that decides dipole moment here. Hence, C—Cl bond has greater dipole moment than the C—F bond.

61. H_2O is V-shaped molecule.



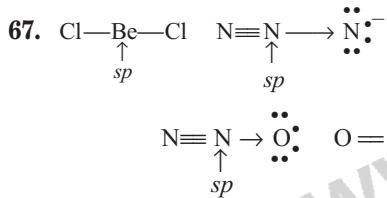
62. False

63. In sp^3 -hybrid orbital, there is 25% s-character and 75% p-character.

64. Carbon in benzene is sp^2 -hybridised, i.e. uses only two of its p-orbitals in hybridisation.

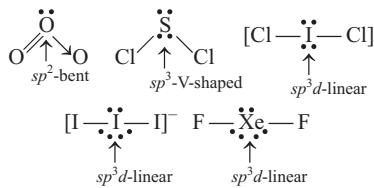
65. Sn in SnCl_2 has sp^2 -hybridisation.

S.N.	Species	No. of σ -bonds with central atom	No. of L.P at central atom
(i)	$\text{In}[\text{TeBr}_6]^{2-}$	6	1
(ii)	$\text{In}[\text{BrF}_2]^+$	2	2
(iii)	$\text{In}[\text{SNF}_3]$	4	0
(iv)	$\text{In}[\text{XeF}_3]^-$	3	3



All the above mentioned molecules/ions have sp -hybridised central atom and no one pair at central atom, hence linear also.

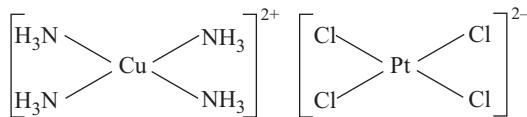
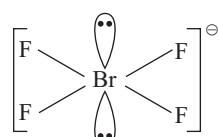
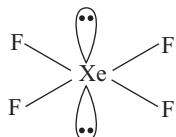
Others are :



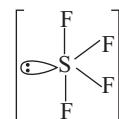
[Although ICl_2^- , I_3^- and XeF_2 all also are linear but in them d-orbital contribute in hybridisation.]

68. **PLAN** This problem includes concept of hybridisation using VBT, VSEPR theory, etc.,

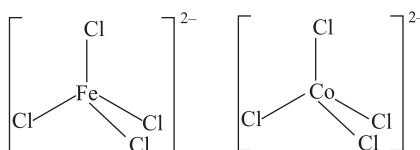
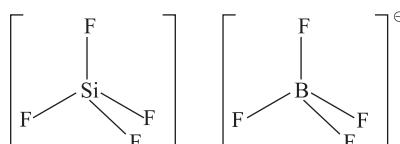
XeF_4 , BrF_4 , $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{PtCl}_4]^{2-}$ are square planar as shown below:



SF_4 (See-saw) as shown below:

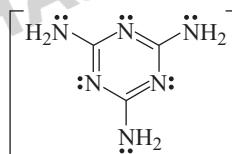


SiF_4 , BF_4^- , $[\text{FeCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$ are tetrahedral as shown below:



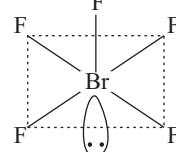
Hence, correct integer is 4.

69. **PLAN** Melamine is a heterocyclic compound.



Each nitrogen atom has one pair of lone pair. Thus, in all six lone pairs.

- 70.



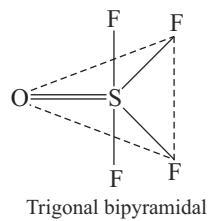
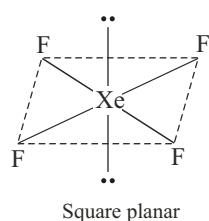
Lone pair would push the Br—F bond pairs in upward direction and all Br—F bond angles will contract.

71. No, (i) NMe_3 is pyramidal while (ii) $\text{N}(\text{SiMe}_3)_3$ is planar. In the latter case, $p\pi - d\pi$ back bonding between N and Si makes N sp^2 -hybridised.

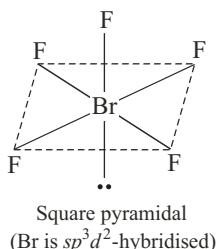
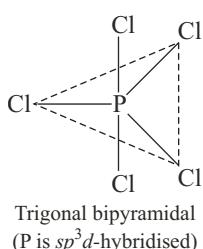
72. Bond order : $\text{O}_2^- = 1.5$, $\text{O}_2 = 2$, $\text{O}_2^+ = 2.5$

Bond length : $\text{O}_2^+ < \text{O}_2 < \text{O}_2^-$

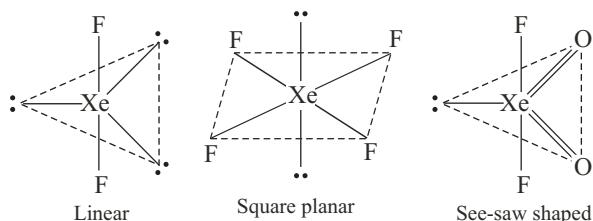
- 73.



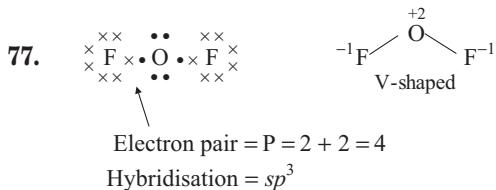
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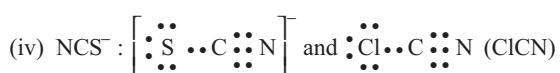
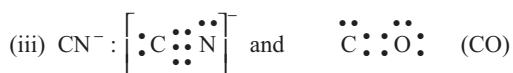
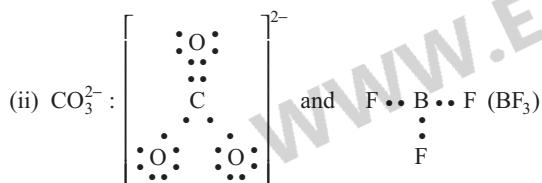
75.



76. In H_2S , S is sp^3 -hybridised with two lone pairs of electrons on it giving V-shaped (water like) shape. In PCl_3 , P is sp^3 -hybridised with one lone pair of electrons on it. Therefore, PCl_3 is pyramidal in shape.



78. (i) $O_2^{2-} : \left[\begin{array}{c:c} \bullet & \bullet \\ \bullet & \bullet \end{array} \right]^{2-}$ and $\ddot{\text{Cl}} - \text{Cl} \ddot{\text{Cl}} : (Cl_2)$



Topic 3 Resonance, LCAO, MOT, Other Bonding Types

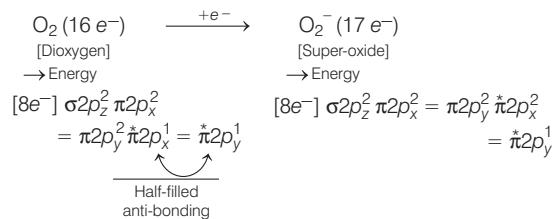
1. (a) $A - B$ has stiffest bond.

This is correct because the potential energy of $A - B$ has maximum negative value [between -500 to -600]. More negative is the potential energy means high energy is released. Higher the released energy higher is the stability and hence the stiffness bond.

- (b) D is more electronegative than other atoms, it is incorrect.
(c) $A - A$ has the largest bond enthalpy, it is incorrect because value of potential energy is more negative in $A - B$.

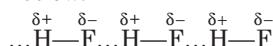
- (d) $A - D$ has shortest bond length, it is incorrect because intermolecular distance in between $A - D$ more than 150 (pm) which is height in all.

2. The change of O_2 to O_2^- can be as follows:



So, in the formation of O_2^- from O_2 , the 17th electron goes to the $\pi^* 2p_x$ or $\pi^* 2p_y$ molecular orbital (anti-bonding) which is half-filled in O_2^- .

3. HF has highest boiling point among hydrogen halides because it has strongest hydrogen bonding. Here, the hydrogen bond exists between hydrogen of one molecule and fluorine atom of another molecule as shown below.



In this molecule, hydrogen bond behaves like a bridge between two atoms that holds one atom by covalent bond and the other by hydrogen bond.

4. **Key Idea** Magnetic nature can be detected by molecular orbital theory. Presence of unpaired electrons means paramagnetic and absence of unpaired electrons means diamagnetic in nature.

Among the given options, CO is a diamagnetic molecule. It can be proved by molecular orbital (MO) theory. The electronic configuration of given diatomic molecules are given below.

- CO (Number of electrons = 14)
Electronic configuration = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2$
Since, there is no unpaired electron in the CO molecule, so it is diamagnetic.
- NO (Number of electrons = 15)
Electronic configuration = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^0$
Since, NO has one unpaired electron in $\pi^* 2p_x^1$ orbital, so it is paramagnetic.
- B_2 (Number of electrons = 10)
Electronic configuration = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi p_y^1$
Since, two unpaired electrons are present in $\pi 2p_x^1$ and $\pi 2p_y^1$ orbital. So, it is paramagnetic.
- O_2 (Number of electrons = 16)
Electronic configuration = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^1$
Since, two unpaired electrons are present in $\pi^* 2p_x^1$ and $\pi^* 2p_y^1$ orbital. So, it is also paramagnetic.

64 Chemical Bonding

5. C_2 will be stabilised after forming anion. The electronic configuration of carbon is $1s^2 2s^2 2p^2$. There are twelve electrons in C_2 . After forming anion (i.e. C_2^-), the electronic configuration is

- $C_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z^1)$ or $KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z^1)$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(9 - 4) = 2.5$$

For other options such as F_2^- , O_2^- , NO^- , the electronic configurations are as follows :

- $F_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2) (\sigma^* 2p_z^1)$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 9) = 0.5$$

- $O_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z^2) (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 7) = 1.5$$

- $NO^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z^2) (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

The value of bond order of C_2^- is highest among the given options. Bond order between two atoms in a molecule may be taken as an approximate measure of the bond length.

The bond length decreases as bond order increases. As a result, stability of a molecule increases.

Species	MO energy order	Bond order (BO)	n, number of unpaired e^-	Magnetic character
$C_2^- (14e^-)$	$[8\bar{e}] \pi_{2p_x^2} = \pi_{2p_y^2} \sigma_{2p_z^2}$	$\frac{6-0}{2} = 3$	0	Diamagnetic
$O_2 (16e^-)$	$[8\bar{e}] \sigma_{2p_z^2} \pi_{2p_x^2} = \pi_{2p_y^2} \pi_{2p_x^1} = \pi_{2p_y^1}$	$\frac{6-2}{2} = 2$	2	Paramagnetic
$O_2^{2-} (18e^-)$	$[8\bar{e}] \sigma_{2p_z^2} \pi_{2p_x^2} = \pi_{2p_y^2} \pi_{2p_x^2} = \pi_{2p_y^1}$	$\frac{6-4}{2} = 1$	0	Diamagnetic
$N_2^{2-} (16e^-)$	$[8\bar{e}] \pi_{2p_x^2} = \pi_{2p_y^2} \sigma_{2p_z^2} \pi_{2p_x^1} = \pi_{2p_y^1}$	$\frac{6-2}{2} = 2$	2	Paramagnetic

Bond length $\propto \frac{1}{\text{BO (Bond order)}}$. So order of bond length

$$C_2^{2-} < O_2^- = N_2^{2-} < O_2^{2-}$$

($\text{BO} = 3$) ($\text{BO} = 2$) ($\text{BO} = 1$)

The diamagnetic species with shortest bond length is C_2^{2-} (option-a).

7. The energy order of MOs of the given species are as follows:

$$O_2 (16e^-)'s = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1,$$

$$O_2^+ (15e^-)'s = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^0$$

$$N_2 (14e^-)'s = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$$

$$\pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$$

$$N_2^+ (13e^-)'s = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$$

$$\pi 2p_x^2 = \pi 2p_z^2 \sigma 2p_z^1$$

Thus, in case of N_2^+ , two π -bonds and half σ -bond are present in the bonding MOs.

8. Considering molecular orbital theory (MOT) :

The electronic configuration of $Li_2^+ (Z = 5) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$

$$\text{Bond order (BO)} = \frac{N_b - N_a}{2} = \frac{3-2}{2} = \frac{1}{2}$$

The electronic configuration of $Li_2^- (Z = 7) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^1$

$$\text{Bond order (BO)} = \frac{N_b - N_a}{2} = \frac{4-3}{2} = \frac{1}{2}$$

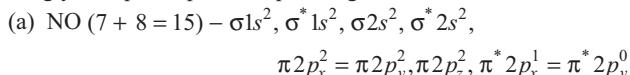
For the species having the same value of BO, the specie having lesser number of antibonding electrons [N_a] will be more stable. Here, N_a of $Li_2^+ (2) < N_a$ of $Li_2^- (3)$. So, their order of stability will be $Li_2^+ > Li_2^-$.

9. Key Idea According to M.O.T, the viability of any molecule can be judged through the calculation of bond order.

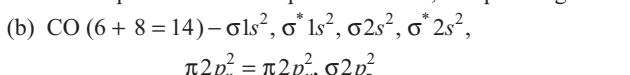
Electronic Configuration	Bond order
He_2^+ $\sigma_{1s^2} \sigma_{1s^1}^*$	$\frac{2-1}{2} = 0.5$
H_2^- $\sigma_{1s^2} \sigma_{1s^1}^*$	$\frac{2-1}{2} = 0.5$
H_2^{2-} $\sigma_{1s^2} \sigma_{1s^2}^*$	$\frac{2-2}{2} = 0$
He_2^{2+} σ_{1s^2}	$\frac{2-0}{2} = 1$

The molecule having zero bond order will not be viable hence, H_2^- (option d) is the correct answer.

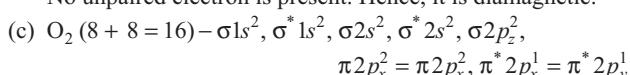
10. To identify the magnetic nature we need to check the molecular orbital configuration. If all orbitals are fully occupied, species is diamagnetic while when one or more molecular orbitals is/are singly occupied, species is paramagnetic.



One unpaired electron is present. Hence, it is paramagnetic.

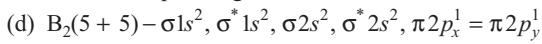


No unpaired electron is present. Hence, it is diamagnetic.



Two unpaired electrons are present.

Hence, it is paramagnetic.

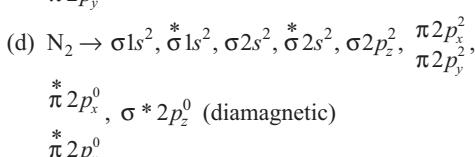
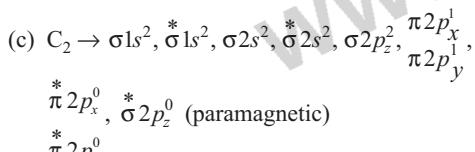
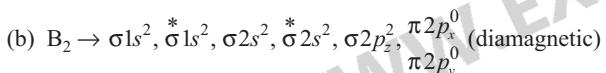
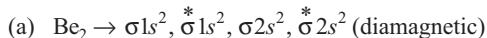
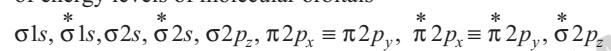


Two unpaired electrons are present.

Hence, it is paramagnetic.

11. PLAN This problem can be solved by using the concept involved in molecular orbital theory. Write the molecular orbital electronic configuration keeping in mind that there is no $2s-2p$ mixing, then if highest occupied molecular orbital contain unpaired electron then molecule is paramagnetic otherwise diamagnetic.

Assuming that no $2s-2p$ mixing takes place the molecular orbital electronic configuration can be written in the following sequence of energy levels of molecular orbitals

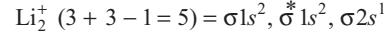


$\pi 2p_y^0$

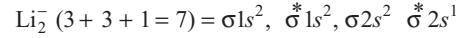
Hence, (c) is the correct choice.

12. Li_2 ($3 + 3 = 6$) = $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$



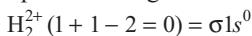
$$\text{Bond order} = \frac{3 - 2}{2} = \frac{1}{2} = 0.5$$



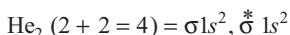
$$\text{Bond order} = \frac{4 - 3}{2} = \frac{1}{2} = 0.5$$

Stability order is $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$ (because Li_2^- has more number of electrons in antibonding orbitals which destabilises the species).

13. Species having zero or negative bond order do not exist.

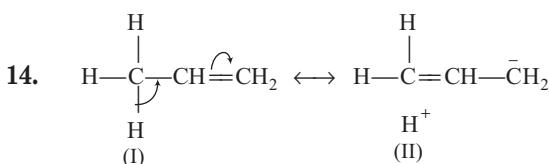


Bond order = 0

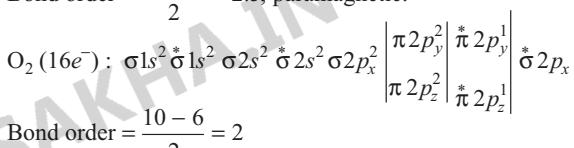
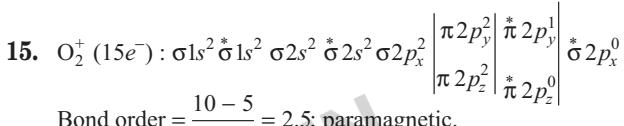


$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$$

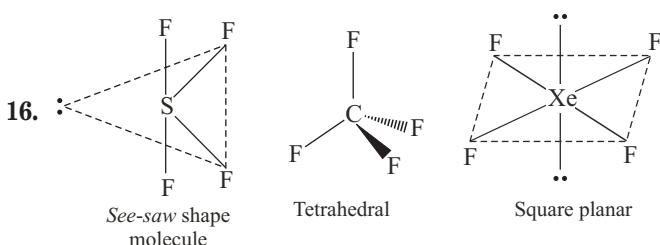
So, both H_2^{2+} and He_2 do not exist.



I and II are hyperconjugation structures of propene and involves σ -electrons of C–H bond and p -orbitals of pi bond in delocalisation.



Hence, (a) is the correct answer.



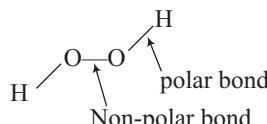
17. When $E = \text{B}$ in BCl_3 , bond angle is 120° . When $E = \text{P}$, As or Bi in ECl_3 , hybridisation at E will be sp^3 . Also, if central atoms are from same group, bond angle decreases down the group provided all other things are similar. Hence, the order of bond angles is $\text{BCl}_3 > \text{PCl}_3 > \text{AsCl}_3 > \text{BiCl}_3$

18. Bond length $\propto \frac{1}{\text{Bond order}}$

$$\text{Bond order : } \text{CO}_2 = 2, \text{CO} = 3, \text{CO}_3^{2-} = 1 + \frac{1}{3} = \frac{4}{3}$$

Therefore, order of bond length is $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$

19. H_2O_2



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20. HCl does not form hydrogen bond. For formation of hydrogen bond, atleast one hydrogen atom must be bonded to one of the three most electronegative atom O , N and F.

21.

Species	Electrons	MOEC	N_B	N_A	BO	Magnetic character
C_2^{2-}	14	$\sigma 1s^2, \sigma^* 1s^2,$ $\sigma 2s^2, \sigma^* 2s^2,$ $\pi 2p_x^2 \approx -\pi 2p_y^2,$ $\sigma 2p_z^2$	10	4	3	Diamagnetic
O_2^{2+}	14	As above according to number of electrons	10	4	3	Diamagnetic
O_2	16		10	6	2	Paramagnetic
N_2^+	13		9	4	2.5	Paramagnetic
N_2^-	15		10	5	2.5	Paramagnetic
He_2^+	3		2	1	0.5	Paramagnetic

Thus, (a) is correct.

(b) Bond order $O_2^{2+} > O_2$ thus,

Bond length of $O_2^{2+} < O_2$ thus, incorrect.

(c) N_2^+ and N_2^- have same bond order thus correct.

(d) He_2^+ with bond order = 0.5 is more stable thus, less energy than isolated He atoms. Thus, (d) is incorrect.

22. **PLAN** This problem can be solved by using concept of H-bonding and applications of H-bonding.

$$C_2 (6 + 6 = 12) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$$

Since, all the electrons are paired, it is a diamagnetic species.

$$N_2 (7 + 7 = 14) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2,$$

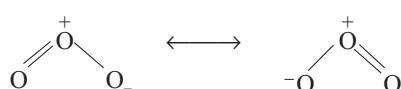
$$\sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$$

It is also a diamagnetic species because of the absence of unpaired electrons.

$$O_2 (8 + 8 = 16) \text{ or } S_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2 \quad \pi^* 2p_x^1 \approx \pi^* 2p_y^1$$

Due to the presence of two unpaired electrons, O_2 and S_2 both are paramagnetic molecules.

24. Statement I is correct, given structure is one of the resonance structure of ozone.



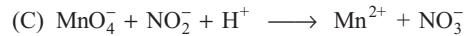
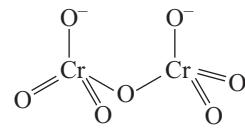
Statement II is also correct because oxygen cannot expand its octet. It is also the explanation for the given structure of ozone.

25. (A) In the reaction : $O_2^- \rightarrow O_2 + O_2^{2-}$

Oxygen on reactant side is in $-1/2$ oxidation state. In product side, one of the oxygen is in zero oxidation state, i.e. oxidised while the other oxygen is in -1 oxidation

state, i.e. reduced. Hence, in the above reaction, oxygen ($O^{-1/2}$) is simultaneously oxidised and reduced disproportionated.

- (B) In acidic medium, CrO_4^{2-} is converted into $Cr_2O_7^{2-}$ which is a dimeric, bridged tetrahedral.

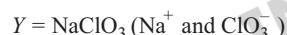
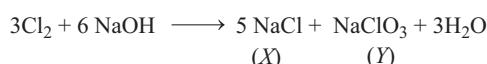


The above is a redox reaction and a product NO_3^- has trigonal planar structure.

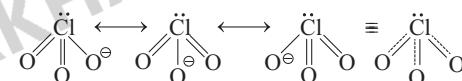


The above is a redox reaction.

26. The reaction is,



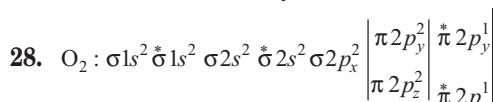
The structure of ClO_3^- (chlorate ion) is,



'Cl—O' bond order in the hybrid

$$= \frac{\text{Number of bonds between Cl and O}}{\text{Total number of O (surrounding atoms)}} \\ = \frac{5}{3} = 1.66 \text{ or } 1.67$$

27. $H_2, Li_2, Be_2, C_2, N_2$ and F_2 are diamagnetic according to molecular orbital theory.



$$\text{Bond order} = \frac{10 - 6}{2} = 2, \text{ paramagnetic.}$$

29. Strength of hydrogen bonding in $X-H-X$ depends on electronegativity as well as size of X . X with higher electronegativity and smaller size forms stronger H-bond. Hence, increasing order of strength of H-bond is



30. Resonance in vinyl chloride increases polar character of the molecule.

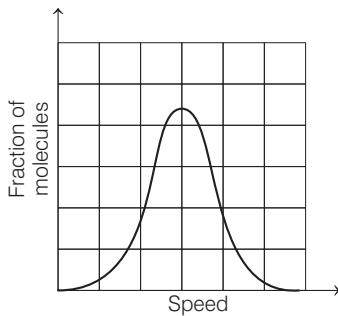
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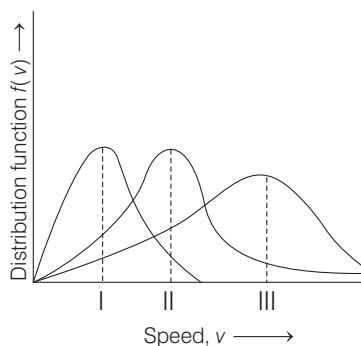
Topic 1 Gaseous State

Objective Questions I (Only one correct option)

1. If the distribution of molecular speeds of a gas is as per the figure shown below, then the ratio of the most probable, the average, and the root mean square speeds, respectively, is
 (2020 Adv.)



- (a) $1 : 1 : 1$
 (b) $1 : 1 : 1.224$
 (c) $1 : 1.128 : 1.224$
 (d) $1 : 1.128 : 1$
2. For one mole of an ideal gas, which of these statements must be true?
 (2020 Main, 4 Sep I)
- (A) U and H each depends only on temperature.
 (B) Compressibility factor Z is not equal to 1.
 (C) $C_{p,m} - C_{V,m} = R$
 (D) $dU = C_V dT$ for any process.
- (a) (B), (C) and (D)
 (b) (A) and (C)
 (c) (A), (C) and (D)
 (d) (C) and (D)
3. Points I, II and III in the following plot respectively correspond to $(v_{mp} : \text{most probable velocity})$
 (2019 Main, 10 April II)



- (a) v_{mp} of $\text{H}_2(300\text{ K})$; v_{mp} of $\text{N}_2(300\text{ K})$; v_{mp} of $\text{O}_2(400\text{ K})$
 (b) v_{mp} of $\text{O}_2(400\text{ K})$; v_{mp} of $\text{N}_2(300\text{ K})$; v_{mp} of $\text{H}_2(300\text{ K})$
 (c) v_{mp} of $\text{N}_2(300\text{ K})$; v_{mp} of $\text{O}_2(400\text{ K})$; v_{mp} of $\text{H}_2(300\text{ K})$
 (d) v_{mp} of $\text{N}_2(300\text{ K})$; v_{mp} of $\text{H}_2(300\text{ K})$; v_{mp} of $\text{O}_2(400\text{ K})$

4. Consider the following table.

Gas	$a/(k\text{ Pa dm}^6\text{ mol}^{-1})$	$b/(\text{dm}^3\text{ mol}^{-1})$
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

a and b are van der Waals' constants. The correct statement about the gases is
 (2019 Main, 10 April I)

- (a) gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D
 (b) gas C will occupy more volume than gas A; gas B will be more compressible than gas D
 (c) gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D
 (d) gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D

5. At a given temperature T , gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour. Their equation of state is given as, $p = \frac{RT}{V-b}$ at T .

Here, b is the van der Waals' constant. Which gas will exhibit steepest increase in the plot of Z (compression factor) vs p ?
 (2019 Main, 9 April II)

- (a) Xe (b) Ar (c) Kr (d) Ne

6. Consider the van der Waals' constants, a and b , for the following gases.

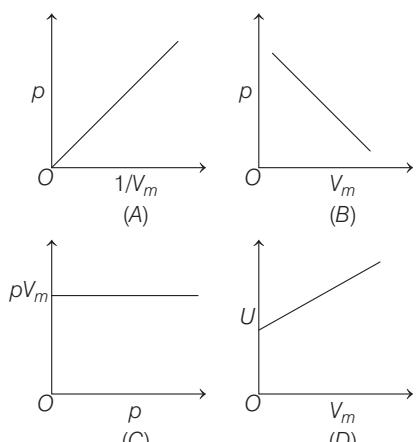
Gas	Ar	Ne	Kr	Xe
$a/(\text{atm dm}^6\text{ mol}^{-2})$	1.3	0.2	5.1	4.1
$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$	3.2	1.7	1.0	5.0

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Which gas is expected to have the highest critical temperature? (2019 Main, 9 April I)

- (a) Kr (b) Xe (c) Ar (d) Ne

7. The combination of plots which does not represent isothermal expansion of an ideal gas is (2019 Main, 12 Jan II)



- (a) (A) and (C) (b) (B) and (C)
(c) (B) and (D) (d) (A) and (D)

8. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is (2019 Main, 12 Jan II)

- (a) 750 K (b) 500 K
(c) 750°C (d) 500°C

9. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are (2019 Main, 12 Jan I)

- (a) $p_A = 2p_B$ (b) $2p_A = 3p_B$
(c) $p_A = 3p_B$ (d) $3p_A = 2p_B$

10. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 mL of CO_2 at $T = 298.15\text{ K}$ and $p = 1\text{ bar}$. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet?

[Molar mass of $\text{NaHCO}_3 = 84\text{ g mol}^{-1}$] (2019 Main, 11 Jan I)

- (a) 8.4 (b) 0.84 (c) 16.8 (d) 33.6

11. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 m^3 at 1000 K. Given R is the gas constant in $\text{JK}^{-1}\text{ mol}^{-1}$, x is (2019 Main, 9 Jan I)

- (a) $\frac{2R}{4-R}$ (b) $\frac{4-R}{2R}$ (c) $\frac{4+R}{2R}$ (d) $\frac{2R}{4+R}$

12. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the

figure below. The temperature of one of the bulbs is then raised to T_2 . The final pressure p_f is (2016 Main)

- (a) $2p_i\left(\frac{T_1}{T_1+T_2}\right)$ (b) $2p_i\left(\frac{T_2}{T_1+T_2}\right)$
(c) $2p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ (d) $p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$

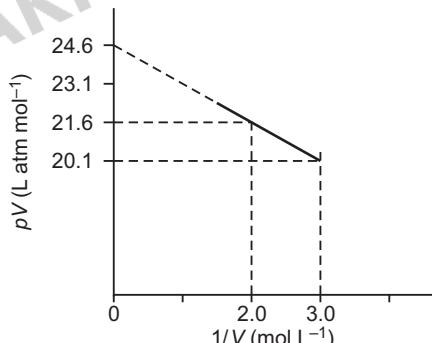
13. If Z is a compressibility factor, van der Waals' equation at low pressure can be written as (2014 Main)

- (a) $Z = 1 + \frac{RT}{pb}$ (b) $Z = 1 - \frac{a}{VRT}$
(c) $Z = 1 - \frac{pb}{RT}$ (d) $Z = 1 + \frac{pb}{RT}$

14. For gaseous state, if most probable speed is denoted by C^* , average speed by \bar{C} and root square speed by C , then for a large number of molecules, the ratios of these speeds are

- (a) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$ (2013 Main)
(b) $C^* : \bar{C} : C = 1.128 : 1.225 : 1$
(c) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$
(d) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$

15. For one mole of a van der Waals' gas when $b = 0$ and $T = 300\text{ K}$, the pV vs $1/V$ plot is shown below. The value of the van der Waals' constant a (atm L mol^{-2}) (2012)

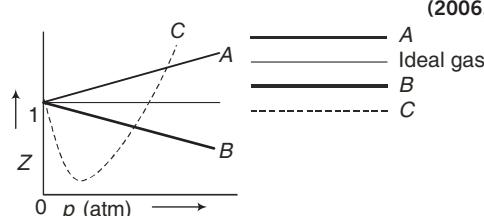


- (a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0

16. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is (2009)

- (a) nb (b) n^2a/V^2
(c) $-(n^2a/V^2)$ (d) $-nb$

17. The given graph represent the variations of Z (compressibility factor ($Z = pV/nRT$)) versus p , for three real gases A, B and C. Identify the only incorrect statement. (2006, 5M)



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35. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be (1988, 1M)
- at the centre of the tube
 - near the hydrogen chloride bottle
 - near the ammonia bottle
 - throughout the length of the tube
36. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular forces is (1988, 1M)
- $(V - b)$
 - RT
 - $\left(p + \frac{a}{V^2} \right)$
 - $(RT)^{-1}$
37. The average velocity of an ideal gas molecule at 27°C is 0.3 m/s. The average velocity at 927°C will be (1986, 1M)
- 0.6 m/s
 - 0.3 m/s
 - 0.9 m/s
 - 3.0 m/s
38. Rate of diffusion of a gas is (1985, 1M)
- directly proportional to its density
 - directly proportional to its molecular weight
 - directly proportional to the square root of its molecular weight
 - inversely proportional to the square root of its molecular weight
39. Equal weights of methane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is (1984, 1M)
- $\frac{1}{2}$
 - $\frac{8}{9}$
 - $\frac{1}{9}$
 - $\frac{16}{17}$
40. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules (1984, 1M)
- are above the inversion temperature
 - exert no attractive forces on each other
 - do work equal to loss in kinetic energy
 - collide without loss of energy
41. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is (1982, 1M)
- two times that of a hydrogen molecule
 - same as that of a hydrogen molecule
 - four times that of a hydrogen molecule
 - half that of a hydrogen molecule
42. Equal weights of methane and oxygen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by oxygen is (1981, 1M)
- $\frac{1}{3}$
 - $\frac{1}{2}$
 - $\frac{2}{3}$
 - $\frac{1}{3} \times \frac{273}{298}$
43. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is (1981, 1M)
- critical temperature
 - Boyle temperature
 - inversion temperature
 - reduced temperature
44. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is (1981, 1M)
- 1.085 : 1
 - 1 : 1.086
 - 2 : 1.086
 - 1.086 : 2

Objective Questions II

(One or more than one correct option)

45. Which of the following statement(s) is(are) correct regarding the root mean square speed (U_{rms}) and average translational kinetic energy (E_{av}) of a molecule in a gas at equilibrium? (2019 Adv.)
- U_{rms} is inversely proportional to the square root of its molecular mass
 - U_{rms} is doubled when its temperature is increased four times
 - E_{av} is doubled when its temperature is increased four times
 - E_{av} at a given temperature does not depend on its molecular mass
46. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where, b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for gas is given by (2015 Adv.)
-
47. According to kinetic theory of gases (2011)
- collisions are always elastic
 - heavier molecules transfer more momentum to the wall of the container
 - only a small number of molecules have very high velocity
 - between collisions, the molecules move in straight lines with constant velocities
48. A gas described by van der Waals' equation (2008, 4M)
- behaves similar to an ideal gas in the limit of large molar volumes
 - behaves similar to an ideal gas in the limit of large pressures
 - is characterised by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature
 - has the pressure that is lower than the pressure exerted by the same gas behaving ideally
49. If a gas is expanded at constant temperature (1986, 1M)
- the pressure decreases
 - the kinetic energy of the molecules remains the same
 - the kinetic energy of the molecules decreases
 - the number of molecules of the gas increases

Numerical Answer Type Questions

50. A spherical balloon of radius 3 cm containing helium gas has a pressure of 48×10^{-3} bar. At the same temperature, the pressure, of a spherical balloon of radius 12 cm containing the same amount of gas will be $\times 10^{-6}$ bar. (2020 Main, 6 Sep I)

51. A closed tank has two compartments *A* and *B*, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Fig. 1). If the old partition is replaced by a new partition which can slide and conduct heat but does not allow the gas to leak across (Fig. 2), the volume (in m^3) of the compartment *A* after the system attains equilibrium is ____.

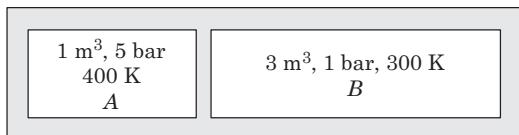


Fig. 1

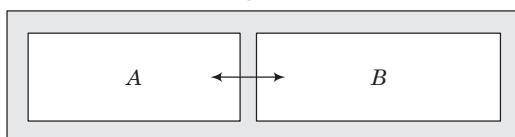


Fig. 2

(2018 Adv.)

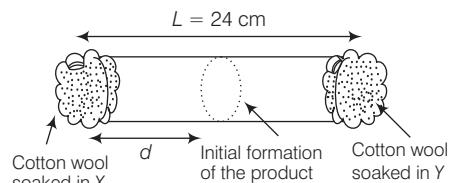
Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
 (c) Statement I is correct; Statement II is incorrect
 (d) Statement I is incorrect; Statement II is correct
52. **Statement I** The pressure of a fixed amount of an ideal gas is proportional to its temperature.
Statement II Frequency of collisions and their impact both increase in proportion to the square root of temperature. (2000)
53. **Statement I** The value of van der Waals' constant '*a*' is larger for ammonia than for nitrogen.
Statement II Hydrogen bonding is present in ammonia. (1998)

Passage Based Questions

X and *Y* are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in *X* and the other soaked in *Y*, are simultaneously placed at the ends of a tube of length $L = 24 \text{ cm}$, as shown in the figure.



The tube is filled with an inert gas at 1 atm pressure and a temperature of 300 K. Vapours of *X* and *Y* react to form a product which is first observed at a distance *d* cm from the plug soaked in *X*. Take *X* and *Y* to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours. (2014 Adv.)

54. The experimental value of *d* is found to be smaller than the estimate obtained using Graham's law. This is due to
 (a) larger mean free path for *X* as compared of that of *Y*
 (b) larger mean free path for *Y* as compared to that of *X*
 (c) increased collision frequency of *Y* with the inert gas as compared to that of *X* with the inert gas
 (d) increased collision frequency of *X* with the inert gas as compared to that of *Y* with the inert gas
55. The value of *d* in cm (shown in the figure), as estimated from Graham's law, is
 (a) 8 (b) 12 (c) 16 (d) 20

Match the Column

56. Match the gases under specified conditions listed in Column I with their properties/laws in Column II.

Column I	Column II
A. Hydrogen gas ($p = 200 \text{ atm}$, $T = 273 \text{ K}$)	p. compressibility factor $\neq 1$
B. Hydrogen gas ($p \sim 0$, $T = 273 \text{ K}$)	q. attractive forces are dominant
C. CO_2 ($p = 1 \text{ atm}$, $T = 273 \text{ K}$)	r. $pV = nRT$
D. Real gas with very large molar volume	s. $p(V - nb) = nRT$

(2007, 6M)

Fill in the Blanks

57. The absolute temperature of an ideal gas is to/than the average kinetic energy of the gas molecules. (1997, 1M)
 58. 8 g each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of (1989, 1M)
 59. The value of pV for 5.6 L of an ideal gas is RT , at NTP. (1987, 1M)
 60. The rate of diffusion of a gas is proportional to both and square root of molecular mass. (1986, 1M)
 61. $C_p - C_V$ for an ideal gas is (1984, 1M)
 62. The total energy of one mole of an ideal monoatomic gas at 27°C is cal. (1984, 1M)

True / False

63. A mixture of ideal gases is cooled up to liquid helium temperature (4.22 K) to form an ideal solution. (1996, 1M)
 64. In the van der Waals' equation, $\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$ the constant '*a*' reflects the actual volume of the gas molecules. (1993, 1M)
 65. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (1985, 1/2 M)
 66. Kinetic energy of a molecule is zero at 0°C . (1985, 1/2 M)

Integer Answer Type Questions

67. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of

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an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is ... (2016 Adv.)

68. A closed vessel with rigid walls contains 1 mole of $^{238}_{92}\text{U}$ and 1 mole of air at 298 K. Considering complete decay of $^{238}_{92}\text{U}$ to $^{206}_{82}\text{Pb}$, the ratio of the final pressure to the initial pressure of the system at 298 K is (2015 Adv.)

69. If the value of Avogadro number is $6.023 \times 10^{-23} \text{ mol}^{-1}$ and the value of Boltzmann constant is $1.380 \times 10^{-23} \text{ JK}^{-1}$, then the number of significant digits in the calculated value of the universal gas constant is (2014 Adv.)

70. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mole of He and 1.0 mole of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to (2011)

Subjective Questions

71. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is (2009)

72. The average velocity of gas molecules is 400 m s^{-1} , find the rms velocity of the gas. (2003, 2M)

73. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3} . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

- (i) Determine, (a) molecular weight (b) molar volume (c) compression factor (Z) of the vapour and (d) which forces among the gas molecules are dominating, the attractive or the repulsive?
(ii) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy of a molecule. (2002, 5M)

74. The compression factor (compressibility factor) for one mole of a van der Waals' gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant ' a '. (2001, 5M)

75. Calculate the pressure exerted by one mole of CO_2 gas at 273 K if the van der Waals' constant $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$. Assume that the volume occupied by CO_2 molecules is negligible. (2000)

76. (i) One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pin-hole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.
(ii) The pressure exerted by 12 g of an ideal gas at temperature $t^\circ\text{C}$ in a vessel of volume V litre is one atm. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V .
(Molecular weight of the gas = 120) (1999, 5M)

77. Using van der Waals' equation, calculate the constant a when two moles of a gas confined in a four litre flask exert a pressure of 11.0 atm at a temperature of 300 K. The value of b is 0.05 L mol^{-1} . (1998, 4M)

78. An evacuated glass vessel weighs 50.0 g when empty 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molar mass of the gas. (1998, 3M)

79. A mixture of ideal gases is cooled up to liquid helium temperature (4.22 K) to form an ideal solution. Is this statement true or false? Justify your answer in not more than two lines. (1996, 1M)

80. The composition of the equilibrium mixture ($\text{Cl}_2 \rightleftharpoons 2\text{Cl}$) which is attained at 1200°C , is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (atomic weight of Kr = 84) (1995, 4M)

81. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 L at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O . Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. (1995, 4M)

82. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C , the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to the *n*-butane with normal boiling point of 0°C. (1994, 3M)

83. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially? (1994, 2M)

84. A gas bulb of 1 L capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3 \text{ Nm}^{-2}$. Calculate the root mean square (rms) speed and the temperature of the gas molecules. If the ratio of the most probable speed to root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature. (1993, 4M)

85. At room temperature, the following reaction proceed nearly to completion. $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4$
The dimer, N_2O_4 , solidifies at 262 K. A 250 mL flask and a 100 mL flask are separated by a stopcock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm.

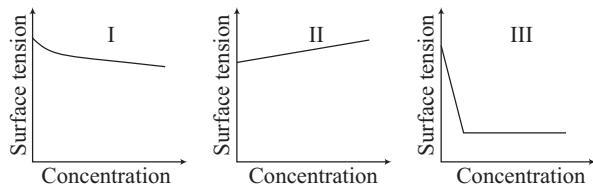
The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled to 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally). (1992, 4M)

86. At 27°C , hydrogen is leaked through a tiny hole into a vessel for 20 min. Another unknown gas at the same temperature and pressure as that of hydrogen is leaked through same hole for 20 min. After the effusion of the gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 L. What is the molecular weight of the unknown gas? (1992, 3M)
87. Calculate the volume occupied by 5.0 g of acetylene gas at 50°C and 740 mm pressure. (1991, 2M)
88. The average velocity at T_1 K and the most probable at T_2 K of CO_2 gas is $9.0 \times 10^4 \text{ cm s}^{-1}$. Calculate the value of T_1 and T_2 (1990, 4M)
89. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm at 27°C . If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up. (1987, 5M)
90. Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure. (1985, 2M)
91. Give reasons for the following in one or two sentences.
- Equal volumes of gases contain equal number of moles. (1984, 1M)
 - A bottle of liquor ammonia should be cooled before opening the stopper. (1983, 1M)
92. Oxygen is present in one litre flask at a pressure of 7.6×10^{-10} mm Hg. Calculate the number of oxygen molecules in the flask at 0°C . (1983, 2M)
93. When 2 g of a gas A is introduced into an evacuated flask kept at 25°C , the pressure is found to be one atmosphere. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$. (1983, 2M)
94. At room temperature, ammonia gas at 1 atm pressure and hydrogen chloride gas at p atm pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of one metre length and of uniform cross-section. Ammonium chloride is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of p ? (1982, 4M)
95. Calculate the average kinetic energy, in joule per molecule in 8.0 g of methane at 27°C . (1982, 2M)
96. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 min when the contained oxygen leaked through a small hole. The bulb was then evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min. (1981, 3M)
97. A hydrocarbon contains 10.5 g of carbon per gram of hydrogen. 1 L of the vapour of the hydrocarbon at 127°C and 1 atm pressure weighs 2.8 g. Find the molecular formula of the hydrocarbon. (1980, 3M)
98. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas? (1979, 2M)
99. 4.215 g of a metallic carbonate was heated in a hard glass tube, the CO_2 evolved was found to measure 1336 mL at 27°C and 700 mm of Hg pressure. What is the equivalent weight of the metal? (1979, 3M)
100. Calculate the density of NH_3 at 30°C and 5 atm pressure. (1978, 2M)

Topic 2 Liquid State

Objective Questions I (Only one correct option)

1. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl , CH_3OH and $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ at room temperature. (2016 Adv.)



The correct assignment of the sketches is

- | I | II | III |
|---|---|---|
| (a) KCl | CH_3OH | $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ |
| (b) $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ | CH_3OH | KCl |
| (c) KCl | $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ | CH_3OH |
| (d) CH_3OH | KCl | $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ |

2. At 100°C and 1 atm if the density of the liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3} , then the volume occupied by water molecules in 1 L of steam at this temperature is (2000, 1M)
- 6 cm^3
 - 60 cm^3
 - 0.6 cm^3
 - 0.06 cm^3
3. The critical temperature of water is higher than that of O_2 because the H_2O molecule has (1997)
- fewer electrons than O_2
 - two covalent bonds
 - V-shape
 - dipole moment
4. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal
- inter-molecular forces
 - potential energy
 - kinetic energy
 - total energy

Answers

Topic 1

- | | | | | |
|---------------|-----------|------------|-----------|---|
| 1. (b) | 2. (c) | 3. (c) | 4. (b) | 56. ($A \rightarrow p, s; B \rightarrow r; C \rightarrow p, q; D \rightarrow r$) |
| 5. (a) | 6. (a) | 7. (c) | 8. (b) | 57. (less) 58. (1 : 16) 59. (0.25) |
| 9. (b) | 10. (a) | 11. (b) | 12. (b) | 60. (inversely, time) 61. (R) 62. (900) |
| 13. (b) | 14. (c) | 15. (c) | 16. (b) | 63. (F) 64. (F) 65. (F) 66. (F) |
| 17. (b) | 18. (a) | 19. (a) | 20. (a) | 67. (4) 68. (9) 69. (4) 70. (7 L) |
| 21. (c) | 22. (d) | 23. (b) | 24. (c) | 71. (4) 72. 435 ms^{-1} 74. (1.25) 75. (0.99 atm) |
| 25. (c) | 26. (c) | 27. (b) | 28. (c) | 77. (6.46) 78. (123 g mol^{-1}) 80. (0.14) |
| 29. (d) | 30. (a) | 31. (d) | 32. (a) | 82. (2.46 m^3) 83. (8:1) 84. (407 ms^{-1}) 85. (0.221 atm) |
| 33. (b) | 34. (c) | 35. (b) | 36. (c) | 86. (1020 g mol^{-1}) 87. (5.23 L) 89. (10) |
| 37. (a) | 38. (d) | 39. (b) | 40. (b) | 90. (390.2 ms^{-1}) 92. ($2.7 \times 10^{10} \text{ g mol}^{-1}$) |
| 41. (b) | 42. (a) | 43. (b) | 44. (a) | 93. (1 : 3) 94. (2.20 atm) 95. ($6.2 \times 10^{-21} \text{ J/molecule}$) |
| 45. (a, b, d) | 46. (c) | 47. (a) | 48. (a,c) | 98. (41.32 g) 99. (12.15) 100. (3.42 gL^{-1}) |
| 49. (a,b) | 50. (750) | 51. (2.22) | 52. (d) | |
| 53. (a) | 54. (d) | 55. (c) | | |

Topic 2

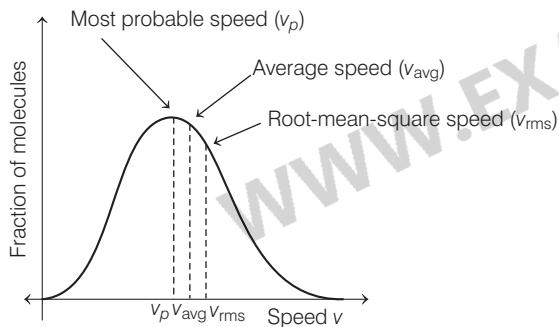
1. (d) 2. (c) 3. (d) 4. (c)

Hints & Solutions

Topic 1 Gaseous State

1. Fraction of molecules vs velocity graph is Maxwell distribution curve.

This curve is slightly unsymmetrical as shown below.



The ratio of most probable, the average and the root mean square speeds for this graph is 1 : 1.128 : 1.224

But the graph in question is completely symmetrical. Therefore, the most probable and the average speed will be same here but root mean square speed will be greater than average speed. So, the correct ratio is 1 : 1 : 1.224.

2. Statements (A), (C) and (D) are true whereas (B) is false.
 (A) For 1 mole, U = internal energy and H = enthalpy.
 Heat capacity at constant volume.

$$nC_V = \frac{dU}{dT}$$

$$dU = nC_V dT \quad (n = 1 \text{ mol})$$

$$dU = 1 \times C_V \times dT \quad (\because C_V = \text{constant})$$

$$U = f(T) \quad (\text{Function of temperature})$$

U depends on temperature.

Heat capacity at constant volume,

$$nC_p = \frac{dH}{dT}$$

$$dH = nC_p dT \quad [n = 1 \text{ mol}]$$

$$dH = 1 \times C_p \times dT$$

In mathematical term,

$$H = f(T) \quad [\because C_p = \text{constant}]$$

Hence, H depends on function of temperature

- (b) Compressibility factor (Z) describe the deviation of real gas from ideal gas behaviour.

$$Z = \frac{pV}{RT} \quad \dots(i)$$

For ideal gas,

$$pV = nRT \quad [n = 1 \text{ mol}]$$

$$pV = RT \quad \dots(ii)$$

Put in the value of pV from Eq. (ii) to Eq. (i)

$$Z = \frac{RT}{RT} = 1$$

Compressibility factor is 1 for ideal gas then option (b) is incorrect.

- (c) For ideal gas,

$$C_p - C_V = nR \quad (n = 1 \text{ mol})$$

$$C_p - C_V = R$$

It is correct statement.

- (d) $\Delta U = C_V dT$
- $$nC_V = \frac{dU}{dT}$$
- $$dU = nC_V dT \quad (n = 1 \text{ mol})$$
- $$dU = C_V dT$$

It is also correct.

3.

Key Idea From kinetic gas equation,

$$\text{Most probable velocity } (v_{\text{mp}}) = \sqrt{\frac{2RT}{M}}$$

where, R = gas constant, T = temperature,
 M = molecular mass

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}}, \text{ i.e. } v_{\text{mp}} \propto \sqrt{\frac{T}{M}}$$

Gas	M	$T(K)$	$\sqrt{T/M}$
H_2	2	300	$\sqrt{300/2} = \sqrt{150}$... III (Highest)
N_2	28	300	$\sqrt{300/28} = \sqrt{10.71}$... I (Lowest)
O_2	32	400	$\sqrt{400/32} = \sqrt{12.5}$... II

So,

- I. corresponds to v_{mp} of N_2 (300 K)
- II. corresponds to v_{mp} of O_2 (400 K)
- III. corresponds to v_{mp} of H_2 (300 K)

4. For 1 mole of a real gas, the van der Waals' equation is

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT$$

The constant ' a ' measures the intermolecular force of attraction of gas molecules and the constant ' b ' measures the volume correction by gas molecules after a perfectly inelastic binary collision of gas molecules.

For gas A and gas C given value of ' b ' is $0.05196 \text{ dm}^3 \text{ mol}^{-1}$. Here,

$a \propto$ intermolecular force of attraction

\propto compressibility \propto real nature

$$\propto \frac{1}{\text{volume occupied}}$$

Value of $a/(\text{kPa dm}^6 \text{ mol}^{-1})$ for gas A (642.32) > gas C (431.91). So, gas C will occupy more volume than gas A . Similarly, for a given value of a say $155.21 \text{ kPa dm}^6 \text{ mol}^{-1}$ for gas B and gas D

$\frac{1}{b} \propto$ intermolecular force of attraction
 b

\propto compressibility \propto real nature

$$\propto \frac{1}{\text{volume occupied}}$$

$b/(\text{dm}^3 \text{ mol}^{-1})$ for gas B (0.04136) < Gas D (0.4382)

So, gas B will be more compressible than gas D .

5. Noble gases such as Ne, Ar, Xe and Kr found to deviate from ideal gas behaviour.

Xe gas will exhibit steepest increase in plot of Z vs p .

Equation of state is given as:

$$p = \frac{RT}{(V - b)} \Rightarrow p(V - b) = RT$$

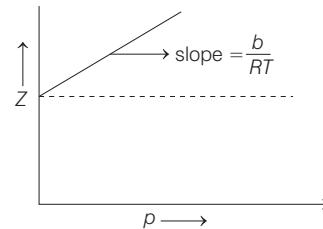
$$pV - pb = RT \Rightarrow pV = RT + pb$$

$$\frac{pV}{RT} = 1 + \frac{pb}{RT}$$

$$\text{As, } Z = \frac{pV}{RT}$$

$$\text{so, } Z = 1 + \frac{pb}{RT} \Rightarrow y = c + mx$$

The plot of Z vs p is found to be



The gas with high value of b will be steepest as slope is directly proportional to b . b is the van der Waals' constant and is equal to four times the actual volume of the gas molecules. Xe gas possess the largest atomic volume among the given noble gases (Ne, Kr, Ar). Hence, it gives the steepest increase in the plot of Z (compression factor) vs p .

6. Critical temperature is the temperature of a gas above which it cannot be liquefied whatever high the pressure may be. The kinetic energy of gas molecules above this temperature is sufficient enough to overcome the attractive forces. It is represented as T_c .

$$T_c = \frac{8a}{27Rb}$$

$$\text{For Ar, } T_c = \frac{8 \times 1.3}{27 \times 8.314 \times 3.2} = 0.0144$$

$$\text{For Ne, } T_c = \frac{8 \times 0.2}{27 \times 8.314 \times 1.7} = 0.0041$$

$$\text{For Kr, } T_c = \frac{8 \times 5.1}{27 \times 8.314 \times 1.0} = 0.18$$

$$\text{For Xe, } T_c = \frac{8 \times 4.1}{27 \times 8.314 \times 5.0} = 0.02$$

The value of T_c is highest for Kr (Krypton).

7. In isothermal expansion, $pV_m = K$ (constant)

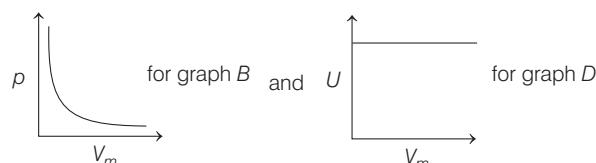
This relation is plotted in graph 'C'

$$\text{Likewise, } p = \frac{K}{V_m}$$

This relation is plotted in graph "A".

Thus, graph B and D are incorrect.

For them the correct graphs are:



8. Given, temperature (T_1) = $27^\circ C = 273 + 27 = 300 K$

Volume of vessel = constant

Pressure in vessel = constant

Volume of air reduced by $\frac{2}{5}$ so the remaining volume of air is $\frac{3}{5}$

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Let at T_1 the volume of air inside the vessel is n so at T_2 the volume of air will be $\frac{3}{5}n$.

Now, as p and V are constant, so

$$n \cdot T_1 = \frac{3}{5}n \cdot T_2 \quad \dots(i)$$

Putting the value of T_1 in equation (i) we get,

$$n \times 300 = \frac{3}{5}n \times T_2$$

$$\text{or} \quad T_2 = 300 \times \frac{5}{3} = 500 \text{ K}$$

9. Given, $Z_A = 3Z_B$

$$\text{Compressibility factor (Z)} = \frac{pV}{nRT} \quad [\text{for real gases}]$$

On substituting in equation (i), we get

$$\frac{p_A V_A}{n_A R T_A} = \frac{3 p_B V_B}{n_B R T_B} \quad \dots(ii)$$

Also, it is given that

$$V_A = 2V_B, n_A = n_B \text{ and } T_A = T_B$$

\therefore Eq. (ii) becomes

$$\begin{aligned} \frac{p_A \times 2V_B}{n_B R T_B} &= \frac{3 p_B V_B}{n_B R T_B} \\ \Rightarrow \quad 2p_A &= 3p_B \end{aligned}$$

10. $2\text{NaHCO}_3 + \text{H}_2\text{C}_2\text{O}_4 \longrightarrow 2\text{CO}_2 + \text{Na}_2\text{C}_4\text{O}_4 + \text{H}_2\text{O}$

\Rightarrow In the reaction, number of mole of CO_2 produced.

$$\begin{aligned} n &= \frac{pV}{RT} = \frac{1 \text{ bar} \times 0.25 \times 10^{-3} \text{ L}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= 1.02 \times 10^{-5} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Number of mole of NaHCO}_3 &= \frac{\text{Weight of NaHCO}_3}{\text{Molecular mass of NaHCO}_3} \\ \therefore w_{\text{NaHCO}_3} &= 1.02 \times 10^{-5} \times 84 \times 10^3 \text{ mg} \\ &= 0.856 \text{ mg} \\ \Rightarrow \text{NaHCO}_3 \% &= \frac{0.856}{10} \times 100 = 8.56\% \end{aligned}$$

11. From the ideal gas equation,

$$pV = \Sigma nRT \quad \dots(i)$$

Given: $p = 200 \text{ Pa}, V = 10 \text{ m}^3, T = 1000 \text{ K}$

$$n_A = 0.5 \text{ moles}, n_B = x \text{ moles}$$

On substituting the given values in equation (i), we get

$$\begin{aligned} 200 \times 10 &= (n_A + n_B) \times R \times 1000 \\ 0.5 + x &= \frac{200 \times 10}{R \times 1000} \\ \frac{1}{2} + x &= \frac{2}{R} = \frac{2}{R} - \frac{1}{2} = \frac{4-R}{2R} \end{aligned}$$

12. Initially,

$$\text{Number of moles of gases in each container} = \frac{p_i V}{RT_1}$$

$$\text{Total number of moles of gases in both containers} = 2 \frac{p_i V}{RT_1}$$

$$\text{After mixing, number of moles in left chamber} = \frac{p_f V}{RT_1}$$

$$\text{Number of moles in right chamber} = \frac{p_f V}{RT_2}$$

$$\text{Total number of moles} = \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2} = \frac{p_f V}{R} \left(\frac{1}{T_1} + \frac{1}{T_2} \right)$$

As total number of moles remains constant.

$$\text{Hence, } \frac{2p_i V}{RT_1} = \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2} \Rightarrow p_f = 2p_i \left(\frac{T_2}{T_1 + T_2} \right)$$

13. PLAN To solve this problem, the stepwise approach required, i.e.

(i) Write the van der Waals' equation, then apply the condition that at low pressure, volume become high,
i.e. $V - b \approx V$

(ii) Now calculate the value of compressibility factor (Z).
[$Z = pV / RT$]

According to van der Waals' equation,

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT$$

$$\text{At low pressure, } \left(p + \frac{a}{V^2} \right) V = RT$$

$$\Rightarrow pV + \frac{a}{V} = RT \text{ or } pV = RT - \frac{a}{V}$$

$$\text{Divide both side by } RT, \frac{pV}{RT} = 1 - \frac{a}{RTV}$$

$$14. C^* = \text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

$$\bar{C} = \text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

C = Root square speed corrected as root means square speed, i.e.

$$\text{rms} = \sqrt{\frac{3RT}{M}} \text{ and as we know } \bar{C} < \bar{C} < C$$

$$\bar{C} : \bar{C} : C = 1 : \sqrt{\frac{4}{p}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225$$

NOTE

As no option correspond to root square speed, it is understood as misprint. It should be root mean square speed.

15. The van der Waals' equation of state is

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

For one mole and when $b = 0$, the above equation condenses to

$$\left(p + \frac{a}{V^2} \right) V = RT$$

$$\Rightarrow pV = RT - \frac{a}{V} \quad \dots(i)$$

Eq. (i) is a straight equation between pV and $\frac{1}{V}$ whose slope is ' $-a'$. Equating with slope of the straight line given in the graph.

$$-a = \frac{20.1 - 21.6}{3 - 2} = -1.5 \Rightarrow a = 1.5$$

16. In the van der Waals' equation

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

The additional factor in pressure, i.e. $\frac{n^2 a}{V^2}$ corrects for intermolecular force while b corrects for molecular volume.

17. Option (b) is incorrect statement because at high pressure slope of the line will change from negative to positive.

$$\frac{r_{(\text{He})}}{r_{(\text{CH}_4)}} = \sqrt{\frac{16}{4}} = 2 : 1$$

19. Kinetic energy (E) = $\frac{3}{2} kT$

$$\text{RMS speed } (u) = \sqrt{\frac{3kT}{m}} \Rightarrow u = \sqrt{\frac{2E}{m}}$$

20. Positive deviation corresponds to $Z > 1$

$$\therefore Z = \frac{pV}{nRT}, \text{ for positive deviation, } \frac{pV}{nRT} > 1.$$

21. Option (b) and (d) are ruled out on the basis that at the initial point of 273 K, 1 atm, for 1.0 mole volume must be 22.4 L, and it should increase with rise in temperature.

Option (a) is ruled out on the basis that initial and final points are not connected by the ideal gas equation $V \propto T$, i.e. V/T do not have the same value at the two points.

In option (c), at the initial point, the volume is 22.4 L as required by ideal gas equation and (V/T) have the same value at both initial and final points.

22. Root mean square velocity (u_{rms}) = $\sqrt{\frac{3RT}{M}}$

Also, $p \cdot M = dRT$

Substituting for RT/M in u_{rms} expression gives,

$$u_{\text{rms}} = \sqrt{\frac{3p}{d}} \Rightarrow u_{\text{rms}} \propto \frac{1}{\sqrt{d}}$$

23. Compressibility factor (Z) = $\frac{V}{V_{\text{id}}} < 1$ (given)

$$\Rightarrow V < 22.4 \text{ L}$$

$$\therefore V_{\text{id}} \text{ (1 mol)} = 22.4 \text{ L at STP}$$

24. Root mean square speed $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$

$$\Rightarrow \frac{u_{\text{rms}}(\text{H}_2)}{u_{\text{rms}}(\text{N}_2)} = \sqrt{7} = \sqrt{\frac{T(\text{H}_2)}{2} \times \frac{28}{T(\text{N}_2)}} \Rightarrow 7 = \frac{14T(\text{H}_2)}{T(\text{N}_2)}$$

$$\Rightarrow T(\text{N}_2) = 2T(\text{H}_2) \text{ i.e. } T(\text{H}_2) < T(\text{N}_2)$$

25. At high temperature and low pressure, the gas volume is infinitely large and both intermolecular force as well as molecular volume can be ignored. Under this condition postulates of kinetic theory applies appropriately and gas approaches ideal behaviour.

26. Rate of effusion $\propto p_i$; $p_i = \text{Partial pressure of } i\text{th component}$

$$\propto \sqrt{\frac{1}{M}}$$

27. Compressibility factor (Z) = $\frac{V}{V_{\text{ideal}}} = 1$

\therefore For ideal gas $V = V_{\text{ideal}}$

28. Expression of rms is, $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$

$$\Rightarrow \frac{u_{\text{rms}}(\text{H}_2 \text{ at } 50 \text{ K})}{u_{\text{rms}}(\text{O}_2 \text{ at } 800 \text{ K})} = \frac{\sqrt{\frac{3R \times 50}{2}}}{\sqrt{\frac{3R \times 800}{32}}} = \sqrt{\frac{50}{2} \times \frac{32}{800}} = 1$$

29. Let x g of each gas is mixed.

$$\text{Mole of ethane} = \frac{x}{30}$$

$$\text{Mole of hydrogen} = \frac{x}{2}$$

$$\text{Mole fraction of hydrogen} = \frac{\frac{x}{2}}{\frac{x}{2} + \frac{x}{30}} = \frac{15}{16}$$

$$\Rightarrow \frac{\text{Partial pressure of H}_2}{\text{Total pressure}} = \text{Mole fraction of hydrogen} = 15 : 16$$

30. Average speed = $\sqrt{\frac{8RT}{\pi M}}$

i.e. at constant volume, for a fixed mass, increasing temperature increases average speeds and molecules collide more frequently to the wall of container leading to increase in gas pressure.

31. The mean translational kinetic energy (ϵ) of an ideal gas is $\epsilon = \frac{3}{2} k_B T$; T = Absolute temperature, i.e. $\epsilon \propto T$

$$32. \frac{r_{\text{CH}_4}}{r_X} = 2 = \sqrt{\frac{M_X}{16}} \Rightarrow M_X = 64$$

33. The ideal gas equation, $pV = nRT = \frac{w}{M} RT$

$$\Rightarrow pM = \left(\frac{w}{V} \right) RT = dRT \quad (d = \text{density})$$

$$\Rightarrow d = \frac{pM}{RT}$$

i.e. density will be greater at low temperature and high pressure.

34. The ease of liquefaction of a gas depends on their intermolecular force of attraction which in turn is measured in terms of van der Waals' constant a . Hence, higher the value of a , greater the intermolecular force of attraction, easier the liquefaction.

In the present case, NH_3 has highest a , can most easily be liquefied.

35. HCl will diffuse at slower rate than ammonia because rate of effusion $\propto \frac{1}{\sqrt{M}}$.

Therefore, ammonia will travel more distance than HCl in the same time interval and the two gas will first meet nearer to HCl end.

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36. In van der Waals' equation of state

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (\text{For 1 mole})$$

The first factor ($p + a/V^2$) correct for intermolecular force while the second term ($V - b$) correct for molecular volume.

37. Expression for average velocity is $u_{av} = \sqrt{\frac{8RT}{\pi M}}$

For the same gas but at different temperature

$$\frac{u_{avg}(T_1)}{u_{avg}(T_2)} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{300}{1200}} = \frac{1}{2}$$

$$\Rightarrow u_{av}(927^\circ\text{C}) = 2 \times u_{av}(27^\circ\text{C}) = 0.6 \text{ ms}^{-1}$$

38. Rate of effusion $\propto \frac{1}{\sqrt{M}}$,

39. Let x grams of each hydrogen and methane are mixed,

$$\text{Moles of H}_2 = \frac{x}{2}$$

$$\text{Moles of CH}_4 = \frac{x}{16}$$

$$\Rightarrow \text{Mole fraction of H}_2 = \frac{\frac{x}{2}}{\frac{x}{2} + \frac{x}{16}} = \frac{8}{9}$$

$$\Rightarrow \frac{\text{Partial pressure of H}_2}{\text{Total pressure}} = \text{Mole fraction of H}_2 = \frac{8}{9}$$

40. According to postulates of kinetic theory, there is no intermolecular attractions or repulsions between the molecules of ideal gases.

41. According to kinetic theory, average kinetic energy (E) = $\frac{3}{2}k_B T$

where, k_B is Boltzmann's constant. Since, it is independent of molar mass, it will be same for He and H₂ at a given temperature.

42. If x g of both oxygen and methane are mixed then :

$$\text{Mole of oxygen} = \frac{x}{32}$$

$$\text{Mole of methane} = \frac{x}{16}$$

$$\Rightarrow \text{Mole fraction of oxygen} = \frac{\frac{x}{32}}{\frac{x}{32} + \frac{x}{16}} = \frac{1}{3}$$

According to law of partial pressure

Partial pressure of oxygen (p_{O_2}) = Mole fraction \times Total pressure

$$\Rightarrow \frac{p_{O_2}}{p} = \frac{1}{3}$$

43. It is the Boyle temperature T_B . At Boyle temperature, the first virial coefficient (B) vanishes and real gas approaches ideal behaviour.

$$T_B = \frac{a}{Rb}$$

Here, a and b are van der Waals' constants.

44. The two types of speeds are defined as;

$$\text{Root mean square speed (}u_{rms}\text{)} = \sqrt{\frac{3RT}{M}}$$

$$\text{Average speed (}u_{av}\text{)} = \sqrt{\frac{8RT}{\pi M}}$$

For the same gas, at a given temperature, M and T are same, therefore

$$\begin{aligned} \frac{u_{rms}}{u_{av}} &= \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} \\ &= \sqrt{3} : \sqrt{\frac{8}{\pi}} = \sqrt{3} : \sqrt{2.54} = 1.085 : 1 \end{aligned}$$

45. The explanation of given statements are as follows:

- (a) U_{rms} is inversely proportional to the square root of its molecular mass.

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

Hence, option (a) is correct.

- (b) When temperature is increased four times then U_{rms} become doubled.

$$\begin{aligned} U_{rms} &= \sqrt{\frac{3R}{M} \times 4T} \\ U_{rms} &= 2 \times \sqrt{\frac{3RT}{M}} \end{aligned}$$

Hence, option (b) is correct.

(c) and (d) E_{av} is directly proportional to temperature but does not depends on its molecular mass at a given temperature as $E_{av} = \frac{3}{2}KT$. If temperature raised four times than E_{av} becomes four time multiple.

Thus, option (c) is incorrect and option (d) is correct.

46. Equation of state $p(V - b) = RT$ indicates absence of intermolecular attraction or repulsion, hence interatomic potential remains constant on increasing ' π ' in the beginning. As the molecules come very close, their electronic and nuclear repulsion increases abruptly.

47. (a) According to a postulate of kinetic theory of gases, collision between the molecules as well as with the wall of container is perfectly elastic in nature.

- (b) If a gas molecule of mass m moving with speed u collide to the wall of container, the change in momentum is $\Delta p = -2mu$. Therefore, heavier molecule will transfer more momentum to the wall as there will be greater change in momentum of the colliding gas molecule. However, this is not postulated in kinetic theory.

- (c) According to Maxwell-Boltzmann distribution of molecular speed, very few molecules have either very high or very low speeds. Most of the molecules moves in a specific, intermediate speed range.

- (d) According to kinetic theory of gases, a gas molecule moves in straight line unless it collide with another molecule or to the wall of container and change in momentum is observed only after collision.

48. Option (a) is correct because in the limit of large volume, both intermolecular force and molecular volume becomes negligible in comparison to volume of gas.

Option (b) is wrong statement because in the limit of large pressure $Z > 1$.

Option (c) is correct statement. For a van der Waals' gas, van der Waals' constants a and b are characteristic of a gas, independent of temperature.

Option (d) is wrong statement because Z can be either less or greater than unity, hence real pressure can be less or greater than ideal pressure.

49. Pressure is inversely proportional to volume at constant temperature, hence (a) is correct.

Average kinetic energy of a gas is directly proportional to absolute temperature, hence (b) is correct.

Expansion at constant temperature cannot change the number of molecules, hence (d) is incorrect.

50. Initial pressure (p_1) = 48×10^{-3} bar

Final pressure (p_2) = $\times 10^{-6}$ bar

$$\text{Initial volume } (V_1) = \frac{4}{3}\pi(3)^3$$

$$\text{Final volume } (V_2) = \frac{4}{3}\pi(12)^3$$

According to Boyle's law $p_1 V_1 = p_2 V_2$

$$p_2 = \frac{p_1 V_1}{V_2}$$

$$p_2 = \frac{48 \times 10^{-3} \times \frac{4}{3}\pi(3)^3}{\frac{4}{3}\pi(12)^3} = \frac{48 \times 10^{-3} \times (3)^3}{(12)^3}$$

$$= \frac{48 \times 10^{-3} \times 27}{1728} = 0.0277 \times 27 \times 10^{-3} = 750 \times 10^{-6} \text{ bar}$$

Hence, the correct answer is 750.

51. Given $p_1 = 5$ bar, $V_1 = 1 \text{ m}^3$, $T_1 = 400 \text{ K}$

$$\text{So, } n_1 = \frac{5}{400R} \quad (\text{from } pV = nRT)$$

$$\text{Similarly, } p_2 = 1 \text{ bar}, V_2 = 3 \text{ m}^3, T_2 = 300 \text{ K}, n_2 = \frac{3}{300R}$$

Let at equilibrium the new volume of A will be $(1+x)$

So, the new volume of B will be $(3-x)$

Now, from the ideal gas equation.

$$\frac{p_1 V_1}{n_1 R T_1} = \frac{p_2 V_2}{n_2 R T_2}$$

and at equilibrium (due to conduction of heat)

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\text{So, } \frac{V_1}{n_1} = \frac{V_2}{n_2} \text{ or } V_1 n_2 = V_2 n_1$$

After putting the values

$$(1+x) \times \frac{3}{300R} = (3-x) \times \frac{5}{400R} \text{ or } (1+x) = \frac{(3-x)5}{4}$$

$$\text{or } 4(1+x) = 15 - 5x \text{ or } 4 + 4x = 15 - 5x \text{ or } x = \frac{11}{9}$$

Hence, new volume of A i.e., $(1+x)$ will come as $1 + \frac{11}{9} = \frac{20}{9}$ or 2.22.

52. Assertion is incorrect because besides amount, pressure also depends on volume. However, reason is correct because both frequency of collisions and impact are directly proportional to root mean square speed which is proportional to square root of absolute temperature

53. a is the measure of intermolecular force of attraction. Greater the intermolecular force of attraction (H-bond in the present case) higher the value of a .

54. X is a lighter gas than Y , hence X has greater molecular speed. Due to greater molecular speed of X , it will have smaller mean free path and greater collision frequency with the incrt gas molecules. As a result X will take more time to travel a given distance along a straight line. Hence X and Y will meet at a distance smaller than one calculated from Graham's law.

Hence, (d) is the correct choice.

55. **PLAN** This problem can be solved by using the concept of Graham's law of diffusion according to which rate of diffusion of non-reactive gases under similar conditions of temperature and pressure are inversely proportional to square root of their density.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{\text{molar weight of gas}}}$$

Let distance covered by X is d , then distance covered by Y is $24-d$.

If r_X and r_Y are the rate of diffusion of gases X and Y ,

$$\frac{r_X}{r_Y} = \frac{d}{24-d} = \sqrt{\frac{40}{10}} = 2$$

[\because Rate of diffusion \propto distance travelled]

$$d = 48 - 2d$$

$$\Rightarrow 3d = 48 \Rightarrow d = 16 \text{ cm}$$

Hence, (c) is the correct choice.

56. A. At $p = 200$ atm, very high pressure, $Z > 1$. Also, at such a high pressure, the pressure correction factor $\left(\frac{n^2 a}{V^2}\right)$ can be ignored in comparison to p .

- B. At $p \sim 0$, gas will behave like an ideal gas, $pV = nRT$.

- C. CO_2 ($p = 1$ atm, $T = 273 \text{ K}$), $Z < 1$.

- D. At very large molar volume, real gas behaves like an ideal gas.

57. Less; $E = \frac{3}{2} RT$

58. 1 : 16, $\text{KE} = \frac{3}{2} nRT$. At same temperature, KE (total) $\propto n$.

59. 0.25 RT because at NTP, $5.6 \text{ L} = \frac{1}{4}$ mole.

60. Inversely, time.

61. For an ideal gas, $C_p - C_V = R$

62. At 27°C , $E = \frac{3}{2} RT = \frac{3}{2} \times 2 \times 300 = 900 \text{ cal}$

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63. An ideal gas cannot be liquefied because there exist no intermolecular attraction between the molecules of ideal gas.
64. a is the measure of intermolecular force.
65. In a close container, gas exert uniform pressure everywhere in the container.
66. $KE = \frac{3}{2} RT$ where, T is absolute temperature (in Kelvin).
67. (DC) Diffusion coefficient $\propto \lambda$ (mean free path) $\propto U_{\text{mean}}$

Thus (DC) $\propto \lambda U_{\text{mean}}$
But, $\lambda = \frac{RT}{\sqrt{2} N_0 \sigma p} \Rightarrow \lambda \propto \frac{T}{p}$

and $U_{\text{mean}} = \sqrt{\frac{8RT}{\pi M}}$

$U_{\text{mean}} \propto \sqrt{T}$
 $\therefore DC \propto \frac{(T)^{3/2}}{p}$

$$\begin{aligned} \frac{(\text{DC})_2}{(\text{DC})_1}(x) &= \left(\frac{p_1}{p_2} \right) \left(\frac{T_2}{T_1} \right)^{3/2} = \left(\frac{p_1}{2p_1} \right) \left(\frac{4T_1}{T_1} \right)^{3/2} \\ &= \left(\frac{1}{2} \right) (8) = 4 \end{aligned}$$

68. $^{92}\text{U}^{238} \longrightarrow {}_{82}\text{Pb}^{206} + 8 {}_2\text{He}^4(g) + 6 {}_{-1}\beta^0$
 $n(\text{gas})[\text{Initial}] = 1$ (air)
 $n(\text{gas})[\text{Final}] = 8(\text{He}) + 1(\text{air}) = 9$
 \Rightarrow At constant temperature and volume;

$p \propto n$
So, $\frac{p_f}{p_i} = \frac{n_f}{n_i} = \frac{9}{1} = 9$

69. **PLAN** This problem can be solved by using the concept involved in calculation of significant figure.

Universal gas constant, $R = kN_A$

where, k = Boltzmann constant

and N_A = Avogadro's number

$$\therefore R = 1.380 \times 10^{-23} \times 6.023 \times 10^{23} \text{ J/Kmol} = 8.31174 \approx 8.312$$

Since, k and N_A both have four significant figures, so the value of R is also rounded off upto 4 significant figures.

[When number is rounded off, the number of significant figure is reduced, the last digit is increased by 1 if following digits ≥ 5 and is left as such if following digits is ≤ 4 .]

Hence, correct integer is (4).

70. Since, the external pressure is 1.0 atm, the gas pressure is also 1.0 atm as piston is movable. Out of this 1.0 atm partial pressure due to unknown compound is 0.68 atm.

Therefore, partial pressure of He

$$= 1.00 - 0.68 = 0.32 \text{ atm.}$$

$$\Rightarrow \text{Volume} = \frac{n(\text{He})RT}{p(\text{He})} = \frac{0.1 \times 0.082 \times 273}{0.32} = 7 \text{ L}$$

\Rightarrow Volume of container = Volume of He.

71. Given, $u_{\text{rms}} = u_{\text{mps}}$
 $\Rightarrow \sqrt{\frac{3RT}{M(X)}} = \sqrt{\frac{2RT}{M(Y)}}$
 $\Rightarrow \frac{3R \times 400}{40} = \frac{2R \times 60}{M(Y)} \Rightarrow M(Y) = 4$

72. $\frac{u_{\text{av}}}{u_{\text{rms}}} = \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{\frac{8}{3\pi}}$
 $\Rightarrow u_{\text{rms}} = \sqrt{\frac{3\pi}{8}} u_{\text{av}} = \sqrt{\frac{3 \times 3.14}{8}} \times 400 = 434 \text{ ms}^{-1}$

73. $\frac{r_{\text{gas}}}{r_{\text{O}_2}} = 1.33 = \sqrt{\frac{32}{M_{\text{gas}}}}$
(i) (a) $M_{\text{gas}} = 18 \text{ g mol}^{-1}$
(b) $V_m = \frac{18}{0.36} = 50 \text{ L mol}^{-1}$
(c) $Z = \frac{pV}{RT} = \frac{1 \times 50}{0.082 \times 500} = 1.22$
(d) $\because Z > 1$, repulsive force is dominating.
(ii) $\bar{E}_k = \frac{3}{2} k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000 \text{ J} = 2.07 \times 10^{-20} \text{ J}$

74. In case of negligible molecular volume, $b = 0$. For 1 mole of gas

$$\begin{aligned} \left(p + \frac{a}{V^2} \right) V = RT &\Rightarrow pV + \frac{a}{V} = RT \\ \Rightarrow \frac{pV}{RT} + \frac{a}{VRT} &= 1 \quad \left[\because \frac{pV}{RT} = Z \right] \\ \Rightarrow Z + \frac{a}{\left(\frac{ZRT}{p} \right) RT} &= 1 \quad \Rightarrow Z + \frac{ap}{ZRT^2} = 1 \\ \Rightarrow a = \frac{ZRT^2(1-Z)}{p} &= \frac{0.5 (0.082 \times 273)^2 (1-0.5)}{100} \\ a &= 1.25 \text{ atm L}^2 \text{ mol}^{-2} \end{aligned}$$

75. In case of negligible molecular volume, $b = 0$ and van der Waals' equation reduces to

$$\begin{aligned} \left(p + \frac{n^2 a}{V^2} \right) V &= nRT \\ \Rightarrow p &= \frac{RT}{V} - \frac{a}{V^2} \quad (n = 1 \text{ mole}) \\ &= \frac{0.082 \times 273}{22.4} - \frac{3.592}{(22.4)^2} = 0.99 \text{ atm} \end{aligned}$$

76. (i) For the same amount of gas being effused

$$\begin{aligned} \frac{t_1}{t_2} = \frac{I_2}{I_1} &= \frac{p_1}{p_2} \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{57}{38} = \frac{0.8}{1.6} \sqrt{\frac{M_2}{28}} \\ \Rightarrow M_2 &= 252 \text{ g mol}^{-1} \end{aligned}$$

Also, one molecule of unknown xenon-fluoride contain only one Xe atom [$M(\text{Xe}) = 131$], formula of the unknown gas can be considered to be XeF_n .

$\Rightarrow 131 + 19n = 252$; $n = 6.3$, hence the unknown gas is XeF_6 .

- (ii) For a fixed amount and volume, $p \propto T$

$$\Rightarrow \frac{1}{1.1} = \frac{T}{T+10} \quad \text{where, } T = \text{Kelvin temperature}$$

$$\Rightarrow T = 100 \text{ K} = t + 273$$

$$\Rightarrow t = -173^\circ\text{C}$$

$$\text{Volume} = \frac{nRT}{p} = \left(\frac{12}{120} \right) \times \frac{0.082 \times 100}{1} = 0.82 \text{ L}$$

77. The van der Waals' equation is

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$\Rightarrow a = \frac{V^2}{n^2} \left[\frac{nRT}{V-nb} - p \right] = \frac{(4)^2}{(2)^2} \left[\frac{2 \times 0.082 \times 300}{4 - 2(0.05)} - 11 \right] = 6.46 \text{ atm L}^2 \text{ mol}^{-2}$$

78. Mass of liquid = $148 - 50 = 98 \text{ g}$

$$\Rightarrow \text{Volume of liquid} = \frac{98}{0.98} = 100 \text{ mL} = \text{volume of flask}$$

$$\text{mass of gas} = 50.5 - 50 = 0.50 \text{ g}$$

$$\text{Now applying ideal gas equation : } pV = \left(\frac{w}{M} \right) RT$$

$$\Rightarrow M = \frac{wRT}{pV} = \frac{0.5 \times 0.082 \times 300}{1 \times 0.1} = 123 \text{ g mol}^{-1}$$

79. False, ideal gas cannot be liquefied as there is no intermolecular attraction between the molecules of ideal gas. Hence, there is no point of forming ideal solution by cooling ideal gas mixture.

80. If ' α ' is the degree of dissociation, then at equilibrium



$$\text{Moles} \quad 1-\alpha \quad 2\alpha \quad \text{Total} = 1+\alpha$$

From diffusion information

$$\frac{r_{(\text{mix})}}{r_{(\text{Kr})}} = 1.16 = \sqrt{\frac{84}{M(\text{mix})}}$$

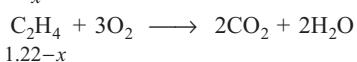
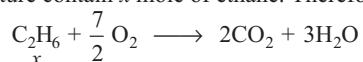
$$\Rightarrow M_{(\text{mix})} = 62.4$$

$$\Rightarrow M_{(\text{mix})} = \frac{71}{1+\alpha} = 62.4$$

$$\Rightarrow \alpha = 0.14$$

81. The total moles of gaseous mixture = $\frac{pV}{RT} = \frac{1 \times 40}{0.082 \times 400}$
 $= 1.22$

Let the mixture contain x mole of ethane. Therefore,



$1.22-x$

$$\text{Total moles of O}_2 \text{ required} = \frac{7}{2}x + 3(1.22-x) = \frac{x}{2} + 3.66$$

$$\Rightarrow \frac{130}{32} = \frac{x}{2} + 3.66$$

$$\Rightarrow x = 0.805 \text{ mole ethane and } 0.415 \text{ mole ethene.}$$

$$\Rightarrow \text{Mole fraction of ethane} = \frac{0.805}{1.22} = 0.66$$

$$\text{Mole fraction of ethene} = 1 - 0.66 = 0.34$$

82. Weight of butane gas in filled cylinder = $29 - 14.8 \text{ kg} = 14.2 \text{ kg}$

⇒ During the course of use, weight of cylinder reduces to 23.2 kg

⇒ Weight of butane gas remaining now = $23.2 - 14.8 = 8.4 \text{ kg}$
 Also, during use, V (cylinder) and T remains same.

$$\text{Therefore, } \frac{p_1}{p_2} = \frac{n_1}{n_2}$$

$$\Rightarrow p_2 = \left(\frac{n_2}{n_1} \right) p_1 = \left(\frac{8.4}{14.2} \right) \times 2.5 \quad \left[\text{Here, } \frac{n_2}{n_1} = \frac{w_2}{w_1} \right]$$

$$= 1.48 \text{ atm}$$

Also, pressure of gas outside the cylinder is 1.0 atm .

$$\Rightarrow pV = nRT$$

$$\Rightarrow V = \frac{nRT}{p} = \frac{(14.2 - 8.4) \times 10^3}{58} \times \frac{0.082 \times 30}{1} \text{ L}$$

$$= 2460 \text{ L} = 2.46 \text{ m}^3$$

$$83. \frac{r_{\text{He}}}{r_{\text{CH}_4}} = \frac{n_{\text{He}}}{n_{\text{CH}_4}} \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \frac{4}{1} \sqrt{\frac{16}{4}} = 8$$

Initial ratio of rates of effusion gives the initial composition of mixture effusing out. Therefore, $n(\text{He}) : n(\text{CH}_4) = 8 : 1$

$$84. \text{Number of moles} = \frac{2 \times 10^{21}}{6 \times 10^{23}} = 0.33 \times 10^{-2}$$

$$p = 7.57 \times 10^3 \text{ Nm}^{-2}$$

$$\text{Now, } pV = nRT$$

$$\Rightarrow T = \frac{pV}{nR} = \frac{7.57 \times 10^3 \times 10^{-3}}{0.33 \times 10^{-2} \times 8.314} = 276 \text{ K}$$

$$\Rightarrow u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 276}{28 \times 10^{-3}}} \text{ ms}^{-1} = 496 \text{ ms}^{-1}$$

$$\text{Also, } \frac{u_{\text{mps}}}{u_{\text{rms}}} = 0.82$$

$$\Rightarrow u_{\text{mps}} = 0.82 \times u_{\text{rms}} = 0.82 \times 496 \text{ ms}^{-1} = 407 \text{ ms}^{-1}$$

85. First we calculate partial pressure of NO and O_2 in the combined system when no reaction taken place.

$$pV = \text{constant} \Rightarrow p_1 V_1 = p_2 V_2$$

$$\Rightarrow p_2(\text{NO}) = \frac{1.053 \times 250}{350} = 0.752 \text{ atm}$$

$$p_2(\text{O}_2) = \frac{0.789 \times 100}{350} = 0.225 \text{ atm}$$

Now the reaction stoichiometry can be worked out using partial pressure because in a mixture.

$p_i \propto n_i$				
2NO	+	O_2	\longrightarrow	$2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4$
Initial	0.752 atm	0.225 atm	0	0
Final	0.302	0	0	0.225 atm

Now, on cooling to 220 K , N_2O_4 will solidify and only unreacted NO will be remaining in the flask.

$$\therefore p \propto T$$

$$\therefore \frac{p_1}{p_2} = \frac{T_1}{T_2}$$

$$\Rightarrow \frac{0.302}{p_2} = \frac{300}{220}$$

$$\Rightarrow p_2(\text{NO}) = 0.221 \text{ atm}$$

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86. Total moles of gas in final mixture = $\frac{pV}{RT} = \frac{6 \times 3}{0.082 \times 300} = 0.731$

\therefore Mole of H_2 in the mixture = 0.70

\therefore Mole of unknown gas (X) = 0.031

Because both gases have been diffused for same time

$$\frac{r(H_2)}{r(X)} = \frac{0.70}{0.031} = \sqrt{\frac{M}{2}} \Rightarrow M = 1020 \text{ g mol}^{-1}$$

87. $V = \frac{nRT}{p}$

For acetylene gas, $5 \text{ g} = \frac{5}{26} \text{ mol}$

$$p = 740 \text{ mm} = \frac{740}{760} \text{ atm}$$

$$T = 50^\circ\text{C} = 323 \text{ K}$$

Substituting in ideal gas equation

$$V = \frac{5}{26} \times \frac{0.082 \times 323}{74} \times 76 = 5.23 \text{ L}$$

88. u_{av} (average velocity) = $\sqrt{\frac{8RT_1}{\pi M}}$

$$\Rightarrow \frac{9 \times 10^4}{100} \text{ ms}^{-1} = \sqrt{\frac{8 \times 8.314 T_1}{3.14 \times 44 \times 10^{-3}}} \Rightarrow$$

$$T_1 = 1682.5 \text{ K}$$

Also, for the same gas

$$\frac{u_{av}}{u_{mps}} = \sqrt{\frac{8RT_1}{\pi M}} : \sqrt{\frac{2RT_2}{M}} = \sqrt{\frac{8T_1}{\pi} \times \frac{1}{2T_2}} = \sqrt{\frac{4T_1}{\pi T_2}}$$

$$\Rightarrow 1 = \sqrt{\frac{4T_1}{\pi T_2}}$$

$$\Rightarrow T_2 = \frac{4T_1}{\pi} = \frac{4 \times 1682.5}{3.14} = 2142 \text{ K}$$

Hence, $T_1 = 1682.5 \text{ K}$, $T_2 = 2142 \text{ K}$

89. Volume of balloon = $\frac{4}{3} \pi r^3 = \frac{4}{3} \times 3.14 \times \left(\frac{21}{2}\right)^3 \text{ cm}^3$
 $= 4847 \text{ cm}^3 \approx 4.85 \text{ L}$

Now, when volume of $H_2(g)$ in cylinder is converted into NTP volume, then

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \Rightarrow \frac{20 \times 2.82}{300} = \frac{1 \times V_2}{273}$$

$$V_2 = \text{NTP volume} \Rightarrow V_2 = 51.324 \text{ L}$$

Also, the cylinder will not empty completely, it will hold 2.82 L of $H_2(g)$ when equilibrium with balloon will be established. Hence, available volume of $H_2(g)$ for filling into balloon is

$$51.324 - 2.82 = 48.504 \text{ L}$$

$$\Rightarrow \text{Number of balloons that can be filled} = \frac{48.504}{4.85} = 10$$

90. $u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 293}{48 \times 10^{-3}}} = 390.2 \text{ ms}^{-1}$

91. (i) $NH_3(l)$ is highly volatile, a closed bottle of $NH_3(l)$ contains large number of molecules in vapour phase maintaining high

pressure inside the bottle. When the bottle is opened, there is chances of bumping of stopper. To avoid bumping, bottle should be cooled that lowers the pressure inside.

(ii) According to Avogadro's hypothesis, "Under identical conditions of pressure and temperature, equal volume of ideal gases contain equal number of molecules."

92. Number of moles (n) = $\frac{pV}{RT}$

and $n = \frac{N \text{ (Number of molecules)}}{N_A \text{ (Avogadro number)}}$

$$\Rightarrow N = nN_A = \left(\frac{pV}{RT} \right) N_A \\ = \left(\frac{7.6 \times 10^{-10}}{760} \times \frac{1}{0.082 \times 273} \right) \times 6.023 \times 10^{23} \\ = 2.7 \times 10^{10} \text{ molecules}$$

93. From the given information, it can be easily deduced that in the final mixture,

partial pressure of $A = 1.0 \text{ atm}$

partial pressure of $B = 0.5 \text{ atm}$

Also

$$n_A = \frac{p_A V}{RT} = \frac{V}{RT}$$

$$n_B = \frac{p_B V}{RT} = \frac{0.5 V}{RT}$$

$$\Rightarrow \frac{n_B}{n_A} = \frac{1}{2} = \frac{w_B}{M_B} \times \frac{M_A}{w_A} = \frac{3}{2} \times \left(\frac{M_A}{M_B} \right)$$

$$\Rightarrow M_A : M_B = 1 : 3$$

94. Rate of effusion (r) $\propto \frac{p}{\sqrt{M}}$

$$\Rightarrow \frac{r(NH_3)}{r(HCl)} = \frac{1}{\sqrt{17}} \times \frac{\sqrt{36.5}}{p} \Rightarrow \frac{40}{60} = \frac{1}{p} \sqrt{\frac{36.5}{17}}$$

$$\Rightarrow p = \frac{3}{2} \sqrt{\frac{36.5}{17}} = 2.20 \text{ atm}$$

95. $KE = \frac{3}{2} k_B T : k_B = \text{Boltzmann's constant}$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 \text{ J} = 6.21 \times 10^{-21} \text{ J/molecule}$$

96. Rate of effusion is expressed as $-\frac{dp}{dt} = \frac{kp}{\sqrt{M}}$

k = constant, p = instantaneous pressure

$$\Rightarrow -\frac{dp}{p} = \frac{k dt}{\sqrt{M}}$$

Integration of above equation gives $\ln \left(\frac{p_0}{p} \right) = \frac{kt}{\sqrt{M}}$

Using first information : $\ln \left(\frac{2000}{1500} \right) = \frac{k 47}{\sqrt{32}}$

$$\Rightarrow k = \frac{\sqrt{32}}{47} \ln \left(\frac{4}{3} \right) \quad \dots(i)$$

Now in mixture, initially gases are taken in equal mole ratio, hence they have same initial partial pressure of 2000 mm of Hg each.

After 74 min :

$$\text{For O}_2 \quad \ln\left(\frac{2000}{p_{O_2}}\right) = \frac{74k}{\sqrt{32}}$$

Substituting k from Eq. (i) gives

$$\ln\left(\frac{2000}{p_{O_2}}\right) = \frac{74}{\sqrt{32}} \times \frac{\sqrt{32}}{47} \ln\left(\frac{4}{3}\right)$$

$$\ln\left(\frac{2000}{p_{O_2}}\right) = \frac{74}{47} \ln\left(\frac{4}{3}\right)$$

Solving gives $p(O_2)$ at 74 min = 1271.5 mm

$$\text{For unknown gas : } \ln\left(\frac{2000}{p_g}\right) = \frac{74 k}{\sqrt{79}}$$

Substituting k from (i) gives

$$\ln\left(\frac{2000}{p_g}\right) = \frac{74}{\sqrt{79}} \times \frac{\sqrt{32}}{47} \ln\left(\frac{4}{3}\right)$$

Solving gives : $p_g = 1500$ mm

\Rightarrow After 74 min, $p(O_2) : p(g) = 1271.5 : 1500$

Also, in a mixture, partial pressure \propto number of moles

$\Rightarrow n(O_2) : n(g) = 1 : 1.18$

97. First we determine empirical formula as

	C	H
Weight	10.5	1
Mole	$\frac{10.5}{12} = 0.875$	1
Simple ratio	1	$1/0.875 = 1.14$
Whole no.	7	8

\Rightarrow Empirical formula = C_7H_8

From gas equation : $pV = \left(\frac{w}{M}\right)RT$

$$M = \frac{wRT}{pV} = \frac{2.8 \times 0.082 \times 400}{1 \times 1} = 91.84 \approx 92$$

\therefore Molar mass (M) is same as empirical formula weight.

Molecular formula = Empirical formula = C_7H_8

98. For same p and V , $n \propto \frac{1}{T}$

$$\Rightarrow \frac{n(\text{gas})}{n(H_2)} = \frac{T(H_2)}{T(\text{gas})}$$

$$n(H_2) = \frac{0.184}{2} = 0.092$$

$$\Rightarrow n(\text{gas}) = \frac{290}{298} \times 0.092 = 0.0895$$

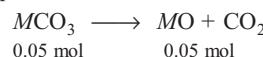
\therefore 0.0895 mole of gas weigh 3.7 g

$$\therefore 1 \text{ mole of gas will weigh } \frac{3.7}{0.0895} = 41.32 \text{ g}$$

99. Moles of CO_2 can be calculated using ideal gas equation as :

$$n = \frac{PV}{RT} = \left(\frac{700}{760}\right) \left(\frac{1336}{1000}\right) \times \frac{1}{0.082 \times 300} = 0.05$$

Also, the decomposition reaction is :



\therefore 0.05 mole $MCO_3 = 4.215 \text{ g}$

$$\therefore 1.0 \text{ mole } MCO_3 = \frac{4.215}{0.05} = 84.3 \text{ g (molar mass)}$$

$$\Rightarrow 84.3 = \text{MW of } M + 12 + 48$$

\Rightarrow Molecular weight of metal = 24.3

\therefore Metal is bivalent, equivalent weight

$$= \frac{\text{Molecular weight}}{2} = 12.15$$

100. The ideal gas equation :

$$pV = nRT = \frac{w}{M} RT$$

$$\Rightarrow pM = \frac{w}{V} RT = dRT \text{ where, 'd' is density.}$$

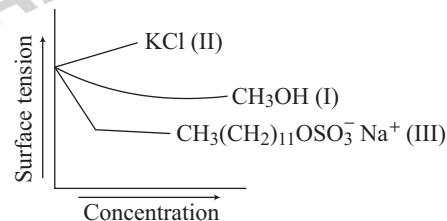
$$\Rightarrow d = \frac{pM}{RT} = \frac{5 \times 17}{0.082 \times 303} = 3.42 \text{ g L}^{-1}$$

Topic 2 Liquid State

1. I (CH_3OH) : Surface tension decreases as concentration increases.
II (KCl) : Surface tension increases with concentration for ionic salt.

III [$CH_3(CH_2)_{11}OSO_3^- Na^+$] : It is an anionic detergent.

There is decrease in surface tension before micelle formation, and after CMC (Critical Micelle Concentration) is attained, no change in surface tension.



2. Let us consider, 1.0 L of liquid water is converted into steam .
 Volume of $H_2O(l) = 1 \text{ L}$, mass = 1000 g
 \Rightarrow Volume of 1000 g steam = $\frac{1000}{0.0006} \text{ cm}^3$
 \therefore Volume of molecules in $\frac{1000}{0.0006} \text{ cm}^3$ steam = 1000 cm^3
 \therefore Volume of molecules in
 1000 cm^3 steam = $\frac{1000}{1000} \times 0.0006 \times 1000 = 0.60 \text{ cm}^3$
3. Critical temperature is directly proportional to intermolecular force of attraction. H_2O is a polar molecule, has greater intermolecular force of attraction than O_2 , hence higher critical temperature.
4. At liquid-vapour equilibrium at boiling point, molecules in two phase posses the same kinetic energy.

6

Chemical and Ionic Equilibrium

Topic 1 Chemical Equilibrium

Objective Questions I (Only one correct option)

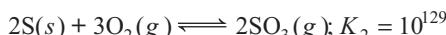
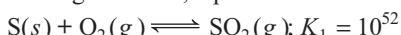
1. Consider the following reaction:



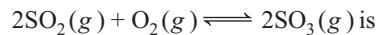
For each of the following cases (A, B), the direction in which the equilibrium shifts is

(2020 Main, 5 Sep I)

- (A) temperature is decreased.
(B) pressure is increased by adding N_2 at constant T .
(a) (A) towards product, (B) towards reactant
(b) (A) towards reactant, (B) no change
(c) (A) towards reactant, (B) towards product
(d) (A) towards product, (B) no change
2. The incorrect match in the following is
- (a) $\Delta G^\circ < 0, K > 1$ (b) $\Delta G^\circ = 0, K = 1$
(c) $\Delta G^\circ > 0, K < 1$ (d) $\Delta G^\circ < 0, K < 1$
3. In which one of the following equilibria, $K_p \neq K_c$?
- (2019 Main, 12 April II)
- (a) $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}(g)$
(b) $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$
(c) $\text{NO}_2(g) + \text{SO}_2(g) \rightleftharpoons \text{NO}(g) + \text{SO}_3(g)$
(d) $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$
4. For the reaction,
- $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g), \Delta H = -57.2 \text{ kJ mol}^{-1}$ and
 $K_c = 1.7 \times 10^{16}$. Which of the following statement is incorrect?
- (2019 Main, 10 April II)
- (a) The equilibrium constant decreases as the temperature increases
(b) The addition of inert gas at constant volume will not affect the equilibrium constant
(c) The equilibrium will shift in forward direction as the pressure increases
(d) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required
5. For the following reactions, equilibrium constants are given :



The equilibrium constant for the reaction,



(2019 Main, 8 April II)

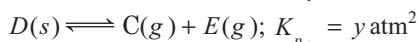
- (a) 10^{25} (b) 10^{77} (c) 10^{154} (d) 10^{181}

6. In a chemical reaction, $A + 2B \xrightleftharpoons{K} 2C + D$, the initial concentration of B was 1.5 times of the concentration of A , but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is

(2019 Main, 12 Jan I)

- (a) $\frac{1}{4}$ (b) 16
(c) 1 (d) 4

7. Two solids dissociate as follows:

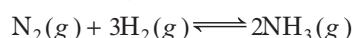


The total pressure when both the solids dissociate simultaneously is

(2019 Main, 12 Jan I)

- (a) $\sqrt{x+y}$ atm (b) $x^2 + y^2$ atm
(c) $(x+y)$ atm (d) $2(\sqrt{x+y})$ atm

8. Consider the reaction,



The equilibrium constant of the above reaction is K_p . If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{\text{NH}_3} << p_{\text{total}}$ at equilibrium)

(2019 Main, 11 Jan I)

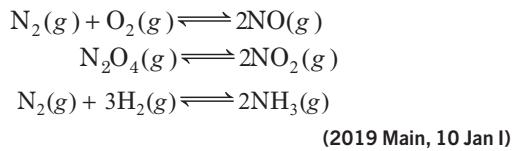
- (a) $\frac{3^{3/2} K_p^{1/2} P^2}{4}$ (b) $\frac{3^{3/2} K_p^{1/2} P^2}{16}$
(c) $\frac{K_p^{1/2} P^2}{16}$ (d) $\frac{K_p^{1/2} P^2}{4}$

9. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327°C . 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is

$(R = 0.082 \text{ atm mol}^{-1}\text{K}^{-1}$, molar mass of S = 32 g mol $^{-1}$, molar mass of N = 14 g mol $^{-1}$)

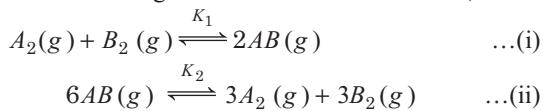
- (a) $0.242 \times 10^{-4} \text{ atm}^2$ (b) 0.242 atm^2
 (c) $4.9 \times 10^{-3} \text{ atm}^2$ (d) $1 \times 10^{-4} \text{ atm}^2$

10. The values of $\frac{K_p}{K_C}$ for the following reactions at 300 K are, respectively (At 300 K, $RT = 24.62 \text{ dm}^3 \text{ atm mol}^{-1}$)



- (a) 1, $24.62 \text{ dm}^3 \text{ atm mol}^{-1}$, $606.0 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2}$
 (b) 1, $24.62 \text{ dm}^3 \text{ atm mol}^{-1}$, $1.65 \times 10^{-3} \text{ dm}^{-6} \text{ atm}^{-2} \text{ mol}^2$
 (c) $24.62 \text{ dm}^3 \text{ atm mol}^{-1}$, $606.0 \text{ dm}^6 \text{ atm}^{-2} \text{ mol}^2$, $1.65 \times 10^{-3} \text{ dm}^{-6} \text{ atm}^{-2} \text{ mol}^2$
 (d) 1, $4.1 \times 10^{-2} \text{ dm}^{-3} \text{ atm}^{-1} \text{ mol}$, $606 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2}$

11. Consider the following reversible chemical reactions,



The relation between K_1 and K_2 is

- (a) $K_2 = K_1^3$ (b) $K_1 K_2 = 3$
 (c) $K_2 = K_1^{-3}$ (d) $K_1 K_2 = \frac{1}{3}$

12. An aqueous solution contains 0.10 M H₂S and 0.20 M HCl. If the equilibrium constants for the formation of HS⁻ from H₂S is 1.0×10^{-7} and that of S²⁻ from HS⁻ ions is 1.2×10^{-13} then the concentration of S²⁻ ions in aqueous solution is :

- (a) $5 \times 10^{-8} \text{ M}$ (b) $3 \times 10^{-20} \text{ M}$
 (c) $6 \times 10^{-21} \text{ M}$ (d) $5 \times 10^{-19} \text{ M}$

13. The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentrations of all the four species were 1 M each, then equilibrium concentration of D (in mol L $^{-1}$) will be

- (a) 0.818 (b) 1.818
 (c) 1.182 (d) 0.182

14. The standard Gibbs energy change at 300 K for the reaction, $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the

$(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}, e = 2.718)$

(2015, Main)

- (a) forward direction because $Q > K_c$
 (b) reverse direction because $Q > K_c$
 (c) forward direction because $Q < K_c$
 (d) reverse direction because $Q < K_c$

15. For the reaction, $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$

if $K_p = K_C (RT)^x$ where, the symbols have usual meaning, then the value of x is (assuming ideality)

- (a) -1 (b) $-\frac{1}{2}$ (c) $\frac{1}{2}$ (d) 1

16. The species present in solution when CO₂ is dissolved in water are

- (a) CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻
 (b) H₂CO₃, CO₃²⁻
 (c) HCO₃⁻, CO₃²⁻
 (d) CO₂, H₂CO₃

17. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

Which is correct statement if N₂ is added at equilibrium condition?

- (a) The equilibrium will shift to forward direction because according to IIInd law of thermodynamics, the entropy must increases in the direction of spontaneous reaction
 (b) The condition for equilibrium is $G(\text{N}_2) + 3G(\text{H}_2) = 2G(\text{NH}_3)$ where, G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent
 (c) The catalyst will increase the rate of forward reaction by α and that of backward reaction by β
 (d) Catalyst will not alter the rate of either of the reaction

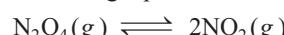
18. $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+$; $K_1 = 3.5 \times 10^{-3}$

$[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$; $K_2 = 1.7 \times 10^{-3}$

then the formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is

- (a) 6.08×10^{-6} (b) 6.08×10^6
 (c) 6.08×10^{-9} (d) None of these

19. Consider the following equilibrium in a closed container



At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

(2002, 3M)

- (a) Neither K_p nor α changes

- (b) Both K_p and α change

- (c) K_p changes but α does not change

- (d) K_p does not change but α changes

20. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, is expressed

by $K_p = \frac{4x^2 p}{(1-x^2)}$, where, p = pressure, x = extent of decomposition. Which one of the following statement is true?

(2001, 1M)

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- (a) K_p increases with increase of p
 (b) K_p increases with increase of x
 (c) K_p increases with decrease of x
 (d) K_p remains constant with change in p and x

21. When two reactants, A and B are mixed to give products, C and D , the reaction quotient, (Q) at the initial stages of the reaction
 (2000)
 (a) is zero
 (b) decreases with time
 (c) is independent of time
 (d) increases with time

22. For the reversible reaction,

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$

 at 500°C , the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol/L is
 (2000, S, 1M)
 (a) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$
 (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
 (c) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$
 (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

23. For the chemical reaction,

$$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$$

 the amount of X_3Y at equilibrium is affected by
 (1999, 2M)
 (a) temperature and pressure
 (b) temperature only
 (c) pressure only
 (d) temperature, pressure and catalyst

24. For the reaction,

$$\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g),$$

 at a given temperature, the equilibrium amount of $\text{CO}_2(g)$ can be increased by
 (1998)
 (a) adding a suitable catalyst
 (b) adding an inert gas
 (c) decreasing the volume of the container
 (d) increasing the amount of $\text{CO}(g)$

25. One mole of $\text{N}_2\text{O}_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $\text{N}_2\text{O}_4(g)$ decomposes to $\text{NO}_2(g)$. The resultant pressure is
 (1996, 1M)
 (a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

26. An example of a reversible reaction is
 (1985, 1M)
 (a) $\text{Pb}(\text{NO}_3)_2(aq) + 2\text{NaI}(aq) \rightarrow \text{PbI}_2(s) + 2\text{NaNO}_3(aq)$
 (b) $\text{AgNO}_3(aq) + \text{HCl}(aq) \rightarrow \text{AgCl}(s) + \text{HNO}_3(aq)$
 (c) $2\text{Na}(s) + 2\text{H}_2\text{O}(l) = 2\text{NaOH}(aq) + \text{H}_2(g)$
 (d) $\text{KNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{KCl}(aq) + \text{NaNO}_3(aq)$

27. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium,

$$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$$

 (1984, 1M)
 (a) K_p does not change significantly with pressure
 (b) α does not change with pressure

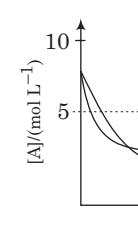
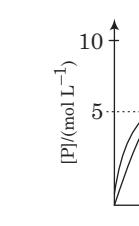
(c) concentration of NH_3 does not change with pressure
 (d) concentration of hydrogen is less than that of nitrogen

28. For the reaction, $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
 the equilibrium constant K_p changes with
 (a) total pressure
 (b) catalyst
 (c) the amount of H_2 and I_2 present
 (d) temperature
 (1981, 1M)

Objective Questions II

(One or more than one correct option)

29. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below.

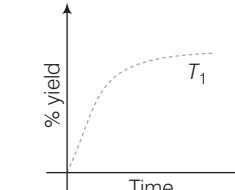



If $T_2 > T_1$, the correct statement(s) is/are
 (Assume ΔH^\ominus and ΔS^\ominus are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2/T_1 . Here H , S , G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)
 (2018 Adv.)
 (a) $\Delta H^\ominus < 0, \Delta S^\ominus < 0$ (b) $\Delta G^\ominus < 0, \Delta H^\ominus > 0$
 (c) $\Delta G^\ominus < 0, \Delta S^\ominus < 0$ (d) $\Delta G^\ominus < 0, \Delta S^\ominus > 0$

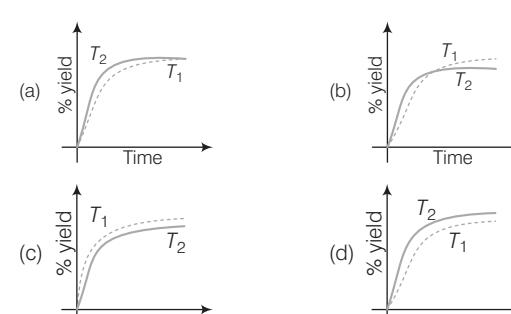
30. The % yield of ammonia as a function of time in the reaction,

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g); \Delta H < 0$$

 at (p, T_1) is given below.



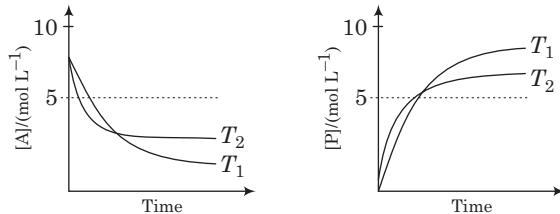
If this reaction is conducted at (p, T_1) , with $T_2 > T_1$ the % yield by of ammonia as a function of time is represented by



Objective Questions II

(One or more than one correct option)

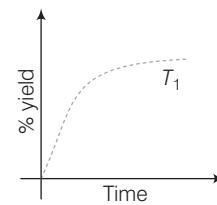
- 29.** For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below.



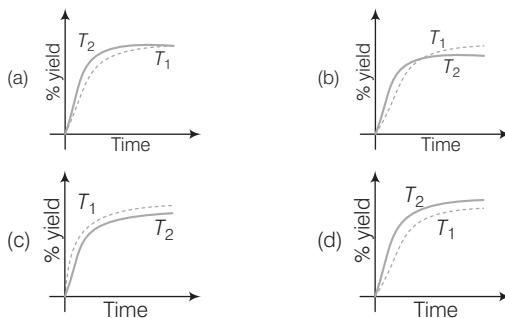
If $T_2 > T_1$, the correct statement(s) is/are

(Assume ΔH^\ominus and ΔS^\ominus are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2 / T_1 . Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.) (2018 Adv.)

- (a) $\Delta H^\ominus < 0$, $\Delta S^\ominus < 0$ (b) $\Delta G^\ominus < 0$, $\Delta H^\ominus > 0$
 (c) $\Delta G^\ominus < 0$, $\Delta S^\ominus < 0$ (d) $\Delta G^\ominus < 0$, $\Delta S^\ominus > 0$



If this reaction is conducted at (p, T_1) , with $T_2 > T_1$ the % yield by of ammonia as a function of time is represented by



Fill in the Blanks

- 37.** For a gaseous reaction $2B \longrightarrow A$, the equilibrium constant K_p is to/than K_c . (1997 C, 1M)

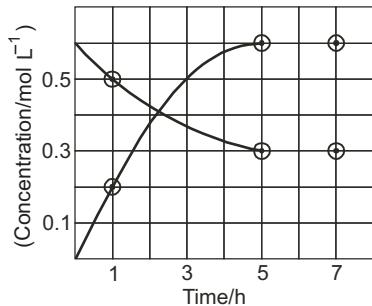
If ammonia is added to a water solution containing excess of $\text{AgCl}(s)$ only. Calculate the concentration of the complex in 1.0 M aqueous ammonia. (1998. 3M+5M)

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47. The progress of reaction,



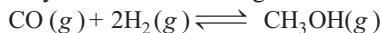
with time, is represented in fig. use given below.



Determine :

- (i) the value of n
- (ii) the equilibrium constant, K and
- (iii) the initial rate of conversion of A . (1994, 3M)

48. 0.15 mole of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place:

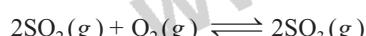


Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. (1993, 5M)

49. For the reaction, $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of $\text{CO}(g)$ and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $\text{CH}_3\text{OH}(g)$ is formed. Calculate the equilibrium constant, K_p and K_c . (1990, 5M)

50. The equilibrium constant K_p of the reaction,



is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. (1989, 3M)

51. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and 37°C. (1988, 4M)

52. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction;

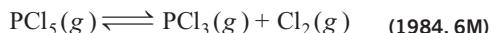


If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and NO_2 ? (1987, 5M)

53. The equilibrium constant of the reaction

$\text{A}_2(g) + \text{B}_2(g) \rightleftharpoons 2\text{AB}(g)$ at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2 , how many moles of AB will be formed at 373 K? (1985, 4M)

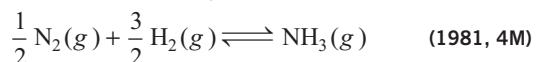
54. One mole of N_2 and 3 moles of PCl_5 are placed in a 100 L vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction,



55. One mole of nitrogen is mixed with three moles of hydrogen in a four litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction



calculate the equilibrium constant, K_c in concentration units. What will be the value of K_c for the following equilibrium?



Passage Based Questions

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:



The standard reaction Gibbs energy, Δ_rG° , of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X . As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given, $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

56. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$ is (2016 Adv.)

- (a) $\frac{8\beta^2_{\text{equilibrium}}}{2 - \beta_{\text{equilibrium}}}$ (b) $\frac{8\beta^2_{\text{equilibrium}}}{4 - \beta^2_{\text{equilibrium}}}$
 (c) $\frac{4\beta^2_{\text{equilibrium}}}{2 - \beta_{\text{equilibrium}}}$ (d) $\frac{4\beta^2_{\text{equilibrium}}}{4 - \beta^2_{\text{equilibrium}}}$

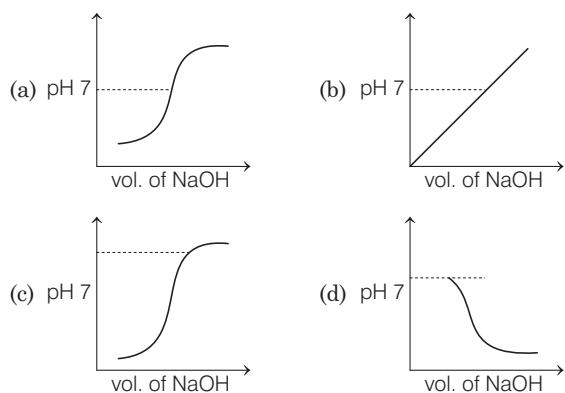
57. The incorrect statement among the following for this reaction, is (2016 Adv.)

- (a) Decrease in the total pressure will result in the formation of more moles of gaseous X
 (b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously
 (c) $\beta_{\text{equilibrium}} = 0.7$
 (d) $K_C < 1$

Topic 2 Ionic Equilibrium

Objective Questions I (Only one correct option)

1. 100 mL of 0.1M HCl is taken in a beaker and to it 100 mL of 0.1 M NaOH is added in steps of 2 mL and the pH continuously measured. Which of the following graphs correctly depicts the change in pH? (2020 Main, 3 Sep II)



2. The molar solubility of Cd(OH)₂ is 1.84×10^{-5} M in water. The expected solubility of Cd(OH)₂ in a buffer solution of pH = 12 is (2019 Main, 12 April II)

- (a) 1.84×10^{-9} M (b) $\frac{2.49}{1.84} \times 10^{-9}$ M
 (c) 6.23×10^{-11} M (d) 2.49×10^{-10} M

3. What is the molar solubility of Al(OH)₃ in 0.2 M NaOH solution? Given that, solubility product of Al(OH)₃ = 2.4×10^{-24} (2019 Main, 12 April II)

- (a) 3×10^{-19} (b) 12×10^{-21}
 (c) 3×10^{-22} (d) 12×10^{-23}

4. The pH of a 0.02 M NH₄Cl solution will be [Given $K_b(\text{NH}_4\text{OH}) = 10^{-5}$ and $\log 2 = 0.301$] (2019 Main, 10 April II)

- (a) 4.65 (b) 2.65
 (c) 5.35 (d) 4.35

5. Consider the following statements.

- I. The pH of a mixture containing 400 mL of 0.1 M H₂SO₄ and 400 mL of 0.1 M NaOH will be approximately 1.3.
 II. Ionic product of water is temperature dependent.
 III. A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.
 IV. The Le-Chatelier's principle is not applicable to common-ion effect.

The correct statements are (2019 Main, 10 April I)

- (a) I, II and IV (b) II and III
 (c) I and II (d) I, II and III

6. If solubility product of Zr₃(PO₄)₄ is denoted by K_{sp} and its molar solubility is denoted by S , then which of the following relation between S and K_{sp} is correct? (2019 Main, 8 April I)

$$(a) S = \left(\frac{K_{sp}}{144} \right)^{1/6} \quad (b) S = \left(\frac{K_{sp}}{6912} \right)^{1/7}$$

$$(c) S = \left(\frac{K_{sp}}{929} \right)^{1/9} \quad (d) S = \left(\frac{K_{sp}}{216} \right)^{1/7}$$

7. If K_{sp} of Ag₂CO₃ is 8×10^{-12} , the molar solubility of Ag₂CO₃ in 0.1 M AgNO₃ is (2019 Main, 12 Jan II)

- (a) 8×10^{-12} M (b) 8×10^{-13} M
 (c) 8×10^{-10} M (d) 8×10^{-11} M

8. 20 mL of 0.1 M H₂SO₄ solution is added to 30 mL of 0.2 M NH₄OH solution. The pH of the resultant mixture is [pK_b of NH₄OH = 4.7] (2019 Main, 9 Jan I)

- (a) 9.3 (b) 5.0
 (c) 9.0 (d) 5.2

9. An aqueous solution contains an unknown concentration of Ba²⁺. When 50 mL of a 1 M solution of Na₂SO₄ is added, BaSO₄ just begins to precipitate. The final volume is 500 mL. The solubility product of BaSO₄ is 1×10^{-10} . What is the original concentration of Ba²⁺? (2018 Main)

- (a) 5×10^{-9} M (b) 2×10^{-9} M
 (c) 1.1×10^{-9} M (d) 1.0×10^{-10} M

10. Which of the following are Lewis acids? (2018 Main)

- (a) PH₃ and BCl₃ (b) AlCl₃ and SiCl₄
 (c) PH₃ and SiCl₄ (d) BCl₃ and AlCl₃

11. Which of the following salts is the most basic in aqueous solution? (2018 Main)

- (a) Al(CN)₃ (b) CH₃COOK
 (c) FeCl₃ (d) Pb(CH₃COO)₂

12. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is (2017 Main)

- (a) 7.2 (b) 6.9
 (c) 7.0 (d) 1.0

13. How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? (2013 Main)

- (a) 0.1 L (b) 0.9 L
 (c) 2.0 L (d) 9.0 L

14. Solubility product constant (K_{sp}) of salts of types MX, MX₂ and M₃X at temperature 'T' are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (mol dm⁻³) of the salts at temperature 'T' are in the order (2008, 3M)

- (a) MX > MX₂ > M₃X (b) M₃X > MX₂ > MX
 (c) MX₂ > M₃X > MX (d) MX > M₃X > MX₂

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- 15.** 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) (2008, 3M)
- (a) 3.7×10^{-13} M (b) 3.2×10^{-7} M
 (c) 3.2×10^{-2} M (d) 2.7×10^{-2} M
- 16.** CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 mole of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is (2005, 1M)
- (a) 1.6×10^{-11} (b) 8×10^{-11}
 (c) 5×10^{-5} (d) 8×10^{-2}
- 17.** HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1M) on reacting with caustic soda. The degree of hydrolysis of NaX is (2004, 1M)
- (a) 0.01% (b) 0.0001% (c) 0.1% (d) 0.5%
- 18.** A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS , FeS , ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first? (2003, 1M)
- (a) FeS (b) MgS (c) HgS (d) ZnS
- 19.** Identify the correct order of solubility of Na_2S , CuS and ZnS in aqueous medium. (2002)
- (a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$
 (c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$
- 20.** For a sparingly soluble salt A_pB_q , the relationship of its solubility product (L_s) with its solubility (S) is (2001, 1M)
- (a) $L_s = S^{p+q} \cdot p^p \cdot q^q$ (b) $L_s = S^{p+q} \cdot p^q \cdot q^p$
 (c) $L_s = S^{pq} \cdot p^p \cdot q^q$ (d) $L_s = S^{pq} \cdot (p \cdot q)^{p+q}$
- 21.** The pH of 0.1 M solution of the following salts increases in the order (1999, 2M)
- (a) $NaCl < NH_4Cl < NaCN < HCl$
 (b) $HCl < NH_4Cl < NaCl < NaCN$
 (c) $NaCN < NH_4Cl < NaCl < HCl$
 (d) $HCl < NaCl < NaCN < NH_4Cl$
- 22.** Which of the following solutions will have pH close to 1.0? (1992, 1M)
- (a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
 (b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
 (c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
 (d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH
- 23.** Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is (1990, 1M)
- (a) $Mg(OH)_2$ (b) $Ca(OH)_2$ (c) $Ba(OH)_2$ (d) $Be(OH)_2$
- 24.** Which of the following is the strongest acid? (1989, 1M)
- (a) $ClO_3(OH)$ (b) $ClO_2(OH)$
 (c) $SO(OH)_2$ (d) $SO_2(OH)_2$
- 25.** When equal volumes of the following solutions are mixed, precipitation of $AgCl$ ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with (1988, 1M)
- (a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
 (b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
 (c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
 (d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)
- 26.** The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be (1988, 1M)
- (a) unionised in the small intestine and in the stomach
 (b) completely ionised in the small intestine and in the stomach
 (c) ionised in the stomach and almost unionised in the small intestine
 (d) ionised in the small intestine and almost unionised in the stomach
- 27.** The compound that is not a Lewis acid is (1985, 1M)
- (a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$
- 28.** The conjugate acid of NH_2^- is (1985, 1M)
- (a) NH_3 (b) NH_2OH (c) NH_4^+ (d) N_2H_4
- 29.** The best indicator for detection of end point in titration of a weak acid and a strong base is (1985, 1M)
- (a) methyl orange (3 to 4) (b) methyl red (5 to 6)
 (c) bromothymol blue (6 to 7.5) (d) phenolphthalein (8 to 9.6)
- 30.** A certain weak acid has a dissociation constant of 1.0×10^{-4} . The equilibrium constant for its reaction with a strong base is (1984, 1M)
- (a) 1.0×10^{-4} (b) 1.0×10^{-10} (c) 1.0×10^{10} (d) 1.0×10^{14}
- 31.** A certain buffer solution contains equal concentration of X^- and HX . The K_b for X^- is 10^{-10} . The pH of the buffer is (1984, 1M)
- (a) 4 (b) 7 (c) 10 (d) 14
- 32.** The precipitate of CaF_2 , ($K_{sp} = 1.7 \times 10^{-10}$) is obtained, when equal volumes of which of the following are mixed? (1982, 1M)
- (a) 10^{-4} M Ca^{2+} + 10^{-4} M F^- (b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
 (c) 10^{-5} M Ca^{2+} + 10^{-3} M F^- (d) 10^{-3} M Ca^{2+} + 10^{-5} M F^-
- 33.** An acidic buffer solution can be prepared by mixing the solution of (1981, 1M)
- (a) acetate and acetic acid
 (b) ammonium chloride and ammonium hydroxide
 (c) sulphuric acid and sodium sulphate
 (d) sodium chloride and sodium hydroxide
- 34.** Of the given anions, the strongest base is (1981, 1M)
- (a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-
- 35.** At 90°C, pure water has $[H_3O^+]$ as 10^{-6} mol L⁻¹. What is the value of K_w at 90°C? (1981, 1M)
- (a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}

36. The pH of 10^{-8} M solution of HCl in water is (1981, 1M)
- 8
 - 8
 - between 7 and 8
 - between 6 and 7

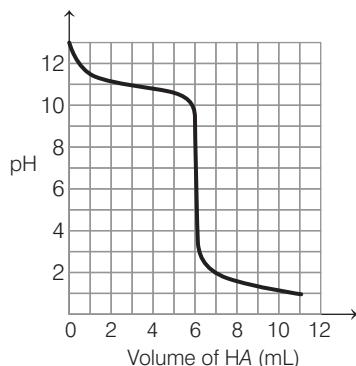
Objective Questions II

(One or more than one correct option)

37. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is
- 1.1×10^{-11}
 - 1.1×10^{-10}
 - 1.1×10^{-12}
 - 1.1×10^{-9}
- (2013 Adv.)
38. Aqueous solutions of HNO_3 , KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are)
- HNO_3 and CH_3COOH
 - KOH and CH_3COONa
 - HNO_3 and CH_3COONa
 - CH_3COOH and CH_3COONa
- (2010)
39. A buffer solution can be prepared from a mixture of
- sodium acetate and acetic acid in water
 - sodium acetate and HCl in water
 - ammonia and ammonium chloride in water
 - ammonia and sodium hydroxide in water
- (1999, 3M)
40. Which of the following statement(s) is (are) correct?
- The pH of 1.0×10^{-8} M solution of HCl is 8
 - The conjugate base of H_2PO_4^- is HPO_4^{2-}
 - Autoprotolysis constant of water increases with temperature
 - When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point $\text{pH} = \left(\frac{1}{2}\right) \text{p}K_a$
- (1998, 2M)

Numerical Answer Type Questions

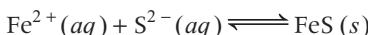
41. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the $\text{p}K_b$ of the base? The neutralisation reaction is given by



42. An acidified solution of 0.05 M Zn^{2+} is saturated with 0.1 M H_2S . What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS ?

Use $K_{sp}(\text{ZnS}) = 1.25 \times 10^{-22}$ and overall dissociation constant of H_2S , $K_{\text{net}} = K_1 K_2 = 1 \times 10^{-21}$. (2020 Adv.)

43. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17} .



When equal volumes of 0.06 M $\text{Fe}^{2+}(aq)$ and 0.2 M $\text{S}^{2-}(aq)$ solutions are mixed, the equilibrium concentration of $\text{Fe}^{2+}(aq)$ is found by $Y \times 10^{-17}$ M. The value of Y is (2019 Adv.)

44. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3}$ mol L⁻¹. The value of Y is _____. (Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionisation constant of HB (K_a) = 1×10^{-8}) (2018 Adv.)

Match the Column

45. Dilution processes of different aqueous solutions, with water, are given in List-I. The effects of dilution of the solution on $[\text{H}^+]$ are given in List-II.

Note Degree of dissociation (α) of weak acid and weak base is $\ll 1$; degree of hydrolysis of salt $\ll 1$; $[\text{H}^+]$ represents the concentration of H^+ ions

List-I	List-II
P. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	1. the value of $[\text{H}^+]$ does not change on dilution
Q. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	2. the value of $[\text{H}^+]$ changes to half of its initial value on dilution
R. (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	3. the value of $[\text{H}^+]$ changes to two times of its initial value on dilution.
S. 10 mL saturated solution of Ni(OH)_2 in equilibrium with excess solid Ni(OH)_2 is diluted to 20 mL (solid Ni(OH)_2 is still present after dilution).	4. the value of $[\text{H}^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
	5. the value of $[\text{H}^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in List-I with one or more effect(s) in List-II. The correct option is (2018 Adv.)

- $P \rightarrow 4; Q \rightarrow 2; R \rightarrow 3; S \rightarrow 1$
- $P \rightarrow 4; Q \rightarrow 3; R \rightarrow 2; S \rightarrow 3$
- $P \rightarrow 1; Q \rightarrow 4; R \rightarrow 5; S \rightarrow 3$
- $P \rightarrow 1; Q \rightarrow 5; R \rightarrow 4; S \rightarrow 1$

92 Chemical and Ionic Equilibrium

Fill in the Blanks

46. In the reaction, $I^- + I_2 \longrightarrow I_3^-$, the Lewis acid is
(1997, 1M)
47. Silver chloride is sparingly soluble in water because its lattice energy is greater than energy.
(1987, 1M)
48. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be.....
(1984, 1M)
49. The conjugate base of HSO_4^- in aqueous solution is
(1982, 1M)

True/False

50. The following species are in increasing order of their acidic property : ZnO , Na_2O_2 , P_2O_5 , MgO .
(1985, 1/2M)
51. Solubility of sodium hydroxide increases with increase in temperature.
(1985, 1/2M)
52. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons.
(1982, 1M)

Integer Answer Type Questions

53. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda_{X^-}^0 \approx \lambda_{Y^-}^0$, the difference in their pK_a values, $pK_a(HX) - pK_a(HY)$, is (consider degree of ionisation of both acids to be $<<1$).
(2015 Adv.)
54. In 1 L saturated solution of $AgCl$ [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mole of $CuCl$ [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of 'x' is
(2011)
55. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is

KCN	K_2SO_4	$(NH_4)_2C_2O_4$	NaCl
$Zn(NO_3)_2$	$FeCl_3$	K_2CO_3	NH_4NO_3
LiCN			(2010)

Subjective Questions

56. The dissociation constant of a substituted benzoic acid at $25^\circ C$ is 1.0×10^{-4} . The pH of 0.01 M solution of its sodium salt is
(2009)
57. 0.1 M of H_4 is titrated with 0.1 M $NaOH$, calculate the pH at end point. Given, $K_a(H_4) = 5 \times 10^{-6}$ and $\alpha << 1$.
(2004)
58. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at $250^\circ C$.
- (i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of $NaOH$ is added to the above solution, determine the final pH (assuming there is no change in volume on mixing, K_a of acetic acid is 1.75×10^{-5} mol/L).
(1984, 1M)

59. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol/L and pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day.
(2000, 5M)
60. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.
(1999, 4M)
61. (a) Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag|Ag^+(saturated, Ag_2CrO_4\ solution.) \parallel Ag^+(0.1\ M)|Ag$ is 0.164 V at 298 K.
(1998, 6M)
- (b) What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of $NaOH$ (pH = 12.0)?
(1998, 6M)
62. A sample of $AgCl$ was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3 . The remaining solution contained 0.0026 g of Cl^- ions per litre. Calculate the solubility product of $AgCl$. [$K_{sp}(Ag_2CO_3) = 8.2 \times 10^{-12}$]
(1997, 5M)
63. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change? ($K_a = 1.0 \times 10^{-5}$)
(1997, 2M)
64. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at $25^\circ C$. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at $25^\circ C$ is 3.4×10^{10} L/mol.s. Calculate the rate constant per proton transfer from water to NH_3 .
(1996, 3M)
65. What is the pH of a 0.50 M aqueous $NaCN$ solution?
(pK_b of $CN^- = 4.70$).
(1996, 2M)
66. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation.
(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)
(1995, 2M)
67. For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$
The equilibrium constant, at $25^\circ C$, is 4.0×10^{-19} . Calculate the silver ion concentration in a solution which was originally 0.10 M in KCN and 0.03 M in $AgNO_3$.
(1994, 3M)

- 68.** An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S . What is the minimum pH at which MS will precipitate? K_{sp} for $MS = 6.0 \times 10^{-21}$, concentration of saturated $H_2S = 0.1\text{ M}$, $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S . (1993, 3M)
- 69.** The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3 , in order to maintain a pH of 7.4? (K_a for H_2CO_3 in blood is 7.8×10^{-7}) (1993, 2M)
- 70.** The solubility product (K_{sp}) of $Ca(OH)_2$ at $25^\circ C$ is 4.42×10^{-5} . A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M $NaOH$. How much $Ca(OH)_2$ in milligrams is precipitated? (1992, 4M)
- 71.** A 40 mL solution of a weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of the acid respectively. Find out the dissociation constant of the base. (1991, 6M)
- 72.** The solubility product of $Ag_2C_2O_4$ at $25^\circ C$ is $1.29 \times 10^{-11} \text{ mol}^3 L^{-3}$. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL water is shaken at $25^\circ C$ with excess of Ag_2CO_3 till the following equilibrium is reached
- $$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$
- At equilibrium, the solution contains 0.0358 mole of K_2CO_3 . Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3 . (1991, 4M)
- 73.** What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given, $K_a = 1.8 \times 10^{-5}$ (1990, 4M)
- 74.** Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 M of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution.
- $$K_b[NH_4OH] = 1.8 \times 10^{-5}$$
- $$K_{sp}[Mg(OH)_2] = 8.9 \times 10^{-12}$$
- $$K_{sp}[Al(OH)_3] = 6 \times 10^{-32}$$
- (1989, 3M)
- 75.** How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing $NaCN$ and HCl) of pH 8.5 using 0.01 g formula weight of $NaCN$?
- $$K_{HCN} = 4.1 \times 10^{-10}$$
- (1988, 4M)
- 76.** What is the pH of the solution when 0.20 mole of HCl is added to one litre of a solution containing
 (i) 1 M each of acetic acid and acetate ion,
 (ii) 0.1 M each of acetic acid and acetate ion?
 Assume the total volume is one litre.
 K_a for acetic acid = 1.8×10^{-5} . (1987, 5M)
- 77.** The solubility of $Mg(OH)_2$ in pure water is $9.57 \times 10^{-3} \text{ g/L}$. Calculate its solubility (in g/L) in 0.02 M $Mg(NO_3)_2$ solution. (1986, 5M)
- 78.** The concentration of hydrogen ions in a 0.20 M solution of formic acid is $6.4 \times 10^{-3} \text{ mol/L}$. To this solution, sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre.
 What will be the pH of this solution? The dissociation constant of formic acid is 2.4×10^{-4} and the degree of dissociation of sodium formate is 0.75. (1985, 3M)
- 79.** A solution contains a mixture of Ag^+ (0.10 M) and Hg^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated? (1984, 4M)
- $$K_{sp} : AgI = 8.5 \times 10^{-17}, HgI_2 = 2.5 \times 10^{-26}$$
- 80.** The dissociation constant of a weak acid HA is 4.9×10^{-8} . After making the necessary approximations, calculate
 (i) pH
 (ii) OH^- concentration in a decimolar solution of the acid.
 (Water has a pH of 7). (1983, 2M)
- 81.** Give reason for the statement that "the pH of an aqueous solution of sodium acetate is more than seven". (1982, 1M)
- 82.** 20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid solution to give 70 mL of the solution. What is the pH of this solution?
 Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74.
 (Ionisation constant of $CH_3COOH = 1.8 \times 10^{-5}$). (1982, 3M)
- 83.** How many moles of sodium propionate should be added to 1 L of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.010 moles of HCl are dissolved in the above buffer solution? Compare the last pH value with the pH of 0.010 M HCl solution. Dissociation constant of propionic acid, K_a at $25^\circ C$ is 1.34×10^{-5} . (1981, 4M)

Answers

Topic 1

1. (b)	2. (d)	3. (a)	4. (d)	13. (d)	14. (d)	15. (d)	16. (b)
5. (a)	6. (d)	7. (d)	8. (b)	17. (a)	18. (c)	19. (d)	20. (a)
9. (b)	10. (b)	11. (c)	12. (b)	21. (b)	22. (d)	23. (d)	24. (a)
13. (b)	14. (b)	15. (b)	16. (a)	25. (a)	26. (d)	27. (c)	28. (a)
17. (b)	18. (a)	19. (d)	20. (d)	29. (d)	30. (c)	31. (a)	32. (b)
21. (d)	22. (d)	23. (a)	24. (d)	33. (a)	34. (a)	35. (b)	36. (d)
25. (b)	26. (d)	27. (a)	28. (d)	37. (b)	38. (c, d)	39. (a, b, c)	40. (b, c)
29. (a,c)	30. (b)	31. (a)	32. (b, c, d)	41. (3.00)	42. (0.20)	43. (8.9)	44. (4.47)
33. (c, d, e)	34. (d)	35. (c, d)	36. (a, b, c, d)	45. (d)	46. I ₂	47. hydration	48. amphoteric
37. smaller	38. no change	39. $K_p = K_c(RT)^{\Delta n}$		49. SO ₄ ²⁻	50. F	51. F	52. F
40. T	41. F	42. F	43. T	53. (3)	54. (1.6 × 10 ⁻⁷)	56. (8)	57. (9)
47. (1.2)	53. (1.86)	54. (0.33)	56. (b)	58. (4.75)	59. (4.86)	60. (1.2 × 10 ⁻³ M)	
57. (c)				62. (2 × 10 ⁻⁸)	65. (11.5)	66. (6.50)	68. (1)

Topic 2

1. (a)	2. (d)	3. (c)	4. (c)
5. (d)	6. (b)	7. (c)	8. (a)
9. (c)	10. (d)	11. (b)	12. (b)

Hints & Solutions

Topic 1 Chemical Equilibrium


Because in case of an endothermic reaction ($\Delta H = +$ ve), the equilibrium constant increases with rise in temperature and hence, the reaction moves in forward direction. On adding N₂, pressure is increased at constant T , and volume would also be constant, so no change is observed.

2. The incorrect match is $\Delta G^\circ < 0, K < 1$.

For an ideal gas $\Delta G^\circ = -RT \ln K$.

$$\therefore \ln K = -\frac{\Delta G^\circ}{RT} \quad \text{and} \quad K = e^{-\Delta G^\circ / RT}$$

The above equation is helpful in predicting the spontaneity of the reaction. e.g.

(i) If $\Delta G^\circ < 0, -\Delta G^\circ / RT = +$ ve and $e^{-\Delta G^\circ / RT} > 1$ and hence, $K > 1$. It means that the reaction occur spontaneously in the forward direction or products predominate over reactants.

(ii) If $\Delta G^\circ > 0; -\Delta G^\circ / RT = -$ ve and

$e^{-\Delta G^\circ / RT} < 1$ and hence, $K < 1$. It means that the reaction is non-spontaneous in forward direction (i.e. product side) but spontaneous in reverse direction (i.e. reactants predominate over products or the reaction occurs rarely).

(iii) When $K = 1$, then $\Delta G^\circ = 0$. This situation generally occur at equilibrium.

3.

Key Idea The relationship between K_p and K_c is

$$K_p = K_c(RT)^{\Delta n_g}$$

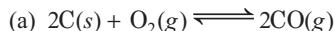
where, $\Delta n_g = n_{\text{products}} - n_{\text{reactants}}$

If $\Delta n_g = 0$ then $K_p = K_c$

If $\Delta n_g = +$ ve then $K_p > K_c$

If $\Delta n_g = -$ ve then $K_p < K_c$

Consider the following equilibria reactions



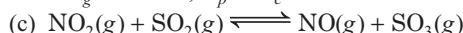
$$\Delta n_g = n_{\text{product}} - n_{\text{reactant}} = 2 - (1) = 1$$

$$\Delta n_g \neq 0 \Rightarrow \text{So, } K_p \neq K_c$$



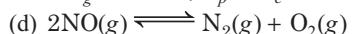
$$\Delta n_g = n_{\text{product}} - n_{\text{reactant}} = 2 - 2 = 0$$

$$\Delta n_g = 0 \Rightarrow \text{So, } K_p = K_c$$



$$\Delta n_g = n_{\text{product}} - n_{\text{reactant}} = 2 - 2 = 0$$

$$\Delta n_g = 0 \Rightarrow \text{So, } K_p = K_c$$



$$\Delta n_g = n_{\text{product}} - n_{\text{reactant}} = 2 - 2 = 0$$

$$\Delta n_g = 0 \Rightarrow \text{So, } K_p = K_c$$

4. The explanation of given statements are as follows:

- (a) For the given equilibrium, ΔH is negative, so the equilibrium constant will decrease with increase in temperature and the equilibrium will shift in the backward direction.

Thus, statement (a) is correct.

- (b) When inert gas is added at constant volume and constant temperature, an equilibrium remains undisturbed.

Thus, statement (b) is correct.

- (c) For the equilibrium,

$$\Delta n_g = 2 - (2 + 1) = -1, \text{ i.e. } (-\text{ve})$$

So, increase in pressure will shift the equilibrium in the forward direction.

Thus, statement (c) is correct.

- (d) The reaction takes place in the presence of a catalyst which is $V_2O_5(s)$ in contact process or $NO(g)$ in chamber process.

Thus, statement (d) is incorrect.

5. $S + O_2 \rightleftharpoons SO_2, K_1$

$$\therefore SO_2 \rightleftharpoons S + O_2, K_1' = \frac{1}{K_1}$$

$$\text{or, } 2SO_2 \rightleftharpoons 2S + 2O_2, K_1'' = (K_1')^2 = \frac{1}{K_1^2} \quad \dots (\text{i})$$

$$\Rightarrow 2S + 3O_2 \rightleftharpoons 2SO_3, K_2 \quad \dots (\text{ii})$$

Now, [(i) + (ii)] gives

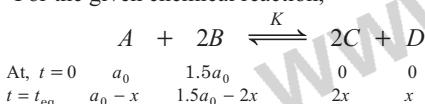


The value of equilibrium constant,

$$K_3 = K_2 \times K_1'' = K_2 \times \frac{1}{K_1^2}$$

$$= 10^{129} \times \frac{1}{(10^{52})^2} = 10^{129-104} = 10^{25}$$

6. For the given chemical reaction,



[x = degree of dissociation]

Given, at equilibrium.

$$[A] = [B]$$

$$a_0 - x = 1.5a_0 - 2x \\ x = 0.5a_0$$

$$\therefore [A] = a_0 - x = a_0 - 0.5a_0 = 0.5a_0$$

$$[B] = 1.5a_0 - 2x = 1.5a_0 - 2 \times 0.5a_0 = 0.5a_0$$

$$[C] = 2x = 2 \times 0.5a_0 = a_0$$

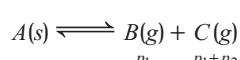
$$[D] = x = 0.5a_0$$

$$\text{Now, } K = \frac{[C]^2[D]}{[A][B]^2}$$

Now, substituting the values in above equation, we get

$$K = \frac{(a_0)^2 \times (0.5a_0)}{(0.5a_0) \times (0.5a_0)^2} = 4$$

7. The equilibrium reaction for the dissociation of two solids is given as:



At equilibrium

$$K_{p_1} = x = p_B \cdot p_C = p_1(p_1 + p_2) \quad \dots (\text{i})$$

Similarly, $D(s) \rightleftharpoons C(g) + E(g)$

At equilibrium $p_1 + p_2 \cdot p_2$

$$K_{p_2} = y = p_C \cdot p_E = (p_1 + p_2)p_2 \quad \dots (\text{ii})$$

On adding Eq. (i) and (ii), we get.

$$K_{p_1} + K_{p_2} = x + y = p_1(p_1 + p_2) + p_2(p_1 + p_2) \\ = (p_1 + p_2)^2$$

$$\text{or } \sqrt{x + y} = p_1 + p_2 \quad \dots (\text{iii})$$

Now, total pressure is given as

$$p_T = p_B + p_C + p_E \\ = p_1 + (p_1 + p_2) + p_2 = 2(p_1 + p_2) \quad \dots (\text{iv})$$

On substituting the value of $p_1 + p_2$ from Eq. (iii) to Eq. (iv), we get

$$p_T = 2\sqrt{x + y} \text{ atm}$$

8. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium: $p_{N_2} = P, p_{H_2} = 3P, p_{NH_3} = 2P$

$$\Rightarrow p_{(\text{total})} = p_{N_2} + p_{H_2} + p_{NH_3} \approx p_{N_2} + p_{H_2} \quad [\because P_{(\text{total})} \gg p_{NH_3}] \\ = p + 3p = 4p$$

$$\text{Now, } K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3} = \frac{p_{NH_3}^2}{p \times (3p)^3} \\ = \frac{p_{NH_3}^2}{27 \times p^4} = \frac{p_{NH_3}^2}{27 \times \left(\frac{P}{4}\right)^4} \quad [\because P = 4p]$$

$$K_p = \frac{p_{NH_3}^2 \times 4^4}{3^2 \times 3 \times P^4} \Rightarrow p_{NH_3}^2 = \frac{3^2 \times 3 \times P^4 \times K_p}{4^4}$$

$$\Rightarrow p_{NH_3} = \frac{3 \times 3^{1/2} \times P^2 \times K_p^{1/2}}{4^2} = \frac{3^{3/2} \times P^2 \times K_p^{1/2}}{16}$$

9. Molar mass of $NH_4SH = 18 + 33 = 51 \text{ g mol}^{-1}$

Number of moles of NH_4SH introduced in the vessel

$$= \frac{\text{Weight}}{\text{Molar mass}} = \frac{5.1}{51} = 0.1 \text{ mol}$$



Number of moles at $t = 0$	0.1	0	0
At $t = t_{eq}$	0.1(l - 0.03)	30% of 0.1 = 0.03	30% of 0.1 = 0.03

Active mass (mol L ⁻¹)	0.03 = 0.01	0.03 = 0.01
	3	3

$$K_C = \frac{[NH_3][H_2S]}{[NH_4HS(s)]} = \frac{0.01 \times 0.01}{1} = 10^{-4} \text{ (mol L}^{-1})^2$$

$$\Rightarrow K_p = K_C(RT)^{\Delta n_g}$$

[where, $\Delta n_g = \Sigma n_{\text{product}} - \Sigma n_{\text{reactant}} = 2 - 0 = 2$

$$\therefore K_p = K_C(RT)^2$$

$$= 10^{-4} \times [0.082 \times (273 + 327)]^2 \text{ atm}^2$$

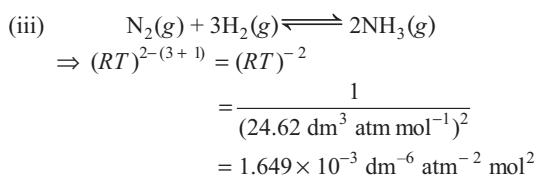
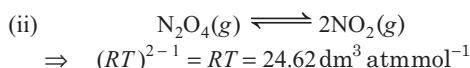
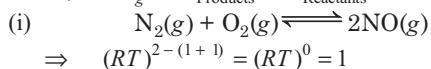
$$= 0.242 \text{ atm}^2$$

96 Chemical and Ionic Equilibrium

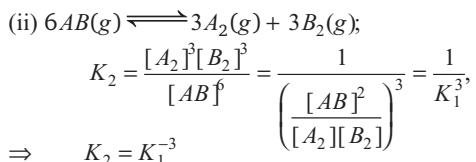
10. We know that, the relationship between K_p and K_C of a chemical equilibrium state (reaction) is

$$K_p = K_C (RT)^{\Delta n_g} \Rightarrow \frac{K_p}{K_C} = (RT)^{\Delta n_g}$$

where, $\Delta n_g = \sum n_{\text{Products}} - \sum n_{\text{Reactants}}$

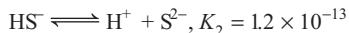


11. (i) $\text{A}_2(g) + \text{B}_2(g) \rightleftharpoons 2\text{AB}(g); \quad K_1 = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]}$



12. Given $[\text{H}_2\text{S}] = 0.10 \text{ M}$

$$[\text{HCl}] = 0.20 \text{ M} \text{ So, } [\text{H}^+] = 0.20 \text{ M}$$



It means for,

$$\begin{aligned} \text{H}_2\text{S} &\rightleftharpoons 2\text{H}^+ + \text{S}^{2-} \\ K &= K_1 \times K_2 = 1.0 \times 10^{-7} \times 1.2 \times 10^{-13} \\ &= 1.2 \times 10^{-20} \end{aligned}$$

Now $[\text{S}^{2-}] = \frac{K \times [\text{H}_2\text{S}]}{[\text{H}^+]^2}$ [according to the final equation]
 $= \frac{1.2 \times 10^{-20} \times 0.1 \text{ M}}{(0.2 \text{ M})^2}$
 $= \frac{1.2 \times 10^{-20} \times 1 \times 10^{-1} \text{ M}}{4 \times 10^{-2} \text{ M}} = 3 \times 10^{-20} \text{ M}$

13. $A + B \rightleftharpoons C + D$

Initially at $t = 0 \quad 1 \quad 1 \quad 1 \quad 1$
At equilibrium $1-x \quad 1-x \quad 1+x \quad 1+x$

$$K_{\text{eq}} = \frac{[C][D]}{[A][B]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2}$$

or $100 = \left(\frac{1+x}{1-x}\right)^2 \text{ or } 10 = \frac{1+x}{1-x}$

or $10 - 10x = 1 + x$
 $10 - 1 = x + 10x$

$$9 = 11x$$

$$x = \frac{9}{11} = 0.818$$

$\therefore [D] = 1 + x = 1 + 0.818 = 1.818$

14. Given, $\Delta G^\circ = 2494.2 \text{ J}$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times \frac{1}{2}}{\left(\frac{1}{2}\right)^2} = 4$$

$$\therefore \text{We know, } \Delta G = \Delta G^\circ + RT \ln Q \\ = 2494.2 + 8.314 \times 300 \ln 4 \\ = 28747.27 \text{ J (+ve value)}$$

Also, we have $\Delta G = RT \ln \frac{Q}{K}$

If ΔG is positive, $Q > K_C$
Therefore, reaction shifts in reverse direction.

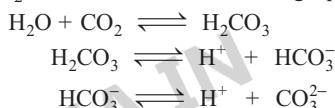
15. For the given reaction, $\Delta n_g = n_P - n_R$

where, n_P = number of moles of products
 n_R = number of moles of reactants

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = -\frac{1}{2}$$

16. When CO_2 is dissolved in water, following equilibria are established:



Therefore, in solution, all of the above mentioned species exist.

17. At equilibrium, $\Delta G = 0$

$$G(\text{reactants}) = G(\text{products})$$

$$G(\text{N}_2) + 3G(\text{H}_2) = 2G(\text{NH}_3)$$

A catalyst does not affect either equilibrium composition or equilibrium constant, it just increases rate of both forward and backward reaction but by the same factor.

18. $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)^+]; \quad K_1 = 3.5 \times 10^{-3}$



$$K = K_1 \times K_2 = 5.95 \times 10^{-6}$$

19. $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad \text{Total}$

$$1-\alpha \quad 2\alpha \quad 1+\alpha$$

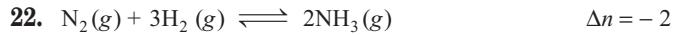
$$p_i: \quad \frac{1-\alpha}{1+\alpha} p \quad \frac{2\alpha}{1+\alpha} p \quad K_p = \frac{4\alpha^2}{1-\alpha^2} p$$

At constant temperature, halving the volume will change both p and α but K_p remains constant.

20. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2, K_p = \frac{4x^2 p}{1-x^2}$. K_p is function of temperature only, does not change with either p or x .

21. $A + B \rightleftharpoons C + D, Q = \frac{[C][D]}{[A][B]}$

As time passes, amount of products 'C' and 'D' increases, hence Q increases.



$$K_p = K_c (RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$$

23. Both temperature and pressure will change the equilibrium amount of $X_3Y(g)$. Temperature changes the value of equilibrium constant.

24. Adding reactant will drive the reaction in forward direction in order to restore equilibrium. Therefore, addition of $CO(g)$ will increase the equilibrium amount of CO_2 .



At 300 K :	1.0 atm	0
At 600 K :	2.0 – 0.40	0.80 Total pressure = 2.40 atm

26. In reactions (a), (b) and (c), atleast one of the product is either insoluble precipitate or a gas that drive the reaction continuously to right and do not allow equilibrium to be established. Following is the reversible reaction.



27. K_p for a given reversible reaction depends only on temperature.

28. Equilibrium constant of a given reversible reaction depends only on temperature.

29. For the reaction, $A \rightleftharpoons P$

Given,

$$\frac{T_1 < T_2}{\ln K_1 > \frac{T_2}{T_1}} \quad \dots(i)$$

It shows, On increasing the temperature, K decreases so reaction is exothermic i.e., $\Delta H^\circ < 0$

Besides, graph shows $K > 1$

$$So \quad \Delta G^\circ < 0$$

Now from equation (i)

$$\begin{aligned} T_1 \ln K_1 &> T_2 \ln K_2 \\ -\Delta G^\circ_1 &> -\Delta G^\circ_2 \end{aligned}$$

Likewise $(-\Delta H^\circ + T_1 \Delta S^\circ) > (-\Delta H^\circ + T_2 \Delta S^\circ)$

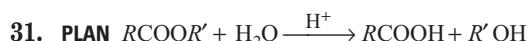
or simply $T_1 \Delta S^\circ > T_2 \Delta S^\circ$

$$So, \quad (T_2 - T_1) \Delta S^\circ < 0$$

$$\therefore \quad \Delta S^\circ < 0$$

In other words, increase of ΔG with increase in temperature is possible only when $\Delta S^\circ < 0$. Hence, options (a) and (c) are correct.

30. Since, the reaction is exothermic, there will be less ammonia at equilibrium and higher temperature. However, rate of reaction increases with rise in temperature, NH_3 will be formed at faster rate in the initial stage when the temperature is high.



Acid hydrolysis of ester is follows first order kinetics.

For same concentration of ester in each case, rate is dependent on $[H^+]$ from acid.

$$Rate = k[RCOOR']$$

Also for weak acid, $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$(Rate)_{HA} = k[H^+]_{HA}$$

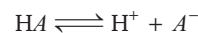
$$(Rate)_{HX} = k[H^+]_{HX}$$

$$(Rate)_{HX} = 100(Rate)_{HA}$$

\therefore Also in strong acid, $[H^+] = [HX] = 1 M$

$$\frac{(Rate)_{HX}}{(Rate)_{HA}} = 100 = \frac{[H^+]_{HX}}{[H^+]_{HA}} = \frac{1}{[H^+]_{HA}}$$

$$\therefore [H^+]_{HA} = \frac{1}{100}$$



$$\begin{array}{ccc} 1 & 0 & 0 \\ (1-x) & x & x \end{array}$$

$$x = 0.01$$

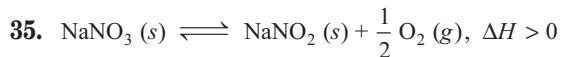
$$\therefore K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.01 \times 0.01}{0.99} = 1.01 \times 10^{-4}$$

32. Cl^- , CN^- and SCN^- forms precipitate with $Cu(I)$, remove $Cu(I)$ ion from equilibrium and reaction shifts in backward direction according to Le-Chatelier's principle.

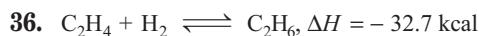
33. If inert gas is introduced at constant pressure, volume of container will have to be increased and this will favour the forward reaction. Also adding $PCl_5(g)$ at constant volume will favour forward reaction because $PCl_5(g)$ is a reactant.



Adding inert gas at constant volume will not affect partial pressure of reactant or products, hence will not affect equilibrium amount of either reactant or products.



$NaNO_3$ and $NaNO_2$ are in solid state, changing their amount has no effect on equilibrium. Increasing temperature will favour forward reaction due to endothermic nature of reaction. Also, increasing pressure will favour backward reaction in which some $O_2(g)$ will combine with $NaNO_2(s)$ forming $NaNO_3$.



The above reaction is exothermic, increasing temperature will favour backward reaction, will increase the amount of C_2H_4 . Decreasing pressure will favour reaction in direction containing more molecules (reactant side in the present case). Therefore, decreasing pressure will increase amount of C_2H_4 .

Removing H_2 , which is a reactant, will favour reaction in backward direction, more C_2H_4 will be formed.

Adding C_2H_6 will favour backward reaction and some of the C_2H_6 will be dehydrogenated to C_2H_4 .

$$37. Smaller : K_p = \frac{K_c}{RT}$$

38. changing pressure has no effect on equilibrium constant.

$$39. K_p = K_c (RT)^{\Delta n}, \text{ where, } \Delta n = \Sigma n(\text{products}) - \Sigma n(\text{reactants})$$

40. Rate of any reaction increases on rising temperature.

41. Catalyst has no effect on thermodynamics of reaction.

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42. It is $\frac{1}{\sqrt{K}}$.

43. Evaporation is an endothermic process.

44. (a) $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

$$\Delta G^\circ = 2\Delta G_f^\circ(\text{NO}_2) - \Delta G_f^\circ(\text{N}_2\text{O}_4) = 0$$

$$\text{Also } \Delta G^\circ = -RT \ln K = 0, \quad K = 1$$

Let the reaction shifts in forward direction.

$$\begin{array}{rcl} \text{N}_2\text{O}_4(g) & \rightleftharpoons & 2\text{NO}_2(g) \quad \text{Total} \\ 5-x & & 5+2x \quad 10+x \\ p_i: \quad \frac{5-x}{10+x} \times 20 & & \frac{5+2x}{10+x} \times 20 \\ \Rightarrow \quad K = \frac{(5+2x)^2}{(10+x)^2} \times \frac{10+x}{5-x} \times 20 = 1 \\ \Rightarrow \quad 81x^2 + 405x + 450 = 0 \\ x = -1.66 \text{ and } -3.33 \end{array}$$

Both values of x indicates that reaction actually proceeds in backward direction.

$$(b) \left(p + \frac{a}{Vm^2}\right)(Vm - b) = RT$$

$$\left(p + \frac{ap^2}{(pV)^2}\right)\left(\frac{pV}{p} - b\right) = RT$$

$$\Rightarrow [(pV^2)p + ap^2][(pV) - b] = p(pV)^2 RT$$

$$\Rightarrow p \cdot [pV^2 + ap](pV - bp) = p(pV^2)RT$$

But $p = 0$

$$\text{Intercept} = RT \Rightarrow (pV)^3 = (pV)^2 RT$$

45. (i) Mole of solid NH_4HS taken initially = $\frac{3.06}{51} = 0.06$

$$\text{At equilibrium } \text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)$$

$$K_c = \left(\frac{0.018}{2}\right)^2 = 8.1 \times 10^{-5}$$

$$p(\text{NH}_3) = \frac{0.018 \times 0.082 \times 300}{2} = 0.22 \text{ atm}$$

$$K_p = (0.22)^2 = 4.84 \times 10^{-2}$$

(ii) Addition of solid NH_4HS will have no effect on equilibrium.

46. (a) $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ Total moles

$$1-\alpha \qquad \qquad \alpha \qquad \qquad \alpha \qquad \qquad 1+\alpha$$

$$\text{Average molar mass} = \frac{208.5}{1.4} = 148.9$$

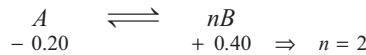
$$\rho \text{ (density)} = \frac{pM}{RT} = \frac{1 \times 148.9}{0.082 \times 400} = 4.54 \text{ g/L}$$

(b) $\text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$

$$K = \frac{K_{sp}}{K_c} = 2.9 \times 10^{-3} = \left(\frac{x}{1-2x}\right)^2$$

$$x = 0.049 \text{ M}$$

47. Observing the graph indicates that when 0.20 mole of A is reacted, 0.40 mole of product is formed.



$$-0.20 \qquad \qquad +0.40 \Rightarrow n=2$$

$$\text{At equilibrium, } [A] = 0.30 \text{ M}, [B] = 0.60 \text{ M}$$

$$K_c = \frac{[B]^2}{[A]} = \frac{0.36}{0.30} = 1.2$$

48. $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$

$$0.15 - 0.08 \qquad x - 0.16 \qquad 0.08$$

$$\text{Total moles at equilibrium} = x - 0.01$$

$$x - 0.01 = \frac{8.5 \times 2.5}{0.082 \times 750} = 0.34 \Rightarrow x = 0.35$$

$$(i) \text{ Partial pressures : } \text{CO} = \frac{0.07}{0.34} \times 8.5$$

$$\text{H}_2 = \frac{0.18}{0.34} \times 8.5$$

$$\text{CH}_3\text{OH} = \frac{0.08}{0.34} \times 8.5$$

$$K_p = \frac{0.08}{(0.07)(0.18)^2} \times \left(\frac{0.34}{8.5}\right)^2 = 0.056$$

$$(ii) \text{ Concentrations : } [\text{CH}_3\text{OH}] = \frac{0.08}{2.5} = 0.032 \text{ M}$$

$$[\text{H}_2] = \frac{0.18}{2.5} = 0.072 \text{ M}$$

$$[\text{CO}] = \frac{0.07}{2.5} = 0.028 \text{ M}$$

$$K_c = \frac{0.032}{(0.028)(0.072)^2} = 213.33$$

49. $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$

$$\text{Mole : } 0.2 - 0.10 \qquad x - 0.20 \qquad 0.10 \Rightarrow \text{Total moles} = x$$

$$\Rightarrow x = \frac{4.92 \times 5}{0.082 \times 600} = 0.5$$

$$\Rightarrow \text{moles of H}_2 \text{ at equilibrium} = x - 0.2 = 0.3$$

$$\text{Partial pressures : } \text{CO} = \frac{0.1}{0.5} p, \quad \text{H}_2 = \frac{0.3}{0.5} p,$$

$$\text{CH}_3\text{OH} = \frac{0.1}{0.5} p$$

$$K_p = \frac{\frac{p}{5}}{\left(\frac{p}{5}\right)\left(\frac{3}{5}p\right)^2} = \frac{25}{9p^2} = \frac{25}{9(4.92)^2} = 0.11 \text{ atm}^{-2}$$

$$\text{Concentrations : } [\text{CO}] = \frac{0.1}{5} \text{ M}, \quad [\text{H}_2] = \frac{0.3}{5} \text{ M},$$

$$[\text{CH}_3\text{OH}] = \frac{0.1}{5} \text{ M} \Rightarrow K_c = \frac{(0.1/5)}{(0.1/5)(0.3/5)^2} = 277.77 \text{ M}^{-2}$$

50. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$

$$\text{Initial } p_i : \quad 0 \qquad 2 \qquad 1$$

$$\text{Equilibrium } p_i : 2p \qquad 2+p \qquad 1-2p$$

$$K_p = 900 = \frac{(1-2p)^2}{(2+p)(2p)^2} \quad [\text{Ignoring } p \text{ in comparison to 2}]$$

$$p = \frac{1}{87} \text{ atm}$$

$$\text{Partial pressure of } \text{SO}_2 = 2p = \frac{2}{87} \text{ atm}$$

$$\text{Partial pressure of } \text{O}_2 = 2 + p = 2 + \frac{1}{87} = \frac{175}{87} \text{ atm}$$

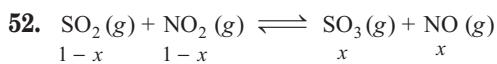
$$\text{Partial pressure of } \text{SO}_3 = 1 - 2p = 1 - 2\left(\frac{1}{87}\right) = \frac{85}{87} \text{ atm}$$



$$p_i : \begin{array}{ccc} \frac{1-\alpha}{1+\alpha} & \frac{2\alpha}{1+\alpha} & 1+\alpha \\ \frac{1-\alpha}{1+\alpha} p & \frac{2\alpha}{1+\alpha} p & \\ K_p = \frac{4\alpha^2}{1-\alpha^2} p = \frac{4(0.25)^2}{1-(0.25)^2} = 0.26 \text{ atm} \end{array}$$

When $p = 0.10 \text{ atm}$

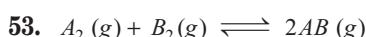
$$0.26 = \frac{4\alpha^2 (0.1)}{1-\alpha^2} \Rightarrow \alpha = 0.62$$



$Q_c = 1 < K_c$, i.e. reaction proceed in forward direction to attain equilibrium.

$$16 = \left(\frac{x}{1-x}\right)^2 \Rightarrow x = 0.80$$

$$[\text{NO}] = 0.80 \text{ M}, [\text{NO}_2] = 0.20 \text{ M}$$



$$K = \frac{[AB]^2}{[A_2][B_2]} = \frac{(n_{AB})^2}{n_{A_2} \cdot n_{B_2}} = \frac{(2x)^2}{(1-x)(2-x)}$$

$$\Rightarrow 50 = \frac{4x^2}{x^2 - 3x + 2} \Rightarrow 23x^2 - 75x + 50 = 0$$

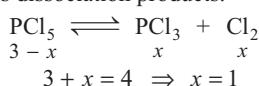
$$\Rightarrow x = \frac{75 \pm \sqrt{75^2 - 4 \times 23 \times 50}}{46} = 0.93, 2.32$$

2.32 is not acceptable because x cannot be greater than 1.

$$\text{Mole of } AB = 2x = 2 \times 0.93 = 1.86$$

54. Total moles of gases at equilibrium = $\frac{pV}{RT} = \frac{2.05 \times 100}{0.082 \times 500} = 5.0$

Out of this 5 moles, 1.0 mole is for $\text{N}_2(g)$ and remaining 4 moles for PCl_5 and its dissociation products.



$$\text{Degree of dissociation} = \frac{1}{3} = 0.33$$

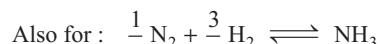


Initial :	1.0	3.0	0
Equilibrium	1 - 0.25	3 - 0.75	0.05
	= 0.75	= 2.25	

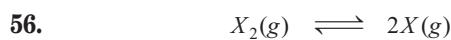
$$[\text{N}_2] = \frac{0.75}{4}, [\text{H}_2] = \frac{2.25}{4}, [\text{NH}_3] = \frac{0.50}{4}$$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.50)^2}{(0.75)(2.25)^3} \times 16$$

$$= 0.468 \text{ L}^2 \text{ mol}^{-2}$$



$$K'_c = \sqrt{K_c} = 0.68$$



$$\text{At } t=0 \quad 1 \quad 0$$

$$\text{At equilibrium} \quad \left(1 - \frac{x}{2}\right) \quad x \quad (\text{where, } x = \beta_{\text{eq}})$$

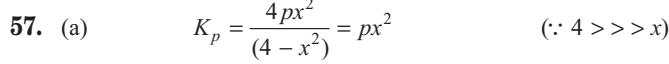
$$\text{Total moles} = \left(1 + \frac{x}{2}\right) \text{ and Mole fraction, } X_2(g) = \frac{\left(1 - \frac{x}{2}\right)}{\left(1 + \frac{x}{2}\right)}$$

$$X(g) = \left(\frac{x}{1 + \frac{x}{2}} \right) \text{ and } p = 2 \text{ bar}$$

$$\text{Partial pressure, } p_{X_2} = \left(\frac{1 - \frac{x}{2}}{1 + \frac{x}{2}} \right) \cdot p \text{ and } p_X = \frac{p \cdot x}{\left(1 + \frac{x}{2}\right)}$$

$$\therefore K_p = p_X^2 / p_{X_2} = \frac{\left[px / \left(1 + \frac{x}{2}\right)\right]^2}{p \left(1 - \frac{x}{2}\right) / \left(1 + \frac{x}{2}\right)}$$

$$= \frac{4px^2}{(4-x^2)} = \frac{8\beta_{\text{eq}}^2}{(4-\beta_{\text{eq}}^2)}$$



$$\therefore x \propto \sqrt{\frac{1}{p}}$$

If p decreases, x increases. Equilibrium is shifted in the forward side. Thus, statement (a) is correct.

(b) At the start of the reaction, $Q = 0$ where, Q is the reaction quotient $\Delta G = \Delta G^\circ + 2.303RT \log Q$

Since, $\Delta G^\circ > 0$, thus ΔG is -ve.

Hence, dissociation takes place spontaneously.

Thus, (b) is correct.

(c) If we use $x = 0.7$ and $p = 2$ bar then $K_p = \frac{4 \times 2(0.7)^2}{[4 - (0.7)^2]} = 1.16 > 1$

Thus, (c) is incorrect.

(d) At equilibrium, $\Delta G = 0$

$$\therefore \Delta G^\circ = -2.303RT \log K_p$$

Since, $\Delta G^\circ = + \text{ve}$

Hence, $K_p < 1$

$$K_C = \frac{K_p}{(RT)}$$

Then $K_C < 1$. Thus, (d) is correct.

100 Chemical and Ionic Equilibrium

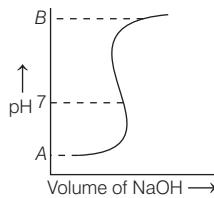
Topic 2 Ionic Equilibrium

1. Given 100 mL of 0.1 M HCl is taken in beaker and to it 100 mL of 0.1 M NaOH is added.

This is acid (HCl) and base (NaOH) titration. Here, phenolphthalein act as an indicator and colour change is pink. The correct graph that depicts the change in pH is as follows.

At first HCl (acid) is taken in beaker and base (NaOH) is taken in burette.

When base is added drop wise then acid-base reaction occurs and following changes are observed.



pH → 0 to 7 is acidic.

pH → 7 is neutral.

pH → 7 to 14 is basic.

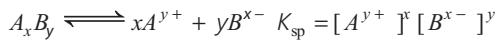
Initially, the graph increases steeply but when concentration of acid becomes equal to base then no change is seen in graph.

This point is called neutral point or equivalence point. Equivalence point, where pH = 7.

After the equivalence point (pH = 7), base (NaOH) is continuously mixed drop by drop then pH increases by 7 and graph also increases slowly. At the point B, solution become basic, again base (NaOH) is mixed drop by drop and the solution becomes basic at point B. Following inference can be seen in the graphs.

- According to this graph, pH = 7 is equivalence point and use of NaOH (base) drop by drop leads to basic solution as a result, value of pH increases slowly. This is correct option.
- According to graph, it shows straight line that mean graph increases instantly but this titration show pH increases slowly because base (NaOH) is mix drop by drop.
- After equivalence point (pH = 7) graph is constant. It is wrong because graph increases and the solution becomes pure basic then graph show constant value.
- According to graph, equivalence point (pH = 7) graph should increase but it decreases.

2. **Key Idea** The concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature.



Solubility of Cd(OH)₂ (S) = 1.84×10^{-5} M

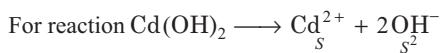
Given, pH = 12 [for Cd(OH)₂ in buffer solution]

$$\text{So, } pOH = 2 \quad (\because pH + pOH = pK_w)$$

$$12 + pOH = 14$$

$$pOH = 14 - 12 = 2$$

$$\therefore [OH^-] = 10^{-2} \text{ in buffer solution.}$$



$$K_{sp} = [\text{Cd}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = (S)(2S)^2 = 4S^3 = 4(1.84 \times 10^{-5})^3$$

$$K_{sp} = 24.9 \times 10^{-15}$$

$$[\text{Cd}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2}$$

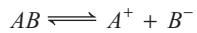
$$[\text{Cd}^{2+}] = \frac{24.9 \times 10^{-15}}{(10^{-2})^2} = 24.9 \times 10^{-15} \times 10^{+4}$$

$$\Rightarrow = 24.9 \times 10^{-11} \text{ M}$$

$$[\text{Cd}^{2+}] = 2.49 \times 10^{-10} \text{ M}$$

The expected solubility of Cd(OH)₂ in a buffer solution of pH = 12 is 2.49×10^{-10} M.

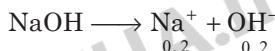
3. **Key Idea** Concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature. For reaction,



$$K_{sp} = [A^+][B^-]$$



Initially	1	0	0
At equilibrium	$1 - S$	S	$3S + 0.2$



$$K_{sp} \text{ of Al(OH)}_3 = 2.4 \times 10^{-24} \text{ (Given)}$$

$$K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3$$

$$2.4 \times 10^{-24} = [S][3S + 0.2]^3$$

$$2.4 \times 10^{-24} = [S][0.008]$$

$$[S] = 3 \times 10^{-22}$$

4. **Key Idea** NH₄Cl is a salt of weak base (NH₄OH) and strong acid (HCl). On hydrolysis, NH₄Cl will produce an acidic solution (pH < 7) and the expression of pH of the solution is

$$\text{pH} = 7 - \frac{1}{2}(\text{p}K_b + \log C)$$

$$\text{Given, } K_b(\text{NH}_4\text{OH}) = 10^{-5}$$

$$\therefore \text{p}K_b = -\log K_b = -\log(10^{-5}) = 5$$

$$C = \text{concentration of salt solution} = 0.02 \text{ M}$$

$$= 2 \times 10^{-2} \text{ M}$$

$$\text{Now, pH} = 7 - \frac{1}{2}(\text{p}K_b + \log C)$$

On substituting the given values in above equation, we get

$$= 7 - \frac{1}{2}[5 + \log(2 \times 10^{-2})] = 7 - \frac{1}{2}[5 + \log 2 - 2]$$

$$= 7 - \frac{1}{2}[5 + 0.301 - 2] = 7 - 1.65 = 5.35$$

5. The explanation of given statements are as follows:

In statement (I), millimoles of H⁺ = $400 \times 0.1 \times 2 = 80$

Millimoles of OH⁻ = $400 \times 0.1 = 40$ (Limiting reagent)

∴ Millimoles of H^+ left = $80 - 40 = 40$

$$\begin{aligned} [H^+] &= \frac{40}{400 + 400} = \frac{40}{800} M = \frac{1}{20} M \\ \Rightarrow \quad pH &= -\log[H^+] = -\log\left(\frac{1}{20}\right) \\ &= -\log 1 + \log 2 + \log 10 = -0 + 0.301 + 1 \\ &\Rightarrow 1.30 \end{aligned}$$

Hence, the option (a) is correct.

In statement (II), ionic product of H_2O is temperature dependent.

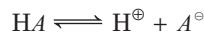
$$K_w = [H^+][OH^-] \approx 10^{-14} (\text{mol/L})^2 \text{ at } 25^\circ\text{C}$$

With increase in temperature, dissociation of H_2O units into H^+ and OH^- ions will also increase. As a result, the value of ionic product, $[H^+] \times [OH^-]$ will be increased. e.g.

Temperature	K_w (mol/L ²)
5°C	0.186×10^{-14}
25°C	1.008×10^{-14}
45°C	4.074×10^{-14}

Hence, the option (b) is correct.

In statement (III), for a weak monobasic acid HA



$$(1-\alpha) C \text{ M} \quad \alpha C \text{ M} \quad \alpha C \text{ M}$$

⇒ pH of the solution is 5, i.e.

$$\begin{aligned} [H^+] &= 10^{-5} \text{ M} = \alpha C \\ \Rightarrow \quad K_a &= \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{10^{-5} \times \alpha}{1-\alpha} \\ \Rightarrow \quad 10^{-5} &= \frac{10^{-5} \times \alpha}{1-\alpha} \\ \Rightarrow \quad \alpha &= 0.5 \Rightarrow \alpha \% = 50 \end{aligned}$$

Hence, the option (c) is correct.

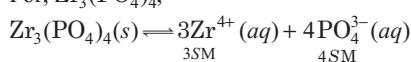
In statement (IV), Le-Chatelier's principle is applicable to common ion effect. Because, in presence of common ion (given) by strong electrolyte (say, $Na^+ \bar{A}$), the product of the concentration terms in RHS increases. For the weaker electrolyte, HA (say) the equilibrium shifts to the LHS, $HA \rightleftharpoons H^+ + A^-$.

As a result dissociation of HA gets suppressed. Hence, the option (d) is incorrect.

6. **Key Idea** The concentration of a substance in a saturated solution is defined as its solubility (S).

$$\text{For } A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}; K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

For, $Zr_3(PO_4)_4$,



$$K_{sp} = [Zr^{4+}]^3 [PO_4^{3-}]^4$$

$$K_{sp} = (3S)^3 (4S)^4 = 6912 S^7 \text{ or } S = \left(\frac{K_{sp}}{6912} \right)^{\frac{1}{7}}$$

Thus, the relation between molar solubility (S) and solubility product (K_{sp}) will be

$$S = \left(\frac{K_{sp}}{6912} \right)^{\frac{1}{7}}$$

7. Let the solubility of Ag_2CO_3 is S . Now, 0.1 M of $AgNO_3$ is added to this solution after which let the solubility of Ag_2CO_3 becomes S' .

$$\therefore [Ag^+] = S + 0.1 \text{ and } [CO_3^{2-}] = S'$$

$$K_{sp} = (S + 0.1)^2 (S') \quad \dots(i)$$

$$\text{Given, } K_{sp} = 8 \times 10^{-12}$$

∴ K_{sp} is very small, we neglect S' against S in Eq. (i)

$$\therefore K_{sp} = (0.1)^2 S'$$

$$\text{or } 8 \times 10^{-12} = 0.01 S'$$

$$\text{or } S' = 8 \times 10^{-12} \times 10^2 = 8 \times 10^{-10} \text{ M}$$

Thus, molar solubility of Ag_2CO_3 in 0.1 M

$AgNO_3$ is 8×10^{-10} M.

8. The reaction takes place when H_2SO_4 is added to NH_4OH is as follows :

H_2SO_4	+ 2 NH_4OH	→ $(NH_4)_2SO_4 + 2H_2O$
Strong acid	Weak base	Salt of strong acid + weak base
Millimoles at $t = 0$	$20 \times 0.1 = 2$	$30 \times 0.2 = 6$
Millimoles at $t = t$	0	2

So, the resulting solution is a basic buffer
[$NH_4OH + (NH_4)_2SO_4$].

According to the Henderson's equation,

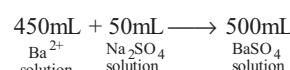
$$pOH = pK_b + \log \frac{[(NH_4)_2SO_4]}{[NH_4OH]}$$

$$= 4.7 + \log \frac{2}{2} = 4.7$$

$$\Rightarrow \quad pH = 14 - pOH = 14 - 4.7 = 9.3$$

9. It's given that the final volume is 500 mL and this final volume was arrived when 50 mL of 1 M Na_2SO_4 was added to unknown Ba^{2+} solution.

So, we can interpret the volume of unknown Ba^{2+} solution as 450 mL i.e.



Ba^{2+} solution Na_2SO_4 solution $BaSO_4$ solution

From this we can calculate the concentration of SO_4^{2-} ion in the solution via

$$M_1 V_1 = M_2 V_2$$

$$1 \times 50 = M_2 \times 500$$

(as 1M Na_2SO_4 is taken into consideration)

$$M_2 = \frac{1}{10} = 0.1 \text{ M}$$

Now for just precipitation,

Ionic product = Solubility product (K_{sp})

$$\text{i.e. } [Ba^{2+}][SO_4^{2-}] = K_{sp} \text{ of } BaSO_4$$

$$\text{Given } K_{sp} \text{ of } BaSO_4 = 1 \times 10^{-10}$$

$$\text{So, } [Ba^{2+}] [0.1] = 1 \times 10^{-10} \text{ or } [Ba^{2+}] = 1 \times 10^{-9} \text{ M}$$

17. $K_h(X^-) = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-5}} = 10^{-9} \Rightarrow \alpha = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-9}}{0.10}} = 10^{-4}$

% hydrolysis = $100\alpha = 0.01$

18. Minimum S^{2-} concentration would be required for precipitation of least soluble HgS .

For HgS , S^{2-} required for precipitation is

$$[S^{2-}] = \frac{K_{sp}}{[Hg^{2+}]} = \frac{10^{-54}}{10^{-3}} = 10^{-51} M$$

19. Alkali metal salts are usually more soluble than the salts of transition metals. Also, CuS is less soluble than ZnS because of $3d^9$ configuration of Cu^{2+} . Therefore, solubility order is



20. $A_pB_q \rightleftharpoons pA + qB$

$$K_{sp} = (pS)^p (qS)^q = S^{(p+q)} \cdot p^p \cdot q^q$$

21. $NaCN$ is basic salt, has highest pH while HCl has lowest pH. $NaCl$ is neutral salt has $pH = 7$ while NH_4Cl is acidic salt, has pH less than 7.



22. $75 \text{ mL } \frac{M}{5} HCl = 15 \text{ mmol HCl}$

$$25 \text{ mL } \frac{M}{5} NaOH = 5 \text{ mmol NaOH}$$

After neutralisation, 10 mmol HCl will be remaining in 100 mL of solution.

$$\text{Molarity of HCl in the final solution} = \frac{10}{100} = 0.10$$

$$pH = -\log [H^+] = -\log (0.10) = 1$$

23. In case of hydroxides of Group II A, solubility increases down the group. Therefore, $Be(OH)_2$ is least soluble, has lowest value of K_{sp} .

24. $HClO_4$ is the strongest acid among these.

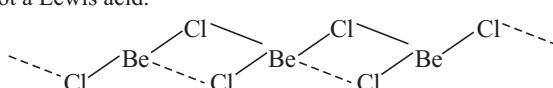
25. For precipitation to occur, $K_{sp} < Q_{sp}$.

$$Q_{sp} = \left(\frac{10^{-4}}{2}\right)\left(\frac{10^{-4}}{2}\right) = 2.5 \times 10^{-9} > K_{sp}$$

Hence, precipitate will be formed in this case. In all other case, $Q_{sp} < K_{sp}$ and no precipitation will occur.

26. In stomach, pH is 2-3, i.e. strongly acidic and aspirin will be almost unionised here due to common ion effect. However, pH in small intestine is 8, basic, aspirin will be neutralised here.

27. $BeCl_2$ exist in polymeric forms and has no electron deficiency, not a Lewis acid.



28. $NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$

Base Conjugate acid

29. When a weak acid (HX) is titrated against a strong base $NaOH$, basic salt (NaX) is present at the end point which makes end point slightly basic with pH around 8. Hence, phenolphthalein, that changes its colour in this pH range, would be the best choice of indicator to detect the end point.

30. The reaction of HA with strong base is



$$K = \frac{[A^-]}{[HA][OH^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

31. $K_a(HX) = \frac{K_w}{K_b} = 10^{-4}$

$$pH = pK_a + \log \frac{[X^-]}{[HX]} \Rightarrow pK_a = 4 \quad [\because [X^-] = [HX]]$$

32. For precipitation reaction, $Q_{IP} > K_{sp}$.

$$Q_{IP} = [Ca^{2+}][F^-]^2 = \left(\frac{10^{-2}}{2}\right) \times \left(\frac{10^{-3}}{2}\right)^2$$

$= 1.25 \times 10^{-9} > K_{sp}$, precipitate will be formed.

33. Acidic buffer is prepared by mixing weak acid with salt of its conjugate base. Therefore, acetic acid and sodium acetate can be used to prepare acidic buffer.

34. The order of acidic strength of conjugate acids is



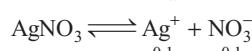
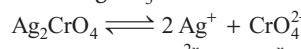
Reverse is the order of basic strength of their conjugate base, i.e. ClO^- is the strongest base.

35. $K_w = [H_3O^+][OH^-] = 10^{-6} \times 10^{-6} = 10^{-12}$

36. No matter, what is the concentration of HCl , its pH will always be less than 7 at $25^\circ C$. In the present case, the solution is very dilute, pH will be between 6 and 7.

37. **PLAN** In presence of common ion (in this case Ag^+ ion) solubility of sparingly soluble salt is decreased.

Let solubility of Ag_2CrO_4 in presence of 0.1 M



$$\text{Total } [Ag^+] = (2x + 0.1)M \approx 0.1 M$$

as $x \lll 0.1 M$

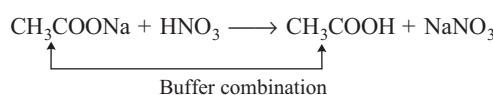
$$[CrO_4^{2-}] = x M$$

$$\text{Thus, } [Ag^+]^2 [CrO_4^{2-}] = K_{sp}$$

$$(0.1)^2(x) = 1.1 \times 10^{-12}$$

$$\therefore x = 1.1 \times 10^{-10} M$$

38. In HNO_3 and CH_3COONa combination, if HNO_3 is present in limiting amount, it will be neutralised completely, leaving behind some excess of CH_3COONa .



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If HCl is taken in limited quantity, final solution will have both CH_3COOH and CH_3COONa needed for buffer solution.

Ammonia and ammonium chloride forms basic buffer.

40. pH of 10^{-8} M solution will be between 6 and 7 but never 8. The conjugate base of an acid is formed by removing a proton (H^+) from acid. Therefore, HPO_4^{2-} is a conjugate base of H_2PO_4^- .



Increasing temperature will increase equilibrium constant of the above endothermic reaction.

At the mid-point of titration $\text{pH} = \text{p}K_a$

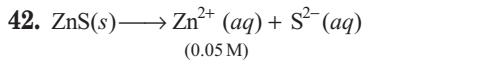
41. From the given diagram, 6 mL volume of HA used till equivalence point. At half of equivalence point, solution will be basic buffer with B and BH^+ .

$$\therefore \text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[\text{B}]}$$

At half equivalence point : $[\text{BH}^+] = [\text{B}]$ ($\because \text{pH} = 11$)

Therefore, $\text{pOH} = \text{p}K_b = 14 - 11 = 3$

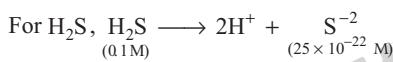
$$\therefore \text{p}K_b = 3.00$$



$$K_{\text{sp}}(\text{ZnS}) = [\text{Zn}^{2+}][\text{S}^{2-}] = 1.25 \times 10^{-22}$$

$$0.05 \times [\text{S}^{2-}] = 1.25 \times 10^{-22}$$

$$\Rightarrow [\text{S}^{2-}] = \frac{1.25 \times 10^{-22}}{0.05} = 25 \times 10^{-22} \text{ M}$$



$$K_{\text{net}} = 1 \times 10^{-21} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$1 \times 10^{-21} = \frac{[\text{H}^+]^2 \times 25 \times 10^{-22}}{[0.1]}$$

$$[\text{H}^+]^2 = \frac{1}{25}$$

$$[\text{H}^+] = \frac{1}{5} \Rightarrow 0.2 \text{ M}$$

43. Given, equilibrium constant (K_C) at 298 K = 1.6×10^{17}

	$\text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightleftharpoons \text{FeS}(s)$	
At initial concentration (Before mixing)	0.06 M	0.2 M
At initial concentration (After mixing)	0.03 M	0.1 M
At equilibrium	$0.03-X$	$0.1 - 0.03 =$ 0.07

[Here, $K_C \gg 10^3$, thus limiting reagent will be consumed almost completely, $0.03 - X = 0 \therefore X = 0.03$]

From equilibrium constant,

$$K_C = \frac{[\text{FeS}]}{[\text{Fe}^{2+}][\text{S}^{2-}]}$$

$$K_C = \frac{1}{X \times 0.07} \quad [\text{For FeS}(s) = 1 \text{ mol L}^{-1}]$$

$$1.6 \times 10^{17} = \frac{1}{X \times 0.07}$$

$$X = \frac{1}{1.6 \times 10^{17} \times 0.07} = 8.9 \times 10^{-17}$$

$$\text{Given, } X = Y \times 10^{-17} = 8.9 \times 10^{-17}$$

$$\therefore Y = 8.9$$

44. **Key Idea** Solubility of salt of weak acid (AB) in presence of H^+ ions from buffer solution can be calculated with the help of following formula.

$$\text{Solubility} = \sqrt{K_{\text{sp}} \left[\frac{[\text{H}^+]}{k_a} + 1 \right]}$$

Given, $\text{pH} = 3$, so $[\text{H}^+] = 10^{-3}$

$$K_a = 1 \times 10^{-8} \Rightarrow K_{\text{sp}} = 2 \times 10^{-10}$$

after putting the values in above formula

$$\text{Solubility} = \sqrt{2 \times 10^{-10} \left(\frac{10^{-3}}{10^{-8}} + 1 \right)} \approx \sqrt{2 \times 10^{-5}} = 4.47 \times 10^{-3} \text{ M}$$

Hence, the value of $y = 4.47$

45. **For P, i.e. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) is diluted to 60 mL**

The correct match is 1, i.e. the value of $[\text{H}^+]$ does not change on dilution due to the formation of following buffer.



Initial millimol 1 2

Final millimol 1 1

Final volume = 30 mL (20 + 10) in which millimoles of CH_3COOH and $\text{CH}_3\text{COO}^-\text{Na}^+$ are counted.

- For Q, i.e. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M CH₃COOH) is diluted to 80 mL**

The correct match is 5, i.e. the value of $[\text{H}^+]$ changes to $\sqrt{2}$ times of its initial value on dilution.

As per the condition given in Q the resultant solution before dilution contain 2 millimoles of $\text{CH}_3\text{COO}^-\text{Na}^+$ in 40 mL solution. Hence, it is the salt of weak acid and strong base. So,

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w K_a}{C}}$$

After dilution to 80 mL, the new 'C' becomes $\frac{C}{2}$, So,

$$[\text{H}^+]_{\text{new}} = \sqrt{\frac{K_w K_a}{C/2}} \text{ or } [\text{H}^+]_{\text{initial}} \times \sqrt{2}$$

- For R, i.e. (20 mL of 0.1 M HCl + 20 mL of 0.1 M NH₃) is diluted to 80 mL**

The correct match is 4, i.e. the value of $[\text{H}^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value of dilution.

As per the condition given in R the resultant solution before dilution contains 2 millimoles of NH_4Cl in 40 mL of solution. Hence, a salt of strong acid and weak base is formed.

For this,

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w \times C}{K_b}}$$

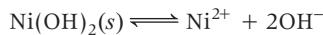
Now on dilution upto 80 mL new conc. becomes $C/2$.

$$\text{So, } [\text{H}^+]_{\text{new}} = \sqrt{\frac{K_w \times \frac{C}{2}}{K_b}}$$

$$\text{or } [\text{H}^+]_{\text{new}} = [\text{H}^+]_{\text{initial}} \times \frac{1}{\sqrt{2}}$$

For S, i.e. 10 mL saturated solution of Ni(OH)_2 in equilibrium with excess solid Ni(OH)_2 is diluted to 20 mL and solid Ni(OH)_2 is still present after dilution.

The correct match is 1.



as per the condition given it is a sparingly soluble salt. Hence, on dilution the concentration of OH^- ions remains constant in saturated solution.

So for this solution,

$$[\text{H}^+]_{\text{new}} = [\text{H}^+]_{\text{initial}}$$

46. $\text{I}_2 : \text{I}^- \longrightarrow \text{I}_2 = \text{I}_3^-$

47. Hydration energy facilitate solubility.

48. Amphoteric

49. SO_4^{2-} Conjugate base is formed by removing a proton from acid.

50. P_2O_5 is strongest acid and MgO is strongest base.

51. $\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{NaOH}(\text{aq}) ; \Delta H < 0$

52. Lewis acid accept lone pair of electron.

53. Degree of ionisation (α) = $\frac{\Lambda_m}{\Lambda^\infty}$

Let $\Lambda_m(HY) = x \Rightarrow \Lambda_m(HX) = \frac{x}{10}$

$$\Rightarrow \frac{\Lambda_m(HX)}{\Lambda_m(HY)} = \frac{1}{10} = \frac{\alpha(HX)}{\alpha(HY)} \quad [\because \Lambda^\infty(HX) = \Lambda^\infty(HY)]$$

Also : $K_a(HX) = (0.01)[\alpha(HX)]^2 \quad \dots (\text{i})$

$$K_a(HY) = (0.10)[\alpha(HY)]^2 \\ = 0.10[10\alpha(HX)]^2 = 10[\alpha(HX)]^2 \quad \dots (\text{ii})$$

$$\Rightarrow \frac{K_a(HX)}{K_a(HY)} = \frac{0.01}{10} = \frac{1}{1000}$$

$$\Rightarrow \log K_a(HX) - \log K_a(HY) = -3$$

$$\Rightarrow -\log K_a(HX) - [-\log K_a(HY)] = 3$$

$$\Rightarrow \text{p}K_a(HX) - \text{p}K_a(HY) = 3$$

54. It is a case of simultaneous solubility of salts with a common ion. Here, solubility product of CuCl is much greater than that of AgCl , it can be assumed that Cl^- in solution comes mainly from CuCl .

$$[\text{Cl}^-] = \sqrt{K_{\text{sp}}(\text{CuCl})} = 10^{-3}\text{M}$$

$$\text{Now, for AgCl, } K_{\text{sp}} = 1.6 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

$$= [\text{Ag}^+] \times 10^{-3}$$

$$\Rightarrow [\text{Ag}^+] = 1.6 \times 10^{-7}$$

55. Basic salts solution will have $\text{pH} > 7$, will change colour of litmus paper red to blue

KCN , K_2CO_3 and LiCN are the only basic salts among these.

56. The hydrolysis reaction is



$$K_h = \frac{K_w}{K_a} = 10^{-10}$$

$$[\text{OH}^-] = \sqrt{K_h C} = 10^{-6}$$

$$\text{pOH} = 6 \quad \text{and} \quad \text{pH} = 8$$

57. At the end-point, $[A^-] = 0.05$

$$K_b(A^-) = K_w / K_a = 2 \times 10^{-9}$$

$$[\text{OH}^-] = \sqrt{K_b C} = \sqrt{2 \times 10^{-9} \times 0.05} = 10^{-5}$$

$$\text{pOH} = 5 \quad \text{and} \quad \text{pH} = 9$$

58. (i) $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

If no HCl is present,

$$[\text{HCl}] = \frac{0.2}{2} = 0.10 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.10 \text{ M}$$

The major contributor of H^+ in solution is HCl .

$$K_a = \frac{C\alpha(0.1)}{C(1-\alpha)} = 1.75 \times 10^{-5}$$

$$\alpha = 1.75 \times 10^{-4}$$

(ii) mmol of NaOH added = $\frac{6}{40} \times 1000 = 150$

$$\text{mmol of HCl} = 500 \times 0.2 = 100$$

$$\text{mmol of CH}_3\text{COOH} = 500 \times 0.2 = 100$$

After neutralisation, mmol of $\text{CH}_3\text{COOH} = 50$

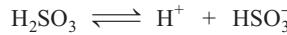
$$\text{mmol of CH}_3\text{COONa} = 50$$

$$\text{pH} = \text{p}K_a = 4.75$$

59. Partial pressure of SO_2 in air = 10^{-5} atm

$$[\text{SO}_2]_{\text{aq}} = 1.3653 \times 10^{-5} \text{ mol L}^{-1}$$

$\because \text{p}K_a = 1.92$ and concentration of H_2SO_3 is very low, it is almost completely ionised as



$$[\text{H}^+] = 1.3653 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log(1.3653 \times 10^{-5}) = 4.86$$

60. In water, $K_{\text{sp}} = 4S^3 = 4(6.7 \times 10^{-6})^3 = 1.2 \times 10^{-15}$

In buffer of $\text{pH} = 8$, $\text{pOH} = 6$, $[\text{OH}^-] = 10^{-6}$

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$$K_{sp} = S [\text{OH}^-]^2$$

$$S = \frac{1.2 \times 10^{-15}}{10^{-12}} = 1.2 \times 10^{-3} \text{ M}$$

61. (a) $E = 0.164 = -0.059 \log \frac{[\text{Ag}^+]_{\text{anode}}}{0.10}$

$$[\text{Ag}^+]_{\text{anode}} = 1.66 \times 10^{-4} \text{ M}$$

$$[\text{CrO}_4^{2-}] = \frac{[\text{Ag}^+]}{2} = 8.3 \times 10^{-5} \text{ M}$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$= (1.66 \times 10^{-4})^2 (8.3 \times 10^{-5}) = 2.3 \times 10^{-12}$$

(b) pH of HCl = 2

$$\therefore [\text{H}^+] = 10^{-2} \text{ M}$$

Moles of H^+ ions in 200 mL of 10^{-2} M HCl solution

$$= \frac{10^{-2}}{1000} \times 200 = 2 \times 10^{-3}$$

Similarly, pH of NaOH = 12

$$\therefore [\text{H}^+] = 10^{-12} \text{ M}$$

$$\text{or } [\text{OH}^-] = 10^{-2} \text{ M} \quad [\because [\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ m}]$$

Moles of OH^- ion in 300 mL of 10^{-2} M NaOH solution

$$= \frac{10^{-2}}{1000} \times 300 = 3 \times 10^{-3}$$

Total volume of solution after mixing = 500 mL

Moles of OH^- ion left in 500 mL of solution

$$= (3 \times 10^{-3}) - (2 \times 10^{-3}) = 10^{-3}$$

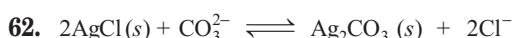
Molar concentration of OH^- ions in the resulting

$$\text{solution} = \frac{10^{-3}}{500} \times 1000 = 2 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(2 \times 10^{-3})$$

$$= -\log 2 + 3 \log 10 = -0.3 \approx 103 = 2.699$$

$$\therefore \text{pH} = 14 - 2.699 = 11.301$$



$$K = \frac{[\text{Cl}^-]^2}{[\text{CO}_3^{2-}]} = \frac{[\text{Cl}^-]^2}{[\text{CO}_3^{2-}]} \times \frac{[\text{Ag}^+]^2}{[\text{Ag}^+]^2} = \frac{K_{sp}(\text{AgCl})^2}{K_{sp}(\text{Ag}_2\text{CO}_3)}$$

$$[\text{Cl}^-] = \frac{0.0026}{35.5} \text{ M} = 7.3 \times 10^{-5} \text{ M}$$

The above concentration of Cl^- indicates that $[\text{CO}_3^{2-}]$ remains almost unchanged.

$$\frac{7.3 \times 10^{-5}}{1.5} = \frac{K_{sp}(\text{AgCl})^2}{8.2 \times 10^{-12}}$$

$$K_{sp}(\text{AgCl}) = 2 \times 10^{-8}$$

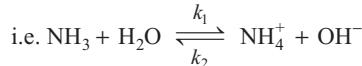
63. $\text{pH} = \text{p}K_{In} + \log 10 = \text{p}K_{In} + 1$

$$= \text{p}K_{In} + \log(0.1) = \text{p}K_{In-1}$$

pH range is $\text{p}K_{In-1}$ to $\text{p}K_{In+1}$.

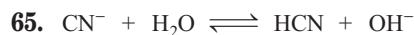
64. $K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$

$$K_b(\text{NH}_3) = K_w / K_a = \frac{10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5}$$



$$K = \frac{k_1}{k_2} = 1.8 \times 10^{-5}$$

$$k_1 = K k_2 = 1.8 \times 10^{-5} \times 3.4 \times 10^{10} = 6.12 \times 10^5$$



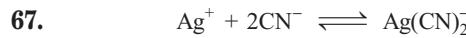
$$K_h = 2 \times 10^{-5}$$

$$[\text{OH}^-] = \sqrt{K_h C} = \sqrt{2 \times 10^{-5} \times 0.5} = \sqrt{10^{-5}}$$

$$\text{pOH} = 2.5 \quad \text{and} \quad \text{pH} = 11.5$$

66. For salts of weak acid and weak base.

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b) = 7 + \frac{1}{2} (3.8 - 4.8) = 6.50$$

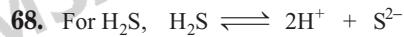


Initial :	0.03	0.10	0
Equilibrium :	x	$0.10 - 0.06$	0.03

$$K = \frac{1}{4 \times 10^{-19}} = 2.5 \times 10^{18}$$

$$\Rightarrow K = 2.5 \times 10^{18} = \frac{0.03}{(0.04)^2 x}$$

$$x = 7.50 \times 10^{-18} \text{ M Ag}^+$$



$$K = K_1 \times K_2 = 1.3 \times 10^{-20}$$

Minimum $[\text{S}^{2-}]$ required to begin precipitation of

$$MS = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}$$

$$K = 1.3 \times 10^{-20} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = [\text{H}^+]^2 \frac{(1.2 \times 10^{-19})}{0.10}$$

$$[\text{H}^+] = 0.10 \text{ M} \Rightarrow \text{pH} = 1$$

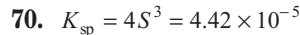
69. Mixing H_2CO_3 with NaHCO_3 results in buffer solution.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NaHCO}_3]}{[\text{H}_2\text{CO}_3]} = \text{p}K_a + \log \frac{n(\text{NaHCO}_3)}{n(\text{H}_2\text{CO}_3)}$$

$$\Rightarrow 7.4 = -\log(7.8 \times 10^{-7}) + \log \frac{x}{20}$$

$$\Rightarrow x = 400 \text{ mmol}$$

$$\text{NaHCO}_3 = 5 \times V \Rightarrow V = 80 \text{ mL}$$



$$S = 0.022 \text{ M}$$

mmol of $\text{Ca}(\text{OH})_2$ in 500 mL saturated solution = 11

mmol of NaOH in 500 mL 0.40 M solution = 200

Total mmol of OH^- = 200 + 2 × 11 = 222

$$[\text{OH}^-] = 0.222 \text{ M}$$

$$\text{Solubility in presence of NaOH} = \frac{K_{\text{sp}}}{[\text{OH}^-]^2}$$

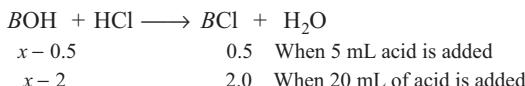
$$= \frac{4.42 \times 10^{-5}}{(0.222)^2} = 9 \times 10^{-4} \text{ M}$$

mmol of Ca^{2+} remaining in solution = 0.9

mmol of $\text{Ca}(\text{OH})_2$ precipitated = 10.1

mg of $\text{Ca}(\text{OH})_2$ precipitated = $10.1 \times 7.4 = 747.4 \text{ mg}$

71. Let 40 mL of base contain x mmol of BOH.



When pH is 10.04, pOH = 3.96 and when pH is 9.14, pOH is 4.86. Therefore,

$$3.96 = \text{p}K_b + \log \frac{0.50}{x - 0.5} \quad \dots(\text{i})$$

$$3.96 = \text{p}K_b + \log \frac{2.0}{x - 2} \quad \dots(\text{ii})$$

Subtracting Eq. (i) from Eq. (ii) gives

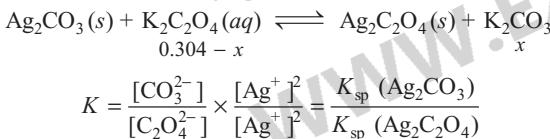
$$0.90 = \log \left(\frac{2}{x - 2} \times \frac{x - 0.5}{0.5} \right) \Rightarrow 28 = \frac{4(x - 0.5)}{x - 2}$$

$\Rightarrow x = 3.5$, substituting in equation (i) gives

$$\begin{aligned} 3.96 &= \text{p}K_b + \log \frac{0.5}{3} \\ K_b &= 1.8 \times 10^{-5} \end{aligned}$$

72. Initial concentration of $\text{K}_2\text{C}_2\text{O}_4 = \frac{0.152}{0.50} = 0.304 \text{ M}$,

Also for the following equilibrium:



Given, $0.304 - x = 0.0358 \Rightarrow x = 0.2682$

$$\Rightarrow K = \frac{0.2682}{0.0358} = 7.5$$

$$\begin{aligned} K_{\text{sp}} (\text{Ag}_2\text{CO}_3) &= K \times K_{\text{sp}} (\text{Ag}_2\text{C}_2\text{O}_4) \\ &= 7.5 \times 1.29 \times 10^{-11} = 9.675 \times 10^{-11} \end{aligned}$$

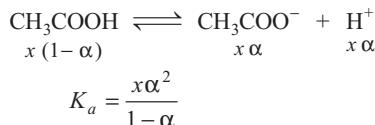
73. $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

When concentration of CH_3COOH is 1.0 M, ' α ' is negligible,

$$[\text{H}^+] = \sqrt{K_a C} = 4.24 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log (4.24 \times 10^{-3}) = 2.37$$

Now, let us assume that solution is diluted to a volume where concentration of CH_3COOH (without considering ionisation) is x .



Also, desired pH = $2 \times 2.37 = 4.74$

$$[\text{H}^+] = 1.8 \times 10^{-5} = x\alpha$$

$$K_a = 1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5}\alpha}{1-\alpha}$$

$$\alpha = 0.5 \text{ and } x = 3.6 \times 10^{-5} \text{ M}$$

$$\text{Volume (final)} = 1/3.6 \times 10^{-5} = 27.78 \times 10^3 \text{ L.}$$

$$\begin{aligned} 74. \text{ pOH of buffer solution} &= \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} \\ &= -\log (1.8 \times 10^{-5}) + \log \frac{0.25}{0.05} = 5.44 \\ [\text{OH}^-] &= 3.6 \times 10^{-6} \text{ M} \\ [\text{Al}^{3+}] &= \frac{K_{\text{sp}}}{[\text{OH}^-]^3} = \frac{6 \times 10^{-32}}{(3.6 \times 10^{-6})^3} = 1.28 \times 10^{-15} \text{ M} \\ [\text{Mg}^{2+}] &= \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{8.9 \times 10^{-12}}{(3.6 \times 10^{-6})^2} = 0.68 \text{ M} \end{aligned}$$

75. HCN for buffer will be formed by the reaction



$$\text{mmol of NaCN present initially} = \frac{0.01}{49} \times 1000 = 0.2$$

Let x mmol of HCl is added so that x mmol of NaCN will be neutralised forming x mmol of HCN.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{NaCN}]}{[\text{HCN}]} \\ 8.5 &= -\log (4.1 \times 10^{-10}) + \log \frac{0.2 - x}{x} \\ x &= 0.177 \text{ mmol} \end{aligned}$$

76. (i) 0.20 mole HCl will neutralise 0.20 mole CH_3COONa , producing 0.20 mol CH_3COOH . Therefore, in the solution moles of $\text{CH}_3\text{COOH} = 0.20$
Moles of $\text{CH}_3\text{COONa} = 0.80$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log (1.8 \times 10^{-5}) + \log \frac{(0.80)}{(1.20)} = 4.56 \end{aligned}$$

- (ii) $\text{CH}_3\text{COONa} + \text{HCl} \longrightarrow \text{CH}_3\text{COOH} + \text{NaCl}$
- | | | | | |
|---------|------|------|------|------|
| Initial | 0.10 | 0.20 | 0 | 0 |
| Final | 0 | 0.10 | 0.10 | 0.10 |

Now, the solution has 0.2 mole acetic acid and 0.1 mole HCl. Due to presence of HCl, ionisation of CH_3COOH can be ignored (common ion effect) and H^+ in solution is mainly due to HCl.

$$[\text{H}^+] = 0.10$$

$$\text{pH} = -\log (0.10) = 1.0$$

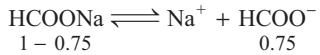
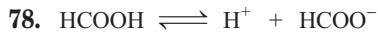
77. In pure water, solubility = $\frac{9.57}{58} \times 10^{-3} \text{ M} = 1.65 \times 10^{-4} \text{ M}$

$$K_{\text{sp}} = 4S^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$$

In 0.02 M $\text{Mg}(\text{NO}_3)_2$:

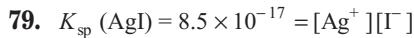
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$$\begin{aligned}\text{solubility of Mg(OH)}_2 &= \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} \times \frac{1}{2} \\ &= 1.5 \times 10^{-5} \text{ mol L}^{-1} \\ &= 1.5 \times 10^{-5} \times 58 \text{ g L}^{-1} \\ &= 8.7 \times 10^{-4} \text{ g L}^{-1}\end{aligned}$$



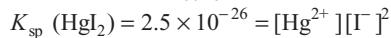
In the above buffer solution, the significant source of formate ion (HCOO^-) is HCOONa. Hence,

$$\begin{aligned}K_a &= 2.4 \times 10^{-4} \\ &= \frac{[\text{H}^+](0.75)}{[\text{HCOOH}]} \\ [\text{H}^+] &= \frac{2.4 \times 10^{-4} \times 0.20}{0.75} = 6.4 \times 10^{-5} \\ \text{pH} &= -\log(6.4 \times 10^{-5}) = 4.20\end{aligned}$$



$[\text{I}^-]$ required to start precipitation of AgI

$$= \frac{8.5 \times 10^{-17}}{0.10} = 8.5 \times 10^{-16} \text{ M}$$



$[\text{I}^-]$ required to start precipitation of HgI_2

$$= \sqrt{\frac{2.5 \times 10^{-26}}{0.10}} = 5 \times 10^{-13} \text{ M}$$

The above calculation indicates that lower $[\text{I}^-]$ is required for precipitation of AgI. When $[\text{I}^-]$ reaches to 5×10^{-13} , AgI gets precipitated almost completely.

When HgI_2 starts precipitating,

$$[\text{Ag}^+] = \frac{8.5 \times 10^{-17}}{5 \times 10^{-13}} = 1.70 \times 10^{-4} \text{ M}$$

$$\% \text{Ag}^+ \text{ remaining} = \frac{1.70 \times 10^{-4} \times 100}{0.10} = 0.17$$

$$\% \text{Ag}^+ \text{ precipitated} = 100 - 0.17 = 99.83$$



$$[\text{H}^+] = \sqrt{K_a \cdot C} = 7 \times 10^{-5} \text{ M} (\alpha \text{ is negligible})$$

$$\begin{aligned}\text{pH} &= 4.15 \\ [\text{OH}^-] &= \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{7 \times 10^{-5}} \\ &= 1.43 \times 10^{-10} \text{ M}\end{aligned}$$

81. Sodium acetate (CH_3COONa) is a basic salt (salt of strong base and weak acid) therefore, its aqueous solution has $\text{pH} > 7$.

82. mmol of NaOH = $20 \times 0.2 = 4$

mmol of acetic acid = $50 \times 0.2 = 10$

After neutralisation, buffer solution is formed which contain 6 mmol CH_3COOH and 4 mmol CH_3COONa .

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= -\log(1.8 \times 10^{-5}) + \log \frac{4}{6} = 4.56\end{aligned}$$

Now, let x mmol of NaOH is further added so that pH of the resulting buffer solution is 4.74.

Now, the buffer solution contains $(4 + x)$ mmol CH_3COONa and $(6 - x)$ mmol of CH_3COOH .

$$\begin{aligned}4.74 &= -\log(1.8 \times 10^{-5}) + \log \frac{4+x}{6-x} \\ \Rightarrow \quad \frac{4+x}{6-x} &= 1 \\ \Rightarrow \quad x &= 1.0 \text{ mmol} = 0.2 \times V \\ \Rightarrow \quad V &= 5.0 \text{ mmol NaOH.}\end{aligned}$$

83. For acidic buffer, the Henderson's equation is

$$\text{pH} = \text{p}K_a + \log \frac{(\text{mole of salt})}{(\text{mole of acid})}$$

$$4.75 = -\log(1.34 \times 10^{-5}) + \log \frac{x}{0.02}$$

$$\Rightarrow x = 0.015 \text{ mole of sodium propionate.}$$

Addition of 0.01 mole HCl will increase moles of propionic acid by 0.01 and moles of sodium propionate will decrease by same amount.

$$\text{New moles of acid} = 0.02 + 0.01 = 0.03$$

$$\text{New moles of salt} = 0.015 - 0.01 = 0.005$$

$$\text{pH} = -\log(1.34 \times 10^{-5}) + \log \left(\frac{0.005}{0.030} \right) = 4.09$$

pH of 0.01 HCl = 2, just half of the pH of final buffer solution.

7

Thermodynamics and Thermochemistry

Topic 1 Thermodynamics

Objective Questions I (Only one correct option)

1. An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is
(2019 Main, 12 April I)

(a) -9.0 (b) +10.0 (c) -0.9 (d) -2.0

2. The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (*l*) is carried out at a temperature T , is equal to
(2019 Main, 10 April II)

(a) $-4 RT$ (b) $3 RT$ (c) $4 RT$ (d) $-3 RT$

3. A process will be spontaneous at all temperature if
(2019 Main, 10 April I)

(a) $\Delta H > 0$ and $\Delta S < 0$ (b) $\Delta H < 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$ (d) $\Delta H > 0$ and $\Delta S > 0$

4. During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, ΔU (in kJ) is
(2019 Main, 9 April II)

(a) 8 (b) -12 (c) 12 (d) -8

5. Among the following the set of parameters that represents path functions, is
(2019 Main, 9 April I)

(A) $q + W$ (B) q (C) W (D) $H - TS$
(a) (A) and (D) (b) (A), (B) and (C)
(c) (B), (C) and (D) (d) (B) and (C)

6. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28 \text{ JK}^{-1} \text{ mol}^{-1}$, calculate ΔU and ΔpV for this process. ($R = 8.0 \text{ JK}^{-1} \text{ mol}^{-1}$)
(2019 Main, 8 April II)

(a) $\Delta U = 2.8 \text{ kJ}$; $\Delta(pV) = 0.8 \text{ kJ}$
(b) $\Delta U = 14 \text{ J}$; $\Delta(pV) = 0.8 \text{ J}$
(c) $\Delta U = 14 \text{ kJ}$; $\Delta(pV) = 4 \text{ kJ}$
(d) $\Delta U = 14 \text{ kJ}$; $\Delta(pV) = 18 \text{ kJ}$

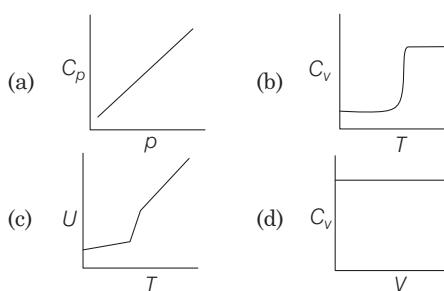
7. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non-expansion work is zero)
(2019 Main, 8 April I)

- (a) Cyclic process : $q = -W$
(b) Adiabatic process : $\Delta U = -W$
(c) Isochoric process : $\Delta U = q$
(d) Isothermal process : $q = -W$

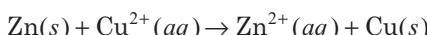
8. For silver, $C_p (\text{J K}^{-1} \text{ mol}^{-1}) = 23 + 0.01 T$. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH will be close to
(2019 Main, 8 April I)

(a) 62 kJ (b) 16 kJ
(c) 21 kJ (d) 13 kJ

9. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?
(2019 Main, 12 Jan I)



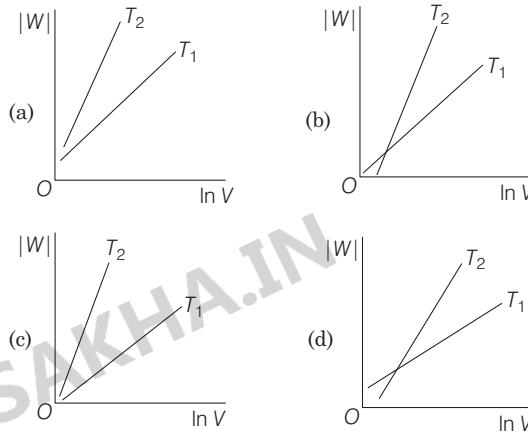
10. The standard electrode potential E^Θ and its temperature coefficient $\left(\frac{dE^\Theta}{dT}\right)$ for a cell are 2V and $-5 \times 10^{-4} \text{ VK}^{-1}$ at 300 K respectively. The cell reaction is



The standard reaction enthalpy ($\Delta_r H^\Theta$) at 300 K in kJ mol^{-1} is, [Use, $R = 8 \text{ JK}^{-1} \text{ mol}^{-1}$ and $F = 96,000 \text{ C mol}^{-1}$]
(2019 Main, 12 Jan I)

(a) -412.8 (b) -384.0
(c) 206.4 (d) 192.0

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[Useful information : $1 \text{ J} = 1 \text{ kg m}^2 \text{s}^{-2}$,

$1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$; $1 \text{ bar} = 10^5 \text{ Pa}$]

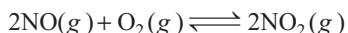
- (a) 58001 bar (b) 1450 bar
 (c) 14501 bar (d) 29001 bar

23. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm.

In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is ($1 \text{ L atm} = 101.3 \text{ J}$) (2016 Adv.)

- (a) 5.763 (b) 1.013 (c) -1.013 (d) -5.763

24. The following reaction is performed at 298K



The standard free energy of formation of $\text{NO}(g)$ is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $\text{NO}_2(g)$ at 298 K? ($K_p = 1.6 \times 10^{12}$) (2015 Main)

- (a) $R(298) \ln(1.6 \times 10^{12}) - 86600$
 (b) $86600 + R(298) \ln(1.6 \times 10^{12})$
 (c) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$
 (d) $0.5[2 \times 86600 - R(298) \ln(1.6 \times 10^{12})]$

25. For the process, $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is

- (a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} > 0$ (2014 Adv.)
 (b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$
 (c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} > 0$
 (d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surrounding}} < 0$

26. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C . As it does so, it absorbs 208 J of heat. The values of q and W for the process will be ($R = 8.314 \text{ J/mol K}$, $\ln 7.5 = 2.01$) (2013 Main)

- (a) $q = +208 \text{ J}$, $W = -208 \text{ J}$
 (b) $q = -208 \text{ J}$, $W = -208 \text{ J}$
 (c) $q = -208 \text{ J}$, $W = +208 \text{ J}$
 (d) $q = +208 \text{ J}$, $W = +208 \text{ J}$

27. For the process $\text{H}_2\text{O}(l)(1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g)$

(1 bar, 373 K), the correct set of thermodynamic parameters is (2007, 3M)

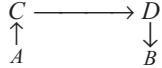
- (a) $\Delta G = 0$, $\Delta S = +\text{ve}$ (b) $\Delta G = 0$, $\Delta S = -\text{ve}$
 (c) $\Delta G = +\text{ve}$, $\Delta S = 0$ (d) $\Delta G = -\text{ve}$, $\Delta S = +\text{ve}$

28. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given : $\Delta_r H^\circ_{298 \text{ K}} = -54.07 \text{ kJ mol}^{-1}$,
 $\Delta_r S^\circ_{298 \text{ K}} = 10 \text{ JK}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$;
 $2.303 \times 8.314 \times 298 = 5705$) (2007, 3M)

- (a) 5 (b) 10 (c) 95 (d) 100

29. The direct conversion of A to B is difficult, hence it is carried out by the following shown path



Given that $\Delta S_{(A \rightarrow C)} = 50 \text{ eu}$
 $\Delta S_{(C \rightarrow D)} = 30 \text{ eu}$

$\Delta S_{(D \rightarrow B)} = -20 \text{ eu}$ where, eu is entropy unit

Then, $\Delta S_{(A \rightarrow B)}$ is (2006, 3M)

- (a) +100 eu (b) +60 eu
 (c) -100 eu (d) -60 eu

30. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas ? (2006, 3M)

- (a) $\frac{4R}{2}$ (b) $\frac{3R}{2}$ (c) $\frac{5R}{2}$ (d) 0

31. One mole of monoatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from 1 L to 2 L. Find out the final temperature ($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$) (2005, 1M)

- (a) T (b) $\frac{T}{(2)^{5/3-1}}$
 (c) $T - \frac{2}{3 \times 0.082}$ (d) $T + \frac{2}{3 \times 0.082}$

32. 2 moles of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change? (2004, 1M)

- (a) 4.98 kJ (b) 11.47 kJ (c) -11.47 kJ (d) 0 kJ

33. Spontaneous adsorption of a gas on solid surface is an exothermic process because (2004, 1M)

- (a) ΔH increases for system (b) ΔS increases for gas
 (c) ΔS decreases for gas (d) ΔG increases for gas

34. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) \rightarrow (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta E = 30.0 \text{ L-atm}$. The change in enthalpy (ΔH) of the process in L-atm is (2002, 3M)

- (a) 40.0 (b) 42.0
 (c) 44.0 (d) not defined, because pressure is not constant

35. Which of the following statements is false? (2001, 1M)

- (a) Work is a state function
 (b) Temperature is a state function
 (c) Change in the state is completely defined when the initial and final states are specified
 (d) Work appears at the boundary of the system

36. In thermodynamics, a process is called reversible when (2001, 1M)

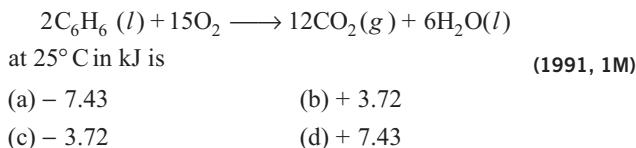
- (a) surroundings and system change into each other
 (b) there is no boundary between system and surroundings
 (c) the surroundings are always in equilibrium with the system
 (d) the system changes into the surroundings spontaneously

37. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol , the minimum value for the energy of activation will be (1992, 1M)

- (a) less than ΔH (b) zero
 (c) more than ΔH (d) equal to ΔH

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38. The difference between heats of reaction at constant pressure and constant volume for the reaction



Objective Questions II

(One or more than one correct option)

39. In thermodynamics, the pV work done is given by

$$w = - \int dV p_{\text{ext}}$$

For a system undergoing a particular process, the work done is

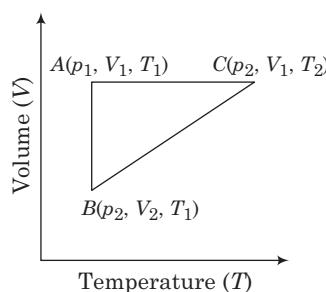
$$w = - \int dV \left(\frac{RT}{V-b} - \frac{a}{V^2} \right)$$

This equation is applicable to a (2020 Adv.)

- (a) system that satisfies the van der Waals' equation of state
 (b) process that is reversible and isothermal
 (c) process that is reversible and adiabatic
 (d) process that is irreversible and at constant pressure
40. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. (2019 Adv.)
- (a) $2\text{C}(g) + 3 \text{ H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g)$
 (b) $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$
 (c) $\frac{3}{2}\text{O}_2(g) \longrightarrow \text{O}_3(g)$
 (d) $\frac{1}{8}\text{S}_8(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$

41. A reversible cyclic process for an ideal gas is shown below. Here, p, V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.

(2018 Adv.)



The correct options is (are)

- (a) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = p_2(V_2 - V_1)$
 (b) $w_{BC} = p_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
 (c) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$
 (d) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

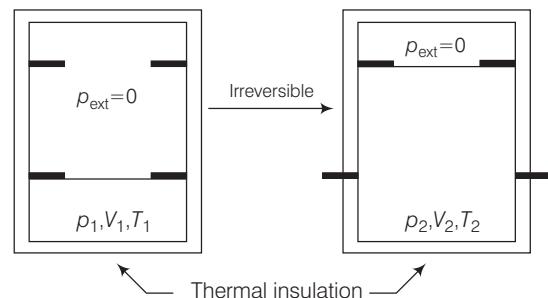
42. An ideal gas is expanded form (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are) (2017 Adv.)

- (a) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.
 (b) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$.
 (c) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.
 (d) The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1 .

43. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by (2017 Adv.)

- (a) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases.
 (b) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surrounding decreases.
 (c) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative.
 (d) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive.

44. An ideal gas in thermally insulated vessel at internal pressure = p_1 , volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2 , respectively. For this expansion



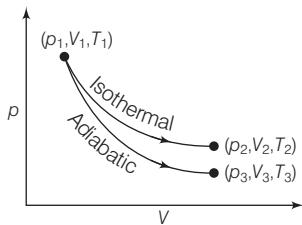
(2014 Adv.)

- (a) $q = 0$ (b) $T_2 = T_1$
 (c) $p_2V_2 = p_1V_1$ (d) $p_2V_2^\gamma = p_1V_1^\gamma$

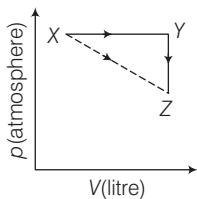
45. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are) (2013 Adv.)

- (a) ΔG is positive (b) ΔS_{system} is positive
 (c) $\Delta S_{\text{surroundings}} = 0$ (d) $\Delta H = 0$

46. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? (2012)



- (a) $T_1 = T_2$
 (b) $T_3 > T_1$
 (c) $W_{\text{isothermal}} > W_{\text{adiabatic}}$
 (d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$
47. For an ideal gas, consider only p - V work in going from initial state X to the final state Z . The final state Z can be reached by either of the two paths shown in the figure.



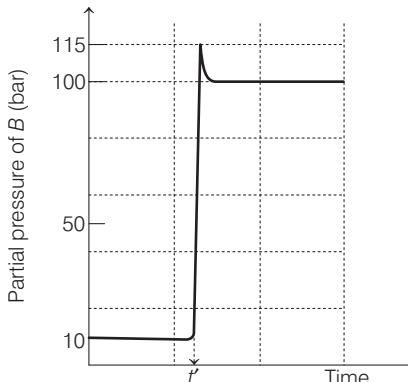
[Take ΔS as change in entropy and W as work done].

- Which of the following choice(s) is (are) correct? (2012)
- (a) $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$
 (b) $W_{X \rightarrow Z} = W_{X \rightarrow Y} + W_{Y \rightarrow Z}$
 (c) $W_{X \rightarrow Y \rightarrow Z} = W_{X \rightarrow Z}$
 (d) $\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Y}$
48. Among the following, extensive property is (properties are) (2010)
- (a) molar conductivity (b) electromotive force
 (c) resistance (d) heat capacity
49. Among the following, the state function(s) is(are) (2009)
- (a) internal energy
 (b) irreversible expansion work
 (c) reversible expansion work
 (d) molar enthalpy
50. Identify the intensive quantities from the following. (1993, 1M)
- (a) enthalpy (b) temperature
 (c) volume (d) refractive index

Numerical Answer Type Questions

51. Consider the reaction, $A \rightleftharpoons B$ at 1000 K. At time t' , the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment the partial pressure of A was maintained at 1 bar. Given, below is the plot of the partial pressure of B with time.

What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K? (2020 Adv.)



Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
 (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
 (c) Statement I is true; Statement II is false
 (d) Statement I is false; Statement II is true

52. **Statement I** There is a natural asymmetry between converting work to heat and converting heat to work.

Statement II No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. (2008, 3M)

53. **Statement I** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

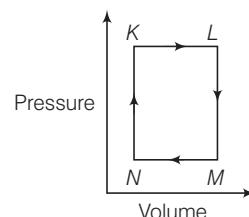
Statement II At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. (2008, 3M)

54. **Statement I** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Statement II The volume occupied by the molecules of an ideal gas is zero. (2000, S, 1M)

Passage Based Questions

A fixed mass m of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. (2013 Adv.)



55. The pair of isochoric processes among the transformation of states is
- (a) K to L and L to M (b) L to M and N to K
 (c) L to M and M to N (d) M to N and N to K

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56. The succeeding operations that enable this transformation of states are
 (a) heating, cooling, heating, cooling
 (b) cooling, heating, cooling, heating
 (c) heating, cooling, cooling, heating
 (d) cooling, heating, heating, cooling

Match the Columns

57. Match the thermodynamic processes given under Column I with the expressions given under Column II.

Column I	Column II
A. Freezing of water at 273 K and 1 atm	p. $q = 0$
B. Expansion of 1 mole of an ideal gas into a vacuum under isolated conditions	q. $W = 0$
C. Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	r. $\Delta S_{\text{sys}} < 0$
D. Reversible heating of $\text{H}_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	s. $\Delta U = 0$
	t. $\Delta G = 0$

58. Match the transformations in Column I with appropriate options in Column II. (2011)

Column I	Column II
A. $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$	p. Phase transition
B. $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$	q. Allotropic change
C. $2\text{H}\bullet \rightarrow \text{H}_2(g)$	r. ΔH is positive
D. $P_{(\text{white, solid})} \rightarrow P_{(\text{red, solid})}$	s. ΔS is positive
	t. ΔS is negative

Fill in the Blanks

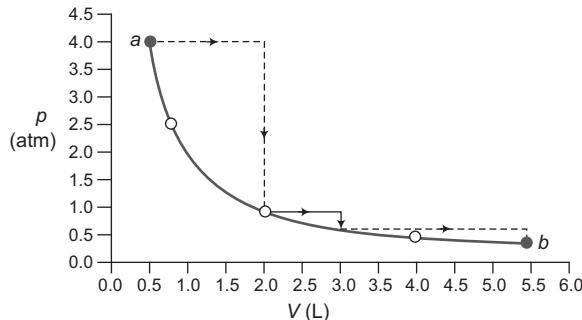
59. Enthalpy is an property. (1997, 1M)
 60. When $\text{Fe}(s)$ is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is (1997)
 61. The heat content of the products is more than that of the reactants in an reaction. (1993, 1M)
 62. A system is said to be if it can neither exchange matter nor energy with the surroundings. (1993, 1M)
 63. $C_p - C_V$ for an ideal gas is (1984, 1M)
 64. The total energy of one mole of an ideal monatomic gas at 27°C is cal. (1984, 1M)

True/False

65. First law of thermodynamics is not adequate in predicting the direction of a process. (1982, 1M)
 66. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985, 1/2 M)

Integer Answer Type Question

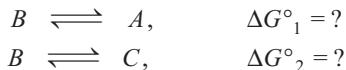
67. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is W_s and that along the dotted line path is W_d , then the integer closest to the ratio W_d / W_s is (2010)



Subjective Questions

68. For the reaction, $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$; $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2 , the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K. (1 L-atm = 0.1 kJ) (2006, 3M)
69. 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the ΔH and ΔU . (2004, 2M)
70. C_V value of He is always $\frac{3R}{2}$ but C_V value of H_2 is $\frac{3R}{2}$ at low temperature and $\frac{5R}{2}$ at moderate temperature and more than $\frac{5R}{2}$ at higher temperature. Explain in two or three lines. (2003, 2M)
71. Two moles of a perfect gas undergo the following processes :
 (a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L)
 (b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L)
 (c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)
 (i) Sketch with labels each of the processes on the same p - V diagram.
 (ii) Calculate the total work (W) and the total heat change (Q) involved in the above processes.
 (iii) What will be the values of ΔU , ΔH and ΔS for the overall process? (2002, 5M)
72. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C , it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of

1, 2-pentadiene (*C*). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria.



From the calculated value of ΔG°_1 and ΔG°_2 indicate the order of stability of (*A*), (*B*) and (*C*). Write a reasonable reaction mechanism showing all intermediates leading to (*A*), (*B*) and (*C*). (2001, 10M)

73. Show that the reaction, $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs' free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively. (2000, 3M)
74. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3 .

Calculate the enthalpy change in this process C_{V_m} for argon is $12.49 \text{ JK}^{-1} \text{ mol}^{-1}$. (2000, 4M)

75. A gas mixture of 3.67 L of ethylene and methane on complete combustion at 25°C produces 6.11 L of CO_2 . Find out the amount of heat evolved on burning 1 L of the gas mixture. The heat of combustion of ethylene and methane are -1423 and -891 kJ mol^{-1} at 25°C. (1991, 5M)
76. An athlete is given 100 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of energy equivalent to 1560 kJ. He utilizes 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol. (1989, 2M)
77. Following statement is true only under some specific conditions. Write the conditions for that in not more than two sentences
“The heat energy q , absorbed by a gas is ΔH .” (1984, 1M)

Topic 2 Thermochemistry

Objective Questions I (Only one correct option)

1. Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1} , respectively. The hydration enthalpy of NaCl is
(2020 Main, 5 Sep II)
(a) -780 kJ mol^{-1} (b) 780 kJ mol^{-1}
(c) -784 kJ mol^{-1} (d) 784 kJ mol^{-1}
2. The variation of equilibrium constant with temperature is given below:
(2020 Main, 6 Sep I)

Temperature	Equilibrium constant
$T_1 = 25^\circ\text{C}$	$K_1 = 10$
$T_2 = 100^\circ\text{C}$	$K_2 = 100$

The values of ΔH° , ΔG° at T_1 and ΔG° at T_2 (in kJ mol^{-1}) respectively, are close to
[use $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$]
(a) 28.4, -7.14 and -5.71
(b) 0.64, -7.14 and -5.71
(c) 28.4, -5.71 and -14.29
(d) 0.64, -5.71 and -14.29
3. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C . If specific heat of $\text{I}_2(s)$ and $\text{I}_2(\text{vap.})$ are 0.055 and $0.031 \text{ cal g}^{-1} \text{ K}^{-1}$ respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is
(2019 Main, 12 April I)
(a) 2.85 (b) 5.7 (c) 22.8 (d) 11.4

4. Given :

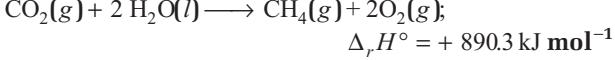
- (i) $\text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g); \Delta_r H^\circ = x \text{ kJ mol}^{-1}$
(ii) $\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g); \Delta_r H^\circ = y \text{ kJ mol}^{-1}$



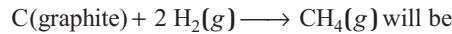
Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?
(2019 Main, 12 Jan II)

- (a) $y = 2z - x$ (b) $x = y - z$
(c) $z = x + y$ (d) $x = y + z$

5. Given, $\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1}$
 $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l); \Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$



Based on the above thermochemical equations, the value of $\Delta_r H^\circ$ at 298 K for the reaction,
(2017 Main)



- will be
(a) $+78.8 \text{ kJ mol}^{-1}$ (b) $+144.0 \text{ kJ mol}^{-1}$
(c) $-74.8 \text{ kJ mol}^{-1}$ (d) $-144.0 \text{ kJ mol}^{-1}$

6. The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is
(2016 Main)
(a) 676.5 (b) -676.5
(c) -110.5 (d) 110.5

7. For the complete combustion of ethanol,
 $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$, the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C . Assuming

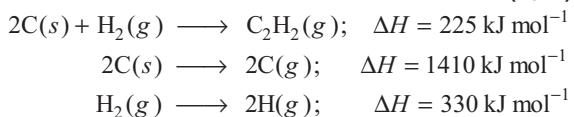
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ideality the enthalpy of combustion, $\Delta_C H$, for the reaction will be ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) (2014 Main)

- (a) $-1366.95 \text{ kJ mol}^{-1}$ (b) $-1361.95 \text{ kJ mol}^{-1}$
 (c) $-1460.50 \text{ kJ mol}^{-1}$ (d) $-1350.50 \text{ kJ mol}^{-1}$

8. The standard enthalpies of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$ and glucose(s) at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is (2013 Adv.)
 (a) $+2900 \text{ kJ}$ (b) -2900 kJ
 (c) -16.11 kJ (d) $+16.11 \text{ kJ}$

9. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $\text{C}\equiv\text{C}$ bond C_2H_2 . That energy is (take the bond energy of a C—H bond as 350 kJ mol^{-1}) (2012)



- (a) 1165 (b) 837 (c) 865 (d) 815

10. The species which by definition has zero standard molar enthalpy of formation at 298 K is (2010)
 (a) $\text{Br}_2(g)$ (b) $\text{Cl}_2(g)$ (c) $\text{H}_2\text{O}(g)$ (d) $\text{CH}_4(g)$

11. The bond energy (in kcal mol $^{-1}$) of C—C single bond is approximately (2010)
 (a) 1 (b) 10 (c) 100 (d) 1000

12. $\Delta H_{\text{vap}} = 30 \text{ kJ/mol}$ and $\Delta S_{\text{vap}} = 75 \text{ J mol}^{-1} \text{ K}^{-1}$. Find the temperature of vapour, at one atmosphere (2004, 1M)
 (a) 400 K (b) 350 K (c) 298 K (d) 250 K

13. Which of the following reactions defines ΔH_f° ? (2003, 1M)
 (a) $\text{C}(\text{diamond}) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
 (b) $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{F}_2(g) \longrightarrow \text{HF}(g)$
 (c) $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
 (d) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$

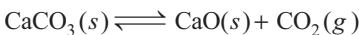
14. The ΔH_f° for $\text{CO}_2(g)$, $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ are -393.5 , -110.5 and $-241.8 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy change (in kJ mol^{-1}) for the reaction $\text{CO}_2(g) + \text{H}_2(g) \longrightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$ is (2000, 1M)
 (a) 524.1 (b) +41.2
 (c) -262.5 (d) -41.2

Objective Question II

(One or more than one correct option)

15. The following is/are endothermic reaction(s) (1999, 3M)
 (a) Combustion of methane
 (b) Decomposition of water
 (c) Dehydrogenation of ethane to ethylene
 (d) Conversion of graphite to diamond

16. The thermal dissociation of equilibrium of $\text{CaCO}_3(s)$ is studied under different conditions. (2013 Adv.)



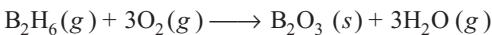
For this equilibrium, the correct statement(s) is/are

- (a) ΔH is dependent on T
 (b) K is independent of the initial amount of CaCO_3
 (c) K is dependent on the pressure of CO_2 at a given T
 (d) ΔH is independent of the catalyst, if any

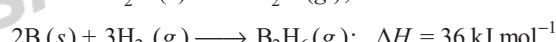
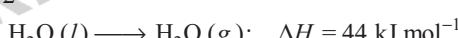
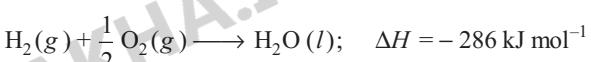
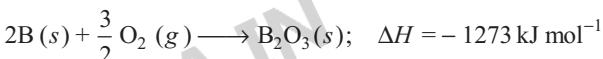
Subjective Questions

17. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K . The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is (2009)

18. Diborane is a potential rocket fuel which undergoes combustion according to the reaction



From the following data, calculate the enthalpy change for the combustion of diborane. (2000, 2M)



19. Estimate the average S—F bond energy in SF_6 . The values of standard enthalpy of formation of $\text{SF}_6(g)$, $\text{S}(g)$ and $\text{F}(g)$ are : -1100 , 275 and 80 kJ mol^{-1} respectively. (1999, 3M)

20. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K . The enthalpy of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$ and propane(g) are -393.5 , -285.8 and $20.42 \text{ kJ mol}^{-1}$ respectively. The enthalpy of isomerisation of cyclopropane to propene is $-33.0 \text{ kJ mol}^{-1}$. (1998, 5M)

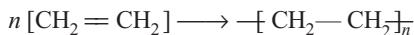
21. Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1} , using the following data. Heat of vaporisation of liquid methyl alcohol = 38 kJ/mol . Heat of formation of gaseous atoms from the elements in their standard states : $\text{H} = 218 \text{ kJ/mol}$, $\text{C} = 715 \text{ kJ/mol}$, $\text{O} = 249 \text{ kJ/mol}$. Average bond energies: (1997, 5M)

$$\text{C—H} = 415 \text{ kJ/mol}, \quad \text{C—O} = 356 \text{ kJ/mol},$$

$$\text{O—H} = 463 \text{ kJ/mol}$$

22. The standard molar enthalpies of formation of cyclohexane(l) and benzene(l) at 25°C are -156 and $+49 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy of hydrogenation of cyclohexene(l) at 25°C is -119 kJ mol^{-1} . Use these data to estimate the magnitude of the resonance energy of benzene. (1996, 2M)

23. The polymerisation of ethylene to linear polyethylene is represented by the reaction,



where, n has large integral value. Given that the average enthalpies of bond dissociation for $\text{C}=\text{C}$ and $\text{C}-\text{C}$ at 298 K are +590 and +311 kJ/mol respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K.

(1994, 2M)

24. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and $6x$ litre/hour of O_2) is to be readjusted for butane, C_4H_{10} .

In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc., are the same for both fuels and that the gases behave ideally. Heats of combustions:

$\text{CH}_4 = -809$ kJ/mol, $\text{C}_4\text{H}_{10} = -2878$ kJ/mol (1993, 3M)

25. Determine the enthalpy of the reaction,

$\text{C}_3\text{H}_8(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) + \text{CH}_4(g)$, at 25°C, using the given heat of combustion values under standard conditions.

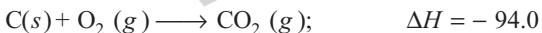
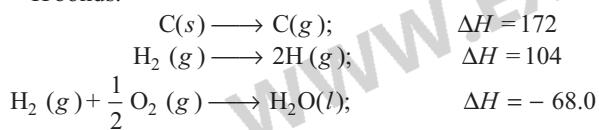
Compound : $\text{H}_2(g)$ $\text{CH}_4(g)$ $\text{C}_2\text{H}_6(g)$ C(graphite)

ΔH° (kJ/mol): -285.8 -890.0 -1560.0 -393.0

The standard heat of formation of $\text{C}_3\text{H}_8(g)$ is -103 kJ/mol.

(1992, 3M)

26. Using the data (all values are in kilocalories per mol at 25°C) given below, calculate the bond energy of $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds.



Heat of combustion of C_2H_6 = -372.0

Heat of combustion of C_3H_8 = -530.0 (1990, 5M)

27. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241, -3800 and -3920 kJ/mol respectively. Calculate the heat of hydrogenation of cyclohexene. (1989, 2M)

28. An intimate mixture of ferric oxide, Fe_2O_3 , and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows:

$$H_f(\text{Al}_2\text{O}_3) = -399 \text{ kcal/mol}$$

$$H_f(\text{Fe}_2\text{O}_3) = -199 \text{ kcal/mol}$$

Density of Fe_2O_3 = 5.2 g/cc, Density of Al = 2.7 g/cc

(1989, 2M)

29. The standard molar heat of formation of ethane, carbon dioxide and liquid water are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. (1986, 2M)

30. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal/mol respectively. Calculate the enthalpy of formation of HCl gas. (1985, 2M)

31. Given the following standard heats of reactions

(i) heat of formation of water = -68.3 kcal

(ii) heat of combustion of acetylene = -310.6 kcal

(iii) heat of combustion of ethylene = -337.2 kcal

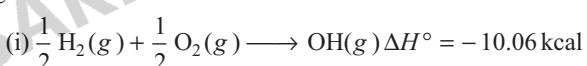
Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C). (1984, 4M)

32. The molar heats of combustion of $\text{C}_2\text{H}_2(g)$, C(graphite) and $\text{H}_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $\text{C}_2\text{H}_2(g)$. (1983, 2M)

33. The standard heats of formation of $\text{CCl}_4(g)$, $\text{H}_2\text{O}(g)$, $\text{CO}_2(g)$ and $\text{HCl}(g)$ at 298 K are -25.5, -57.8, -94.1 and -22.1 kcal/mol respectively. Calculate ΔH° (298 K) for the reaction



34. The enthalpy for the following reactions (ΔH°) at 25°C are given below



Calculate the O—H bond energy in the hydroxyl radical. (1981, 2M)

Passage Based Questions

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (-57.0 kJ mol⁻¹), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

35. Enthalpy of dissociation (in kJ mol⁻¹) of acetic acid obtained from the Expt. 2 is

(a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4

36. The pH of the solution after Expt. 2 is

(a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

Answers

Topic 1 Thermodynamics

1. (c) 2. (a) 3. (b) 4. (a)
 5. (d) 6. (c) 7. (b) 8. (a)
 9. (a) 10. (a) 11. (d) 12. (d)
 13. (c) 14. (c) 15. (a) 16. (d)
 17. (c) 18. (a) 19. (c) 20. (d)
 21. (c) 22. (c) 23. (c) 24. (d)
 25. (b) 26. (a) 27. (a) 28. (b)
 29. (b) 30. (a) 31. (c) 32. (d)
 33. (c) 34. (c) 35. (a) 36. (c)
 37. (c) 38. (a) 39. (a, b, c) 40. (c, d)
 41. (b,c) 42. (a, c, d) 43. (a, b) 44. (a,b,c)
 45. (b,c,d) 46. (a,c,d) 47. (a,c) 48. (c,d)
 49. (a,c,d) 50. (b, d) 51. (0.25) 52. (b)
 53. (d) 54. (b) 55. (b) 56. (c)
57. A → r, t; B → p, q, s; C → p, q, s; D → p,q, s, t
 58. A → p, r, s; B → r, s; C → t; D → p, q, t

59. (extensive) 60. (zero) 61. (exothermic reaction)
 62. (isolated) 63. (R) 64. (900) 65. (T)
 66. (T) 67. (2) 68. (-563 kJ) 72. (12.3 kJ)
 73. (-285.4 kJ) 74. (-116.4 J) 75. (49.82 kJ) 76. (318.96 g)

Topic 2 Thermochemistry

1. (c) 2. (c) 3. (c) 4. (d)
 5. (c) 6. (c) 7. (a) 8. (c)
 9. (d) 10. (b) 11. (c) 12. (a)
 13. (b) 14. (b) 15. (b,c,d) 16. (a, b, c, d)
 17. (9 kJ) 18. (-2035 kJ) 19. (309.16 kJ) 20. (-2091.32 kJ)
 21. (-116.4 kJ) 22. (-152 kJ/mol)
 23. (-32 kJ/mol) 24. (5.46 xL/h)
 25. (-55 kJ) 27. (-121 kJ/mol)
 29. (-372 kcal/mol) 30. (-22 kcal/mol)
 31. (-41.7 kcal) 32. (54.2 kcal)
 33. (-41.4 kcal) 34. (121.31 kcal)
 35. (1 kJ/mol) 36. (4.7)

Hints & Solutions

Topic 1 Thermodynamics

1. **Key Idea** Work done during isothermal expansion of an ideal gas is given by the equation.

$$W = -p_{\text{ext}}(V_2 - V_1)$$

According to the given conditions, the expansion is against constant external pressure. So, the work done is given by following formula;

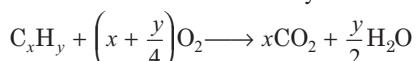
$$\begin{aligned} W &= -p_{\text{ext}}(V_2 - V_1) \\ &= -1 \text{ bar} (10 \text{ L} - 1 \text{ L}) = -9 \text{ L bar} \quad (\because 1 \text{ L bar} = 100 \text{ J}) \\ &= -9 \times 100 \text{ J} = -900 \text{ J} \end{aligned}$$

2. **Key Idea** The relation between ΔH and ΔU is

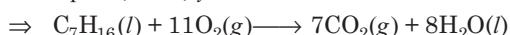
$$\Delta H = \Delta U + \Delta n_g RT$$

where, $\Delta n_g = \Sigma n_p - \Sigma n_R$
 = number of moles of gaseous products – number of moles of gaseous reactants.

The general combustion reaction of a hydrocarbon is as follows :



For heptane, $x = 7$, $y = 16$



$$\therefore \Delta n_g = 7 - 11 = -4$$

Now, from the principle of thermochemistry,

$$\begin{aligned} \Delta H &= \Delta U + \Delta n_g RT \\ \Rightarrow \Delta H - \Delta U &= \Delta n_g RT = -4RT \end{aligned}$$

3. A process will be spontaneous when its free energy (Gibb's energy) change will be negative, i.e. $\Delta G < 0$.

Spontaneity of a process is decided by the value of ΔG , which can be predicted from the Gibb's equation, $\Delta G = \Delta H - T\Delta S$ for positive/negative signs of ΔH and ΔS at any/higher/lower temperature as:

ΔH	ΔS	Comment on temperature (T)	ΔG	Comment on the process
< 0	> 0	at any temp.	< 0	spontaneous
> 0	< 0	at any temp.	> 0	non-spontaneous
< 0	< 0	at lower temp.	< 0	spontaneous
> 0	> 0	at higher temp.	< 0	spontaneous

4. In the given system, during the compression of a spring the workdone is 10 kJ and 2 kJ of heat is escaped to the surroundings. So, $q = -2 \text{ kJ}$ and $W = 10 \text{ kJ}$

According to the first law of thermodynamics,

$$\begin{aligned} \Delta U &= q + W = -2 \text{ kJ} + 10 \text{ kJ} \\ \Delta U &= 8 \text{ kJ} \end{aligned}$$

The change in internal energy, ΔU (in kJ) is 8 kJ.

5. q (heat) and W (work) represents path functions. These variables are path dependent and their values depends upon the path followed by the system in attaining that state. They are inexact differentials whose integration gives a total quantity depending upon the path.

Option (a), i.e. $q + W$ and option (d), i.e. $H - TS$ are state functions. The value of state functions is independent to the way in which the state is attained. All the state functions are exact differentials and cyclic integration involving a state functions is zero.

6. Given,

$$\begin{aligned} n &= 5 \text{ mol}, T_2 = 200 \text{ K}, T_1 = 100 \text{ K} \\ C_V &= 28 \text{ JK}^{-1}\text{mol}^{-1} \\ \Delta U &= nC_V\Delta T = nC_V(T_2 - T_1) \\ &= 5 \text{ mol} \times 28 \text{ JK}^{-1}\text{mol}^{-1} \times (200 - 100) \text{ K} \\ &= 14,000 \text{ J} = 14 \text{ kJ} \\ \Delta pV &= nR\Delta T = nR(T_2 - T_1) \\ &= 5 \text{ mol} \times 8 \text{ JK}^{-1}\text{mol}^{-1} \times (200 - 100) \text{ K} \\ &= 4000 \text{ J} = 4 \text{ kJ} \end{aligned}$$

7. From the 1st law of thermodynamics,

$$\Delta U = q + W$$

where, ΔU = change in internal energy

q = heat

W = work done

The above equation can be represented for the given processes involving ideal gas as follows:

(a) **Cyclic process** For cyclic process, $\Delta U = 0$

$$\therefore q = -W$$

Thus, option (a) is correct.

(b) **Adiabatic process** For adiabatic process,

$$q = 0$$

$$\therefore \Delta U = W$$

Thus, option (b) is incorrect.

(c) **Isochoric process** For isochoric process, $\Delta V = 0$.

$$\text{Thus, } W = 0 \quad (\because W = p\Delta V).$$

$$\therefore \Delta V = q$$

Thus, option (c) is correct.

(d) **Isothermal process** For isothermal process, $\Delta U = 0$

$$\therefore q = -W$$

Thus, option (d) is correct.

8. According to Kirchoff's relation,

$$\Delta H = n \int_{T_1}^{T_2} C_p dT \quad \dots(i)$$

where, ΔH = Change in enthalpy.

C_p = Heat capacity at constant pressure.

Given, $n = 3$ moles, $T_1 = 300 \text{ K}$, $T_2 = 1000 \text{ K}$, $C_p = 23 + 0.01T$

On substituting the given values in Eq. (i), we get

$$\begin{aligned} \Delta H &= 3 \int_{300}^{1000} (23 + 0.01T) dT = 3 \int_{300}^{1000} 23dT + 0.01T dT \\ &= 3 \left[23T + \frac{0.01T^2}{2} \right]_{300}^{1000} \\ &= 3 \left[23(1000 - 300) + \frac{0.01}{2} (1000^2 - 300^2) \right] \\ &= 3 [16100 + 4550] = 61950 \text{ J} \approx 62 \text{ kJ} \end{aligned}$$

9. For diatomic ideal gases,

$$C_V = \frac{f}{2}R \text{ and } C_p = \left(\frac{f}{2} + 1 \right)R$$

where, f = degree of freedom

f = translational degree of freedom + rotational degree of freedom

$$= 3 + 2 = 5 \text{ [at normal temperature]}$$

The explanation of various plots are as follows.

(a) We know that, C_p is heat capacity at constant pressure. Thus, it does not vary with the variation in pressure. Hence, plot given in option (a) is incorrect.

(b) In this plot, C_V first increases slightly with increase in temperature and then increases sharply with temperature. The sharp increase is due to increase in degree of freedom. Thus, plot given in option (b) is correct.

(c) For ideal gases,

$$\text{Internal energy } (U) \propto T$$

Thus, as temperature increases internal energy also increases. As temperature increases further degree of freedom also increases thus, there is slight variation in the graph. First translational degree of freedom is present followed by rotational and vibrational degree of freedom. Hence, plot given in option (c) is also correct.

(d) C_V is heat capacity at constant volume. Thus, it does not vary with variation in volume. Hence, plot given in option (d) is correct.

10. Given,

$$E^\circ = 2V, \left(\frac{dE^\circ}{dT} \right) = -5 \times 10^{-4} \text{ VK}^{-1}$$

$$T = 300 \text{ K}, R = 8 \text{ JK}^{-1}\text{mol}^{-1},$$

$$F = 96000 \text{ C mol}^{-1}$$

According to Gibbs-Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S \quad \dots(i)$$

$$\text{Also, } \Delta G = -nFE^\circ_{\text{cell}} \quad \dots(ii)$$

On substituting the given values in equation (ii), we get

$$\Delta G = -2 \times 96000 \text{ C mol}^{-1} \times 2 \text{ V}$$

[$\because n = 2$ for the given reaction]

$$= -4 \times 96000 \text{ J mol}^{-1}$$

$$= -384000 \text{ J mol}^{-1}$$

$$\text{Now, } \Delta S = nF \left(\frac{dE^\circ}{dT} \right)$$

$$\text{or } \Delta S = 2 \times 96000 \text{ C mol}^{-1} \times (-5 \times 10^{-4} \text{ VK}^{-1}) \\ = -96 \text{ JK}^{-1} \text{ mol}^{-1}$$

Thus, on substituting the values of ΔG and ΔS in Eq. (i), we get

$$-384000 \text{ J mol}^{-1}$$

$$= \Delta H - 300 \text{ K} \times (-96 \text{ JK}^{-1} \text{ mol}^{-1})$$

$$\Delta H = -384000 - 28800 \text{ J mol}^{-1}$$

$$= -412800 \text{ J mol}^{-1}$$

$$= -412.800 \text{ kJ mol}^{-1}$$

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11. According to Gibbs-Helmholtz equation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

For a reaction to be feasible (spontaneous)

$$\Delta_r G^\circ < 0$$

$$\Delta_r H^\circ - T\Delta_r S^\circ < 0$$

Given, $\Delta_r H^\circ = + 491.1 \text{ kJ mol}^{-1}$,

$$\Delta_r S^\circ = 198 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\therefore 491.1 \times 10^3 - T \times 198 < 0$$

$$T > \frac{491.1 \times 10^3}{198} = 2480.3 \text{ K}$$

\therefore Above 2480.3 K reaction will become spontaneous.

12. According to Gibb's Helmholtz equation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

Given, $\Delta_r G^\circ = A - BT$

On comparing above two equations, we get,

$$A = \Delta H^\circ \text{ and } \Delta S^\circ = B$$

We know that, if ΔH° is negative, reaction is exothermic and when it is positive, reaction is endothermic.

\therefore If $A > 0$, i.e. positive, reaction is endothermic.

13. For a given value of T ,

(i) If $\Delta_r G^\circ$ becomes < 0 , the forward direction will be spontaneous and then the major and minor components will be Y and X respectively.

(ii) If $\Delta_r G^\circ$ becomes > 0 , the forward direction will be non-spontaneous and then the major and minor components will be X and Y respectively.

$$(a) \Delta_r G^\circ = 120 - \frac{3}{8} \times 280 = 15$$

i.e. $\Delta_r G^\circ > 0$, major component = X ;

$$(b) \Delta_r G^\circ = 120 - \frac{3}{8} \times 350 = -11.25$$

i.e. $\Delta_r G^\circ < 0$, major component = Y

$$(c) \Delta_r G^\circ = 120 - \frac{3}{8} \times 315 = 1.875$$

i.e. $\Delta_r G^\circ > 0$, major component = X

$$(d) \Delta_r G^\circ = 120 - \frac{3}{8} \times 300 = 7.5$$

i.e. $\Delta_r G^\circ > 0$, major component = X

14. At the thermal equilibrium,

$$\text{final temperature } T_f = \frac{T_1 + T_2}{2}$$

$$\Rightarrow \text{for the 1st block, } \Delta S_I = C_p \ln \frac{T_f}{T_1}$$

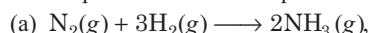
$$\Rightarrow \text{for the 2nd block, } \Delta S_{II} = C_p \ln \frac{T_f}{T_2}$$

When brought in contact with each other,

$$\Delta S = \Delta S_I + \Delta S_{II} = C_p \ln \frac{T_f}{T_1} + C_p \ln \frac{T_f}{T_2}$$

$$\begin{aligned} &= C_p \ln \left(\frac{T_f}{T_1} \times \frac{T_f}{T_2} \right) = C_p \ln \left[\frac{T_f^2}{T_1 T_2} \right] \\ &= C_p \ln \left[\frac{\left(\frac{T_1 + T_2}{2} \right)^2}{T_1 T_2} \right] = C_p \ln \left[\frac{(T_1 + T_2)^2}{4 T_1 T_2} \right] \end{aligned}$$

15. The explanation of all the options are as follows :



$$\Delta n_g = 2 - (1 + 3) = -2$$

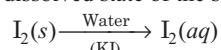
So, ΔS is also negative (entropy decreases)



$$\Delta n_g = (1 + 0) - 0 = +1$$

So, $\Delta S = + \text{ve}$

(c) In dissolution, $\Delta S = + \text{ve}$ because molecules/ions of the solid solute (here, iodine) become free to move in solvated/dissolved state of the solution,



(d) In sublimation process, molecules of solid becomes quite free when they become gas,



Dry ice

So, ΔS will be positive.

16. It is an irreversible isothermal compression of an ideal gas.

(i) $dE = dq + p(V_f - V_i)$

where, dE = Internal energy change

dq = amount of heat released

$$\Rightarrow 0 = dq + p(V_f - V_i)$$

[$\because dE = 0$ for an isothermal process]

$$\Rightarrow dq = -4(1 - 5) = 16 \text{ J}$$

(ii) $dq = n \times C \times \Delta T$ (for Al)

$$\Rightarrow 16 \text{ J} = 1 \text{ mol} \times 24 \text{ J mol}^{-1} \text{ K}^{-1} \times \Delta T$$

$$\Rightarrow \Delta T = \frac{16}{24} \text{ K} = \frac{2}{3} \text{ K}$$

17. $\Delta G = \Delta H - T\Delta S$

The process will be spontaneous, when

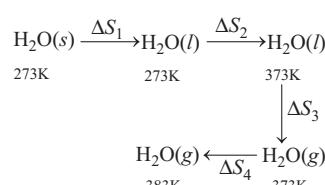
$$\Delta G = - \text{ve}, \text{ i.e. } |\Delta S| > |\Delta H|$$

Given : $\Delta H = 200 \text{ J mol}^{-1}$ and $\Delta S = 40 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\Rightarrow T > \frac{|\Delta H|}{|\Delta S|} = \frac{200}{40} = 5 \text{ K}$$

So, the minimum temperature for spontaneity of the process is 5 K.

18. The conversion of 1 kg of ice at 273 K into water vapours at 383 K takes place as follows:



$$\begin{aligned}\Delta S_1 &= \frac{\Delta H_{\text{Fusion}}}{\Delta T_{\text{Fusion}}} = \frac{334 \text{ kJ kg}^{-1}}{273 \text{ K}} = 1.22 \text{ kJ kg}^{-1} \text{ K}^{-1} \\ \Delta S_2 &= C \ln \frac{T_2}{T_1} = 4.2 \text{ kJ K}^{-1} \text{ kg}^{-1} \ln \left(\frac{373 \text{ K}}{273 \text{ K}} \right) \\ &= 4.2 \times 2.303 (\log 373 - \log 273) \text{ kJ K}^{-1} \text{ kg}^{-1} \\ &= 4.2 \times 2.303 (2.572 - 2.436) = 1.31 \text{ kJ K}^{-1} \text{ kg}^{-1} \\ \Delta S_3 &= \frac{\Delta H_{\text{vap.}}}{\Delta T_{\text{vap.}}} = \frac{2491 \text{ kJ kg}^{-1}}{373 \text{ K}} = 6.67 \text{ kJ kg}^{-1} \text{ K}^{-1} \\ \Delta S_4 &= C \ln \frac{T_2}{T_1} = 2 \text{ kJ K}^{-1} \text{ kg}^{-1} \ln \left(\frac{383 \text{ K}}{373 \text{ K}} \right) \\ &= 2 \times 2.303 (\log 383 - \log 373) \text{ kJ K}^{-1} \text{ kg}^{-1} \\ &= 2 \times 2.303 (2.583 - 2.572) \text{ kJ K}^{-1} \text{ kg}^{-1} = 0.05 \text{ kJ K}^{-1} \text{ kg}^{-1} \\ \Delta S_{\text{Total}} &= \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \\ &= 1.22 + 1.31 + 6.67 + 0.05 = 9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}\end{aligned}$$

19. For isothermal reversible expansion,

$$|W| = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{V}{V_i}$$

where, V = final volume, V_i = initial final.

or $|W| = nRT \ln V - nRT \ln V_i$

On comparing with equation of straight line, $y = mx + c$, we get

$$\text{slope} = m = +nRT$$

$$\text{intercept} = -nRT \ln V_i$$

Thus, plot of $|W|$ with $\ln V$ will give straight line in which slope of $2(T_2)$ is greater than slope of $1(T_1)$ which is given in all options.

Now, if $V_i < 1$ then y intercept ($-nRT \ln V_i$) becomes positive and if it is positive for one case then it is positive for other case also. Thus, it is not possible that one y -intercept goes above and other y -intercept goes below. Thus, option (b) and (d) are incorrect. If we extent plot given in option (a) it seems to be merging which is not possible because if they are merging they give same +ve y -intercept. But they cannot give same y -intercept because value of T is different.

Now, if we extent the line of T_1 and T_2 given in option (c) it seems to be touching the origin. If they touch the origin then y -intercept becomes zero which is not possible. Thus, it is not the exactly correct answer but among the given options it is the most appropriate one.

20. **Key idea** Calculate the heat of combustion with the help of following formula

$$\Delta H_p = \Delta U + \Delta n_g RT$$

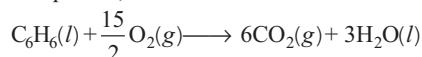
where, ΔH_p = Heat of combustion at constant pressure

ΔU = Heat at constant volume (It is also called ΔE)

Δn_g = Change in number of moles (In gaseous state).

R = Gas constant; T = Temperature.

From the equation,



Change in the number of gaseous moles i.e.

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ or } -1.5$$

Now we have Δn_g and other values given in the question are

$$\Delta U = -3263.9 \text{ kJ/mol}$$

$$T = 25^\circ \text{ C} = 273 + 25 = 298 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}\text{So, } \Delta H_p &= (-3263.9) + (-1.5) \times 8.314 \times 10^{-3} \times 298 \\ &= -3267.6 \text{ kJ mol}^{-1}\end{aligned}$$

21. According to first law of thermodynamics,

$$\Delta U = q + W = q - p\Delta V$$

In isochoric process ($\Delta V = 0$), $\Delta U = q$

In isobaric process ($\Delta p = 0$), $\Delta U = q$

In adiabatic process ($q = 0$), $\Delta U = W$

In isothermal process ($\Delta T = 0$) and $\Delta U = 0$

$\therefore \Delta U$ is equal to adiabatic work.

22. $G = H - TS = U + pV - TS$

$$\Rightarrow dG = dU + pdV + Vdp - TdS - SdT = Vdp - SdT$$

$[\because dU + pdV = dq = TdS]$

$$\Rightarrow dG = Vdp \text{ if isothermal process (}dT = 0\text{)}$$

$$\Rightarrow \Delta G = V\Delta p$$

Now taking initial state as standard state

$$\begin{aligned}G_{gr}^{\circ} - G_{gr}^{\circ} &= V_{gr} \Delta p \\ G_d^{\circ} - G_d^{\circ} &= V_d \Delta p\end{aligned} \quad \dots(i)$$

Now (ii)-(i) gives,

$$(V_d - V_{gr}) \Delta p = G_d - G_{gr} + (G_{gr}^{\circ} - G_d^{\circ})$$

At equilibrium, $G_d = G_{gr}$

$$\Rightarrow (V_{gr} - V_d) \Delta p = G_d^{\circ} - G_{gr}^{\circ} = 2.9 \times 10^3 \text{ J}$$

$$\Rightarrow \Delta p = \frac{2.9 \times 10^3}{2 \times 10^{-6}} \text{ Pa} = \frac{29}{2} \times 10^8 \text{ Pa} = \frac{29000}{2} \text{ bar}$$

$$p = p_0 + \frac{29000}{2} = 1 + \frac{29000}{2} = 14501 \text{ bar}$$

23. By first law,

$$\Delta E = Q + W$$

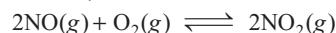
For isothermal expansion, $\Delta E = 0$

$$\therefore Q = -W$$

$$-Q_{\text{irrev}} = W_{\text{irrev}} = p\Delta V = 3(2 - 1) = 3 \text{ L atm}$$

$$\text{Also, } \Delta S_{\text{surr}} = \frac{Q_{\text{irrev}}}{T} = \frac{(-3 \times 101.3) \text{ J}}{300 \text{ K}} = -\frac{303.9}{300} = -1.013 \text{ JK}^{-1}$$

24. For the given reaction,



$$\text{Given, } \Delta G_f^{\circ}(\text{NO}) = 86.6 \text{ kJ/mol}$$

$$\Delta G_f^{\circ}(\text{NO}_2) = ?$$

$$K_p = 1.6 \times 10^{12}$$

Now, we have,

$$\begin{aligned}\Delta G_f^{\circ} &= 2\Delta G_f^{\circ}(\text{NO}_2) - [2\Delta G_f^{\circ}(\text{NO}) + \Delta G_f^{\circ}(\text{O}_2)] \\ &= -RT \ln K_p = 2\Delta G_f^{\circ}(\text{NO}_2) - [2 \times 86,600 + 0]\end{aligned}$$

$$\Delta G_f^{\circ}(\text{NO}_2) = \frac{1}{2} [2 \times 86600 - R \times 298 \ln (1.6 \times 10^{12})]$$

$$\Delta G_f^{\circ}(\text{NO}_2) = 0.5 [2 \times 86,600 - R \times (298) \ln (1.6 \times 10^{12})]$$

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- 25. PLAN** This problem is based on assumption that total entropy change of universe is zero.

At 100°C and 1 atmosphere pressure,



For equilibrium, $\Delta S_{\text{total}} = 0$
and $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

As we know during conversion of liquid to gas entropy of system increases, in a similar manner entropy of surrounding decreases.

$$\therefore \Delta S_{\text{system}} > 0 \text{ and } \Delta S_{\text{surrounding}} < 0$$

- 26.** The process is isothermal expansion, hence

$$q = -W$$

$$\Delta E = 0$$

$$W = -2.303 nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 0.04 \times 8.314 \times 310 \times \log \frac{335}{50} = -208 \text{ J}$$

$$q = +208 \text{ J}$$

$W = -208 \text{ J}$ (expansion work)

- 27.** At transition point (373 K, 1.0 bar), liquid remains in equilibrium with vapour phase, therefore $\Delta G = 0$. As vaporisation occurs, degree of randomness increases, hence $\Delta S > 0$.

$$28. \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -54.07 \times 10^3 \text{ J} - 298 \times 10 \text{ J}$$

$$= -57.05 \times 10^3 \text{ J}$$

$$\text{Also, } \Delta G^\circ = -2.303 RT \log K$$

$$\Rightarrow \log K = \frac{-\Delta G^\circ}{2.303 RT} = \frac{57.05 \times 10^3}{5705} = 10$$

- 29.** Entropy is a state function hence,

$$\begin{aligned} \Delta S_{A \rightarrow B} &= \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow D} + \Delta S_{D \rightarrow B} \\ &= 50 \text{ eu} + 30 \text{ eu} + (-20 \text{ eu}) = 60 \text{ eu} \end{aligned}$$

- 30.** Given, $\frac{P}{V} = 1 \Rightarrow p = V$... (i)

Also from first law : $dq = C_V dT + pdV$

For one mole of an ideal gas : $pV = RT$

$$\Rightarrow pdV + Vdp = RdT \quad \dots (\text{ii})$$

$$\text{From (i)} \quad pdV = Vdp$$

Substituting in Eq. (ii) gives

$$2pdV = RdT \Rightarrow pdV = \frac{R}{2}dT$$

$$\Rightarrow dq = C_V dT + \frac{R}{2}dT$$

$$\Rightarrow \int \frac{dq}{dT} = C_V + \frac{R}{2} = \frac{3}{2}R + \frac{R}{2} = 2R$$

- 31.** For an irreversible, adiabatic process;

$$0 = C_V(T_2 - T_1) + p_e(V_2 - V_1)$$

Substituting the values

$$C_V(T - T_2) = 1(2 - 1)\text{atm L}$$

$$\Rightarrow T - T_2 = \frac{1}{C_V} = \frac{2}{3R} \Rightarrow T_2 = T - \frac{2}{3 \times 0.082}$$

- 32.** In case of reversible thermodynamic process,

$$\Delta H = nC_p \Delta T$$

\therefore Process is isothermal, $\Delta T = 0 \Rightarrow \Delta H = 0$

- 33.** For a spontaneous process $\Delta G < 0$

Also; $\Delta G = \Delta H - T\Delta S$

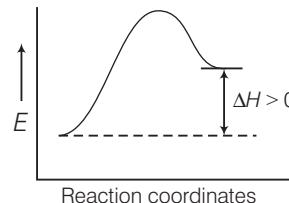
For adsorption of gas on solid surface, $\Delta S < 0$. Therefore, in order to be $\Delta G < 0$, ΔH must be negative.

$$34. \Delta H = \Delta U + \Delta(pV) = 30 + 2(5 - 3) + 5(4 - 2) = 44 \text{ L atm.}$$

- 35.** Work is not a state-function, it depends on path followed.

- 36.** In a reversible thermodynamic process, system always remains in equilibrium with surroundings.

37.



Minimum value of activation energy must be greater than ΔH .

$$38. \Delta H = \Delta E + \Delta n_g RT \Rightarrow \Delta H - \Delta E = \Delta n_g RT = -3RT = -3 \times 8.314 \times 298 = -7433 \text{ J} = -7.43 \text{ kJ}$$

- 39.** Given, $w = - \int p_{\text{ext}} dV$

For 1 mole van der Waals' gas

$$p = \left(\frac{RT}{V - b} - \frac{a}{V^2} \right)$$

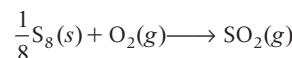
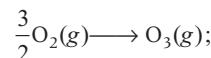
For reversible process, $p_{\text{ext}} = p_{\text{gas}}$

$$w = - \int \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) dV$$

But, it is not applicable for irreversible process which are carried out very fast. So, work done is calculated assuming final pressure remains constant throughout the process.

Thus, statement (a), (b) and (c) correct while statement (d) is incorrect.

- 40.** The standard enthalpy of formation is defined as standard enthalpy change for formation of 1 mole of a substance from its elements, present in their most stable state of aggregation.



In the above two reactions standard enthalpy of reaction is equal to standard enthalpy of formation.

- 41.** In the given curve AC represents **isochoric process** as volume at both the points is same i.e., V_1

Similarly, AB represents **isothermal process** (as both the points are at T_1 temperature) and BC represents **isobaric process** as both the points are at p_2 pressure.

Now (i) for option (a)

$$q_{AC} = \Delta U_{BC} = nC_V(T_2 - T_1)$$

where, n = number of moles

C_v = specific heat capacity at constant volume

However, $W_{AB} \neq p_2(V_2 - V_1)$ instead

$$W_{AB} = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

So, this option is incorrect.

(ii) For option (b)

$$q_{BC} = \Delta H_{AC} = nC_p(T_2 - T_1)$$

where, C_p = specific heat capacity at constant pressure

Likewise,

$$W_{BC} = -p_2(V_1 - V_2)$$

Hence, this option is correct.

(iii) For option (c)

$$\text{as } nC_p(T_2 - T_1) < nC_V(T_2 - T_1)$$

$$\text{so } \Delta H_{CA} < \Delta U_{CA}$$

$$\text{and } q_{AC} = \Delta U_{BC}$$

Hence, this option is also correct.

(iv) For option (d)

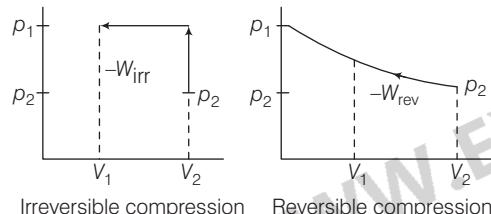
$$\text{Although } q_{BC} = \Delta H_{AC}$$

$$\text{but } \Delta H_{CA} \neq \Delta U_{CA}$$

Hence, this option is incorrect.

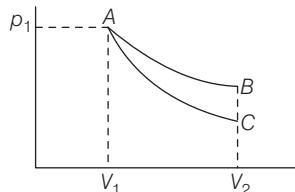
42.

(a)



Maximum work is done on the system when compression occurs irreversibly and minimum work is done in reversible compression.

(b)



AB is isothermal and AC is adiabatic path. Work done is area under the curve. Hence,

(c) It is incorrect. In adiabatic expansion cooling is observed, hence $\Delta U = nC_v\Delta T < 0$.

(d) $q = 0$ (adiabatic), $W = 0$ (Free expansion)
Hence, $\Delta U = 0, \Delta T = 0$ (Isothermal)

$$43. \Delta S_{\text{surr}} = \frac{-\Delta H}{T_{\text{surr}}}$$

For endothermic reaction, if T_{surr} increases, ΔS_{surr} will increase.
For exothermic reaction, if T_{surr} increases, ΔS_{surr} will decrease.

44. **PLAN** This problem includes concept of isothermal adiabatic irreversible expansion.

Process is adiabatic because of the use of thermal insulation therefore, $q = 0$

$$\therefore p_{\text{ext}} = 0 \\ w = p_{\text{ext}} \cdot \Delta V = 0 \times \Delta V = 0$$

Internal energy can be written as

$$\Delta U = q + W = 0$$

The change in internal energy of an ideal gas depends only on temperature and change in internal energy (ΔU) = 0 therefore, $\Delta T = 0$ hence, process is isothermal and

$$T_2 = T_1 \text{ and } p_2 V_2 = p_1 V_1$$

(d) $p_2 V_2^\gamma = p_1 V_1^\gamma$ is incorrect, it is valid for adiabatic reversible process.

Hence, only (a), (b) and (c) are correct choices.

45. **PLAN** When an ideal solution is formed process is spontaneous thus According to Raoult's law, for an ideal solution

$$\Delta H = 0, \Delta V_{\min} = 0$$

From the relation

$$\Delta G = \Delta H - T\Delta S$$

Since,

$$\Delta H = 0$$

i.e. less than zero. and $\Delta S_{\text{surroundings}} = 0$

Therefore, $\Delta S_{\text{sys}} = + \text{ve}$

i.e. more than zero.

46. (a) Since, change of state (p_1, V_1, T_1) to (p_2, V_2, T_2) is isothermal therefore, $T_1 = T_2$.

(b) Since, change of state (p_1, V_1, T_1) to (p_3, V_3, T_3) is an adiabatic expansion it brings about cooling of gas, therefore, $T_3 < T_1$.

(c) Work done is the area under the curve of p - V diagram. As obvious from the given diagram, magnitude of area under the isothermal curve is greater than the same under adiabatic curve, hence $W_{\text{isothermal}} > W_{\text{adiabatic}}$

$$(d) \Delta U = nC_v\Delta T$$

In isothermal process, $\Delta U = 0$ as $\Delta T = 0$

In adiabatic process, $\Delta U = nC_v(T_3 - T_1) < 0$ as $T_3 < T_1$.

$$\Rightarrow \Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$$

NOTE Here only magnitudes of work is being considered otherwise both works have negative sign.

47. (a) Entropy is a state function, change in entropy in a cyclic process is zero.

$$\text{Therefore, } \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z} + \Delta S_{Z \rightarrow X} = 0$$

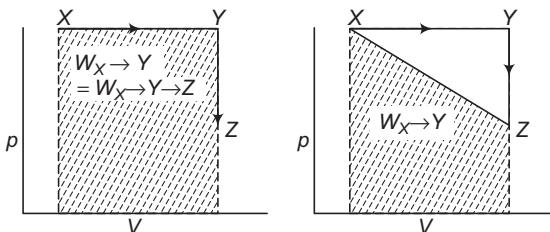
$$\Rightarrow -\Delta S_{Z \rightarrow X} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z} = \Delta S_{X \rightarrow Z}$$

Analysis of options (b) and (c)

Work is a non-stable function, it does depends on the path followed. $W_{Y \rightarrow Z} = 0$ as $\Delta V = 0$.

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Therefore, $W_{X \rightarrow Y \rightarrow Z} = W_{X \rightarrow Y}$. Also, work is the area under the curve on pV diagram.



As shown above $W_{X \rightarrow Y} + W_{Y \rightarrow Z} = W_{X \rightarrow Y} = W_{X \rightarrow Y \rightarrow Z}$ but not equal to $W_{X \rightarrow Z}$.

48. Resistance and heat capacity are mass dependent properties, hence they are extensive.
49. Internal energy, molar enthalpy are state function. Also, reversible expansion work is a state function because between given initial and final states, there can be only one reversible path.
50. Intensive properties are those property which do not depends on amount of sample. Both temperature and refractive index are intensive properties while enthalpy and volumes are extensive properties as they depends on amount of sample.

51. Given : $A \rightleftharpoons B$ ($p_A = 1$ bar)

Using $\Delta G = \Delta G^\circ + RT \ln K_p$

At equilibrium : $\Delta G^\circ = -RT \ln K_p$

$$\Delta G_1^\circ = -RT_1 \ln K_{p_1} \quad \dots (i)$$

$$\Delta G_2^\circ = -RT_2 \ln K_{p_2} \quad \dots (ii)$$

From Eqs. (i) and (ii),

$$\frac{\Delta G_1^\circ}{\Delta G_2^\circ} = \frac{T_1}{T_2} \times \frac{\ln K_{p_1}}{\ln K_{p_2}} = \frac{1000}{2000} \times \frac{\ln(10)}{\ln(100)} = \frac{1}{4} = 0.25$$

52. Statement I is true, it is statement of first law of thermodynamics.

Statement II is true, it is statement of second law of thermodynamics. However, Statement II is not the correct explanation of statement I.

53. Statement I is false. At equilibrium

$$\Delta G = 0, G \neq 0.$$

Statement II is true, spontaneous direction of reaction is towards lower Gibbs free energy.

54. Statement I is true.

$$dq = dE + p_{\text{ext}} dV = 0$$

$$\Delta T = 0$$

$$\therefore dE = 0; \quad p_{\text{ext}} = 0$$

$$\therefore p_{\text{ext}} dV = 0$$

Statement II is true. According to kinetic theory of gases, volume occupied by molecules of ideal gas is zero.

However, Statement II is not the correct explanation of Statement I.

55. $L \rightarrow M$ At constant V — isochoric,

$$N \rightarrow K$$

56. **PLAN** By Boyle's law at constant temperature, $p \propto \frac{1}{V}$

By Charles' law at constant pressure, $V \propto T$

Process taking place at

Constant temperature — isothermal

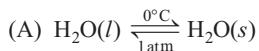
Constant pressure — isobaric

Constant volume — isochoric

Constant heat — adiabatic

$K \rightarrow L$	At constant p , volume increases	thus, heating
$L \rightarrow M$	At constant V , pressure decreases	thus, cooling
$M \rightarrow N$	At constant p , volume decreases	thus, cooling
$N \rightarrow K$	At constant V , pressure increases	thus, heating

57. (A) $\rightarrow r, t$; (B) $\rightarrow p, q, s$; (C) $\rightarrow p, q, s$; (D) $\rightarrow q, s, t$



$q < 0, W < 0$ (expansion)

$\Delta S_{\text{sys}} < 0$ (solid state is more ordered than liquid state)

$\Delta U < 0; \Delta G = 0$ (At equilibrium)

- (B) $q = 0$ (isolated), $W = 0$ ($p_{\text{ext}} = 0$)

$\Delta S_{\text{sys}} > 0 \because V_2 > V_1$

$\Delta U = 0 \because q = W = 0$

$\Delta G < 0 \because p_2 < p_1$

- (C) $q = 0$ (isothermal mixing of ideal gases at constant p)

$W = 0 \because \Delta U = 0; q = 0, \Delta S_{\text{sys}} > 0$

$\because V_2 > V_1, \Delta U = 0$

$\because \Delta T = 0$

$\Delta G < 0 \because$ mixing is spontaneous.

- (D) $q = 0$ (returning to same state and by same path)

$$W = 0$$

$\Delta S_{\text{sys}} = 0$ (same initial and final states)

$\Delta U = 0$

$\because T_i = T_f, \Delta G = 0$

58. (A) $CO_2(s) \longrightarrow CO_2(g)$

It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence ΔS is positive.

- (B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

It is a chemical decomposition, not a phase change. Thermal decomposition occur at the expense of energy, hence endothermic. Product contain a gaseous species, hence, $\Delta S > 0$.

- (C) $2H \longrightarrow H_2(g)$

A new H—H covalent bond is being formed, hence, $\Delta H < 0$.

Also, product is less disordered than reactant, $\Delta S < 0$.

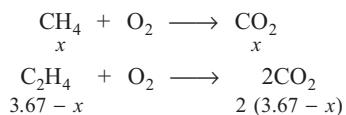
- (D) Allotropes are considered as different phase, hence $P_{(\text{white, solid})} \rightarrow P_{(\text{red, solid})}$ is a phase transition as well as allotropic change.
Also, red phosphorus is more ordered than white phosphorus, $\Delta S < 0$.
- 59.** Extensive : Enthalpy is an extensive property while molar enthalpy is an intensive property.
- 60.** Zero : $-W = p\Delta V = 0 \because \Delta V = 0$
- 61.** Exothermic reaction.
- 62.** Isolated This system neither exchange matter nor energy with surroundings.
- 63.** R : For an ideal gas, $C_p - C_V = R$
- 64.** 900 cal : $E = \frac{3}{2}RT = \frac{3}{2} \times 2 \times 300 \text{ cal}$
- 65.** True First law deals with conservation of energy while second law deals with direction of spontaneous change.
- 66.** True Diatomic gases have more degree of freedom than a monatomic gas.
- 67.** Work done along dashed path $|W| = \Sigma p\Delta V$
 $= 4 \times 1.5 + 1 \times 1 + \frac{2}{3} \times 2.5 = 8.65 \text{ L atm}$
 Work done along solid path $-W = nRT \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{V_2}{V_1}$
 $= 2 \times 2.3 \log \frac{5.5}{0.5} = 2 \times 2.3 \log 11 = 4.79$
 $\Rightarrow \frac{W_d}{W_s} = \frac{8.65}{4.79} = 1.80 \approx 2$
- 68.** $\Delta H = \Delta U + \Delta(pV) = \Delta U + V\Delta p$
 $\Rightarrow \Delta U = \Delta H - V\Delta p$
 $= -560 - 1 \times 30 \times 0.1 = -563 \text{ kJ}$
- 69.** $\Delta U = q + W$
 For adiabatic process, $q = 0$, hence $\Delta U = W$
 $W = -p(\Delta V) = -p(V_2 - V_1)$
 $\Rightarrow \Delta U = -100(99 - 100) = 100 \text{ bar mL}$
 $\Delta H = \Delta U + \Delta(pV)$
 where, $\Delta pV = p_2 V_2 - p_1 V_1$
- 70.** He is monatomic, so it has only three degree of freedom (translational only) at all temperature hence, C_V value is always $\frac{3}{2}R$.
 Hydrogen molecule is diatomic, has three translational, two rotational and one vibrational degree of freedom. The energy spacing between adjacent levels are in the order of :
 translational < rotational < vibrational
 At lower temperature only translational degree of freedom contribute to heat capacity while at higher temperature rotational and vibrational degree of freedom starts contributing to heat capacity.

- 71.** (i)
- (ii) $-W_1 = p\Delta V = 20 \text{ L atm}$
 $W_2 = 0 \quad \because \Delta V = 0$
 $W_3 = nRT \ln \frac{40}{20} = 20 \ln 2$
 Total work done $= W_1 + W_2 + W_3$
 $= -20 \text{ L atm} + 0 + 20 \ln 2$
 $= -6.14 \text{ atm}$
 From first law : $q = \Delta E + (-W) = -W$
 $(\because \Delta E = 0 \text{ for cyclic process})$
 $\Rightarrow q = 6.14 \text{ L atm} = 622.53 \text{ J}$
 (iii) All the states function, ΔU , ΔH and ΔS are zero for cyclic process.
- 72.** At equilibrium : $B \rightleftharpoons A$
 $\Rightarrow K_1 = \frac{95.2\%}{1.3\%} = \frac{13}{952}$
 $B \rightleftharpoons C$
 $\Rightarrow K_2 = \frac{95.2\%}{3.5\%} = \frac{35}{952}$
 $\Rightarrow \Delta G_1^\circ = -RT \ln K_1$
 $= -8.314 \times 448 \times 2.303 \log \frac{13}{952} = 16 \text{ kJ}$
 $\Delta G_2^\circ = -RT \ln K_2$
 $= -8.314 \times 448 \times 2.303 \log \frac{35}{952} = 12.3 \text{ kJ}$
- 73.** $\Delta_r G^\circ = \Delta_f G^\circ (\text{products}) - \Delta_f G^\circ (\text{reactants})$
 $= -394.4 - (-137.2) = -257.2 \text{ kJ} < 0$
 The above negative value of ΔG indicates that the process is spontaneous.
 Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 $\Rightarrow \Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$
 $= -257.2 + 300(-0.094)$
 $= -285.4 \text{ kJ} < 0$
- 74.** Given : $C_V = 12.49 \Rightarrow C_p = 20.8$
 $\Rightarrow \frac{C_p}{C_V} = \gamma = 1.66$
 In case of reversible adiabatic expansion :
 $TV^{\gamma-1} = \text{constant}$

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$$\begin{aligned}\Rightarrow \quad T_2 &= \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{V_1}{V_2}\right)^{0.66} \\ \Rightarrow \quad T_2 &= T_1 \left(\frac{V_1}{V_2}\right)^{0.66} \\ &= 300 \left(\frac{1}{2}\right)^{0.66} = 189.86 \text{ K} \\ \Rightarrow \quad \Delta H &= nC_p\Delta T \\ &= \frac{1 \times 1.25}{0.082 \times 300} \times 20.8 \times (189.86 - 300) \text{ J} \\ &= -116.4 \text{ J}\end{aligned}$$

75. Let the mixture contain x litre of CH_4 and $3.67 - x$ litre of ethylene.



$$\text{Given : } x + 2(3.67 - x) = 6.11 \text{ L}$$

$$\Rightarrow x = 1.23 \text{ L}$$

Volume of ethylene = 2.44 L

$$\text{Total moles of gases in 1 litre} = \frac{PV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.04$$

Also, CH_4 and ethylene are in 1 : 2 volume (or mole) ratio, moles of $\text{CH}_4 = \frac{0.04}{3}$ and moles of ethylene = $\frac{2 \times 0.04}{3}$

$$\Rightarrow \text{Heat evolved due to methane} = \frac{0.04}{3} \times 891 = 11.88 \text{ kJ}$$

$$\text{Heat evolved due to ethylene} = \frac{2 \times 0.04}{3} \times 1423 = 37.94 \text{ kJ}$$

\Rightarrow Total heat evolved on combustion of 1.0L gaseous mixture at 25°C is $11.88 + 37.94 = 49.82 \text{ kJ}$

76. Moles of H_2O needs to perspire = $\frac{1560}{2 \times 44} = 17.72$

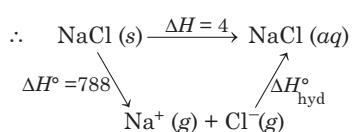
Weight of water needs to perspire = $17.72 \times 18 = 318.96 \text{ g}$

77. At constant pressure, $q = \Delta H$.

Topic 2 Thermochemistry

1. The enthalpy of solution of an ionic solid is numerically equal to the sum of its hydration and lattice energies,

$$\text{i.e. } \Delta H_{\text{sol}}^\circ = \Delta H_{\text{lattice}}^\circ + \Delta H_{\text{hyd}}^\circ$$



$$\Delta_{\text{sol}}H^\circ = \Delta_{\text{lattice}}H^\circ + \Delta_{\text{hyd}}H^\circ$$

$$4 = 788 + \Delta_{\text{hyd}}H^\circ$$

$$\Delta_{\text{hyd}}H^\circ = -784 \text{ kJ/mol}$$

2. $T_1 = 298 \text{ K}, T_2 = 373 \text{ K}, K_1 = 10, K_2 = 100$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \log\left(\frac{100}{10}\right) = \frac{\Delta H^\circ}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{373}\right)$$

$$\therefore \Delta H^\circ = 28.4 \text{ kJ/mol}$$

We know that, $\Delta G^\circ = -RT \ln K$

$$\therefore \Delta G^\circ \text{ at } T_1 = -8.314 \times 298 \times 2.303 \times \log(10)$$

$$\Rightarrow -5.71 \text{ kJ/mol}$$

$$\Delta G^\circ \text{ at } T_2 = -8.314 \times 373 \times 2.303 \times \log(100)$$

$$\Rightarrow -14.29 \text{ kJ/mol}$$

Hence, the correct option is (c).

Key Idea When q is the amount of heat involved in a system then at constant pressure
 $q = q_p$ and $C_p\Delta T = \Delta H$

Given reaction :



Specific heat of $\text{I}_2(s) = 0.055 \text{ cal g}^{-1} \text{ K}^{-1}$.

Specific heat of $\text{I}_2(\text{vap}) = 0.031 \text{ cal g}^{-1} \text{ K}^{-1}$.

Enthalpy (H_1) of sublimation of iodine = 24 cal g^{-1}

If q is the amount of heat involved in a system then at constant pressure $q = q_p$ and

$$\Delta H = C_p\Delta T$$

$$H_2 - H_1 = C_p(T_2 - T_1)$$

$$H_2 = H_1 + \Delta C_p(T_2 - T_1)$$

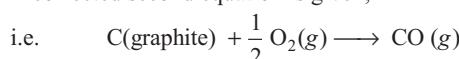
$$H_2 = 24 + (0.031 - 0.055)(250 - 200)$$

$$H_2 = 24 + (-0.024)(50) = 24 - 1.2 = 22.8 \text{ cal/g}$$

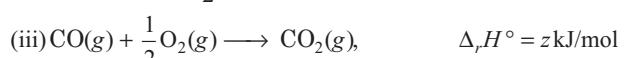
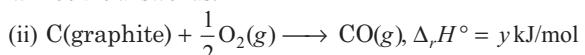
Thus, the enthalpy of sublimation of iodine at 250°C is 22.8 cal/g.

4. Second equation given in this question is wrong. Hence, No answer is correct.

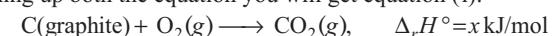
If corrected second equation is given,



and if we take the above reaction in consideration then $x = y + z$ will be the answer as:



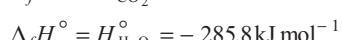
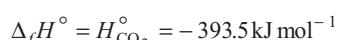
Summing up both the equation you will get equation (i):



Hence, x, y and z are related as:

$$x = y + z$$

5. Based on given $\Delta_r H^\circ$



$$\Delta_f H^\circ = H_{O_2}^\circ = 0.00 \text{ (elements)} \quad \dots \text{(iii)}$$

Required thermal reaction is for $\Delta_f H^\circ$ of CH_4

Thus, from III

$$\begin{aligned} 890.3 &= [\Delta_f H^\circ(\text{CH}_4) + 2\Delta_f H^\circ(\text{O}_2)] \\ &\quad - [\Delta_f H^\circ(\text{CO}_2) + 2\Delta_f H^\circ(\text{H}_2\text{O})] \\ &= \Delta_f H^\circ(\text{CH}_4) + 0 - [-393.5 - 2 \times 285.5] \\ &\therefore \Delta_f H^\circ(\text{CH}_4) = -74.8 \text{ kJ/mol} \end{aligned}$$

$$6. \text{ C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \Delta H = -393.5 \text{ kJ mol}^{-1} \quad \dots \text{(i)}$$

$$\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2(g); \Delta H = -283.5 \text{ kJ mol}^{-1} \quad \dots \text{(ii)}$$

On subtracting Eq. (ii) from Eq. (i), we get

$$\begin{aligned} \text{C}(s) + \frac{1}{2}\text{O}_2(g) &\longrightarrow \text{CO}(g); \\ \Delta H &= (-393.5 + 283.5) \text{ kJ mol}^{-1} \\ &= -110 \text{ kJ mol}^{-1} \text{ (approx.)} \end{aligned}$$

$$7. \text{ C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$$

$$\Delta U = -1364.47 \text{ kJ/mol}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta n_g = -1$$

$$\Delta H = -1364.47 + \frac{-1 \times 8.314 \times 298}{1000}$$

[Here, value of R in unit of J must be converted into kJ]

$$= -1364.47 - 2.4776$$

$$= -1366.9476 \text{ kJ/mol}$$

or

$$= -1366.95 \text{ kJ/mol}$$

8. **PLAN** $\Delta_c H^\circ$ (Standard heat of combustion) is the standard enthalpy change when one mole of the substance is completely oxidised.

Also standard heat of formation ($\Delta_f H^\circ$) can be taken as the standard of that substance.

$$H_{\text{CO}_2}^\circ = \Delta_f H^\circ(\text{CO}_2) = -400 \text{ kJ mol}^{-1}$$

$$H_{\text{H}_2\text{O}}^\circ = \Delta_f H^\circ(\text{H}_2\text{O}) = -300 \text{ kJ mol}^{-1}$$

$$H_{\text{glucose}}^\circ = \Delta_f H^\circ(\text{glucose}) = -1300 \text{ kJ mol}^{-1}$$

$$H_{\text{O}_2}^\circ = \Delta_f H^\circ(\text{O}_2) = 0.00$$



$$\begin{aligned} \Delta_c H^\circ(\text{glucose}) &= 6[\Delta_f H^\circ(\text{CO}_2) + \Delta_f H^\circ(\text{H}_2\text{O})] \\ &\quad - [\Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + 6\Delta_f H^\circ(\text{O}_2)] \\ &= 6[-400 - 300] - [-1300 + 6 \times 0] \\ &= -2900 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Molar mass of } \text{C}_6\text{H}_{12}\text{O}_6 = 180 \text{ g mol}^{-1}$$

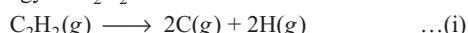
Thus, standard heat of combustion of glucose per gram

$$= \frac{-2900}{180} = -16.11 \text{ kJ g}^{-1}$$

To solve such problem, students are advised to keep much importance in unit conversion. As here, value of R

(8.314 J K $^{-1}$ mol $^{-1}$) in JK $^{-1}$ mol $^{-1}$ must be converted into kJ by dividing the unit by 1000.

9. For calculation of C≡C bond energy, we must first calculate dissociation energy of C_2H_2 as



Using the given bond energies and enthalpies :



Adding Eqs. (ii), (iii) and (iv) gives Eq. (i).



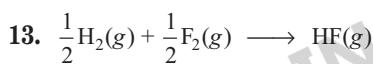
$$= 2 \times 350 + (\text{C} \equiv \text{C}) \text{ BE}$$

$$\Rightarrow (\text{C} \equiv \text{C}) \text{ BE} = 1515 - 700 = 815 \text{ kJ/mol}$$

10. Elements in its standard state have zero enthalpy of formation. Cl_2 is gas at room temperature, therefore $\Delta_f H^\circ$ of $\text{Cl}_2(g)$ is zero.

11. C—C bond energy is approximately 100 kcal.

$$12. T = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30,000}{75} = 400 \text{ K}$$

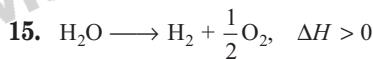


Here ΔH° = Standard molar enthalpy of formation of $\text{HF}(g)$.

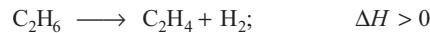


$$\Delta H = \Sigma \Delta_f H^\circ(\text{products}) - \Sigma \Delta_f H^\circ(\text{reactants})$$

$$= -110.5 - 241.8 - (-393.5) = +41.20 \text{ kJ}$$



It is reverse of combustion of $\text{H}_2(g)$, hence endothermic.



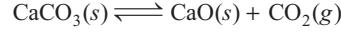
Here, more stable (saturated) hydrocarbon is being transformed to less stable (unsaturated) hydrocarbon, hence endothermic.



More stable allotrope is being converted to less stable allotrope.

16. **PLAN** Heat of reaction is dependent on temperature (Kirchhoff's equation) in heterogeneous system, equilibrium constant is independent on the molar concentration of solid species.

Heat of reaction is not affected by catalyst. It lowers activation energy.



By Kirchhoff's equation,

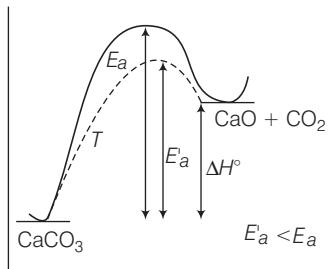
$$\Delta H_2^\circ(\text{at } T_2) = \Delta H_1^\circ(\text{at } T_1) + \Delta C_p(T_2 - T_1)$$

ΔH° varies with temperature. Thus, (a) is correct.

$$K = p_{\text{CO}_2}$$

K is dependent on pressure of CO_2 but independent of molar concentration of CaCO_3 . Thus, (b) and (c) are correct. At a given temperature, addition of catalysis lowers activation energy, ΔH remaining constant. Thus, (d) is also correct.

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E_a = Activation energy in absence of catalyst

E'_a = Activation energy in presence of catalyst

17. Temperature rise = $T_2 - T_1 = 298.45 - 298 = 0.45 \text{ K}$

$$q = \text{heat capacity} \times \Delta T = 2.5 \times 0.45 = 1.125 \text{ kJ}$$

$$\Rightarrow \text{Heat produced per mole} = \frac{1.125}{3.5} \times 28 = 9 \text{ kJ}$$

18. $\Delta H_r^\circ = \Delta H_f^\circ (\text{B}_2\text{O}_3) + 3\Delta H_f^\circ (\text{H}_2\text{O}) - \Delta H_f^\circ (\text{B}_2\text{H}_6)$

$$\Delta H_f^\circ (\text{H}_2\text{O})(g) = \Delta H_f^\circ (\text{H}_2\text{O})(l) + 44 = -242 \text{ kJ}$$

$$\Rightarrow \Delta H_r^\circ = -1273 - 3 \times 242 - 36 \\ = -2035 \text{ kJ}$$

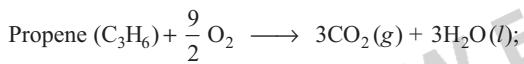
19. $\text{SF}_6(g) \longrightarrow \text{S}(g) + 6\text{F}(g)$

$$\Delta H = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants})$$

$$= 275 + 6 \times 80 + 1100 = 1855 \text{ kJ}$$

$$\Rightarrow \text{Average S—F bond energy} = \frac{1855}{6} = 309.16 \text{ kJ/mol}$$

20. Given : Cyclopropane \longrightarrow Propene (C_3H_6); $\Delta H = -33 \text{ kJ}$



$$\Delta H = -3(393.5 + 285.8) - 20.42 = -2058.32 \text{ kJ}$$

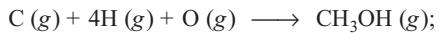
Adding :



$$\Delta H = H_1 + H_2 \\ = -33 + (-2058.32) \text{ kJ}$$

$$\Delta H = -2091.32 \text{ kJ}$$

21. Given : $\text{CH}_3\text{OH}(g) \longrightarrow \text{CH}_3\text{OH}(l); \quad \Delta H = -38 \text{ kJ}$



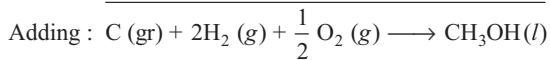
$$\Delta H = -(3 \times 415 + 356 + 463)$$

$$\therefore H = H_1 + H_2 = -2064 \text{ kJ}$$

$$\text{C}(g) \longrightarrow \text{C}(g); \quad \Delta H = 715 \text{ kJ}$$

$$2\text{H}_2(g) \longrightarrow 4\text{H}(g); \quad \Delta H = 2 \times 2 \times 218 = 872 \text{ kJ}$$

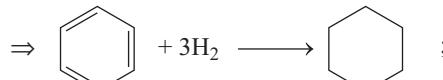
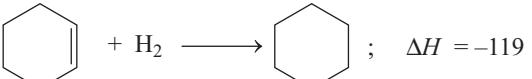
$$\frac{1}{2} \text{O}_2(g) \longrightarrow \text{O}(g); \quad \Delta H = 249 \text{ kJ}$$



$$\Delta H = -266 \text{ kJ/mol}$$

$$= \frac{1 \times 1.25}{0.082 \times 300} \times 20.8 \times (189.86 - 300) \text{ J} = -116.4 \text{ J}$$

22.



$$\Delta H = -119 \times 3 = -357 \text{ kJ} \text{ (Theoretical)}$$

$$-357 \text{ kJ} = \Delta H_f^\circ (\text{cyclohexane}) - \Delta H_f^\circ (\text{C}_6\text{H}_6)$$

$$\Rightarrow \Delta H_f^\circ (\text{C}_6\text{H}_6)_{\text{Theoretical}} = -156 + 357 = 201 \text{ kJ}$$

$$\Rightarrow \text{Resonance energy} = \Delta H_f^\circ (\text{exp.}) - \Delta H_f^\circ (\text{Theoretical}) \\ = 49 - 201 = -152 \text{ kJ/mol}$$

23. Per mole of ethylene polymerized, one C=C bond is broken and two C—C bonds are formed.

$$\Delta H^\circ (\text{Polym.}) = 590 - 2 \times 311 = -32 \text{ kJ/mol}$$

24. At same temperature and pressure, equal volumes contain equal moles of gases.

Let 1.0 L of CH_4 contain ' n ' mol

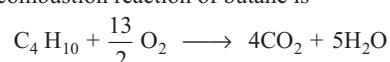
$$\Rightarrow x \text{ L of } \text{CH}_4 \text{ contain } nx \text{ mol}$$

$$\Rightarrow \text{Heat evolved in combustion by } x \text{ L } \text{CH}_4 = 809 nx \text{ kJ}$$

$$\text{Now, } 2878 \text{ kJ energy is evolved from 1 mole } \left(\frac{1}{n} \text{ L}\right) \text{C}_4\text{H}_{10}.$$

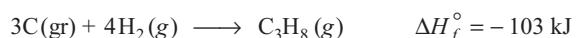
$$\Rightarrow 809 nx \text{ kJ energy will be evolved from } \frac{809 nx}{2878 n} \text{ L of } \text{C}_4\text{H}_{10} \\ = 0.28 x \text{ L of } \text{C}_4\text{H}_{10}$$

Also, the combustion reaction of butane is



$$\Rightarrow \text{Rate of supply of oxygen} = \frac{13}{2} \times 0.28 x \times 3 = 5.46 x \text{ L/h}$$

25. First we need to determine heat of combustion of C_3H_8 .

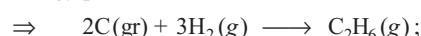


$$\Rightarrow -103 \text{ kJ} = -3 \times 393 - 4 \times 285.80 - \Delta H_{\text{comb}}^\circ (\text{C}_3\text{H}_8)$$

$$\Rightarrow \Delta H_{\text{comb}}^\circ (\text{C}_3\text{H}_8) = -2219.20 \text{ kJ}$$

$$\Rightarrow \Delta H_r^\circ = \Sigma \Delta H_{\text{comb}}^\circ (\text{reactants}) - \Sigma \Delta H_{\text{comb}}^\circ (\text{products}) \\ = -2219.20 - 285.80 + 1560 + 890 \\ = -55 \text{ kJ}$$

26. Let x kcal be the C—C bond energy and y kcal be the C—H bond energy per mole.



$$\Delta H^\circ = -2 \times 94 - 3 \times 68 + 372 \\ = -20 \text{ kcal}$$

$$\Rightarrow -20 \text{ kcal} = 2 \times 172 + 3 \times 104 - \text{BE} (\text{C}_2\text{H}_6)$$

$$\Rightarrow \text{BE} (\text{C}_2\text{H}_6) = 676 \text{ kcal}$$

Similarly, $3\text{C(gr)} + 4\text{H}_2(\text{g}) \longrightarrow \text{C}_3\text{H}_8(\text{g})$;

$$\Delta H^\circ = -3 \times 94 - 4 \times 68 + 530 = -24 \text{ kcal}$$

$$\Rightarrow -24 \text{ kcal} = 3 \times 172 + 4 \times 104 - \text{BE}(\text{C}_3\text{H}_8)$$

$$\Rightarrow \text{BE}(\text{C}_3\text{H}_8) = 956 \text{ kcal}$$

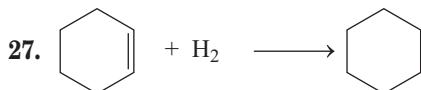
$$\text{Also, } \text{BE}(\text{C}_2\text{H}_6) = 676 \text{ kcal} = x + 6y \quad \dots(\text{i})$$

$$\text{BE}(\text{C}_3\text{H}_8) = 956 \text{ kcal} = 2x + 8y \quad \dots(\text{ii})$$

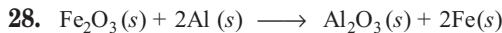
Solving Eqs. (i) and (ii) gives

$$y = 99 \text{ kcal (C—H) BE}$$

$$x = 82 \text{ kcal (C—C) BE}$$



$$\Delta H = \Sigma \Delta H_{\text{comb}}^\circ (\text{reactants}) - \Sigma \Delta H_{\text{comb}}^\circ (\text{products}) \\ = -3800 - 241 - (-3920) = -121 \text{ kJ/mol}$$



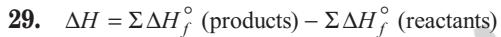
$$\Delta H_r^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ = -399 - (-199) = -200 \text{ kcal}$$

Mass of reactants = $56 \times 2 + 16 \times 3 + 27 \times 2 = 214 \text{ g}$

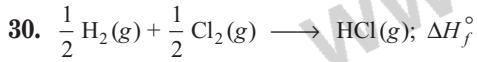
$$\Rightarrow \text{Fuel value/gram} = \frac{200}{214} = 0.93 \text{ kcal/g}$$

$$\text{Volume of reactants} = \frac{160}{5.2} \text{ cc} + \frac{54}{2.7} \text{ cc} = 50.77 \text{ cc}$$

$$\Rightarrow \text{Fuel value/cc} = \frac{200}{50.77} = 3.94 \text{ kcal/cc}$$

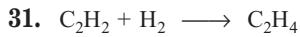


$$= -2 \times 94.1 - 3 \times 68.3 - (-21.1) = -372 \text{ kcal/mol}$$



$$\Delta H_f^\circ = \Sigma \text{BE} (\text{reactants}) - \Sigma \text{BE} (\text{products})$$

$$= \frac{1}{2} (104 + 58) - 103 = -22 \text{ kcal/mol}$$



$$\Delta H^\circ = \Sigma \Delta H_{\text{comb}}^\circ (\text{reactants}) - \Sigma \Delta H_{\text{comb}}^\circ (\text{products})$$

$$= -310.6 - 68.3 - (-337.2)$$

$$= -41.7 \text{ kcal}$$

32. The standard state formation reaction of $\text{C}_2\text{H}_2(\text{g})$ is :

$$2\text{C(g)} + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_2(\text{g}); \Delta H_f^\circ \\ \Delta H_r^\circ = \Sigma \Delta H_{\text{comb}}^\circ (\text{reactants}) - \Sigma \Delta H_{\text{comb}}^\circ (\text{products}) \\ = -2 \times 94.05 - 68.32 - (-310.62) \\ = 54.2 \text{ kcal} = \Delta H_f^\circ (\text{C}_2\text{H}_2)$$

33. $\Delta H_r^\circ = \Sigma \Delta_f H^\circ (\text{products}) - \Sigma \Delta_f H^\circ (\text{reactants})$

$$= -94.1 + 4(-22.1) - (-25.5 - 2 \times 57.8) \\ = -41.4 \text{ kcal}$$

34. $\Delta H^\circ = \Sigma \text{BE} (\text{reactants}) - \Sigma \text{BE} (\text{products})$

$$\Rightarrow -10.06 = \frac{1}{2} (104.18) + \frac{1}{2} (118.32) - \text{BE}(\text{O—H}) \\ \text{BE}(\text{O—H}) = 121.31 \text{ kcal}$$

35. Let $C \text{ JK}^{-1}$ be the heat capacity of calorimeter.

Mass of solution = $200 \text{ mL} \times 1 \text{ g mL}^{-1} = 200 \text{ g}$

Heat evolved in Expt.1

$$= 57 \times 1000 \times 0.1(\text{mol}) = 5700 \text{ J}$$

$$\Rightarrow 5700 \text{ J} = (200 \times 4.2 + C) \times 5.7$$

$$\Rightarrow 1000 = 200 \times 4.2 + C \quad \dots(\text{i})$$

Let $x \text{ kJ/mol}$ is heat evolved in neutralisation of acetic acid.

$$\Rightarrow x \times 1000 \times 0.10 = (200 \times 4.2 + C) \times 5.6$$

$$\Rightarrow \frac{x \times 100}{5.6} = 200 \times 4.2 + C \quad \dots(\text{ii})$$

From (i) and (ii) : $x = 56 \text{ kJ/mol}$

\Rightarrow Enthalpy of ionisation of acetic acid

$$= -56 - (-57) = 1 \text{ kJ/mol}$$

36. $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

200 mmol	100 mol	0	0
100 mmol	0	100 mmol	

A buffer is now formed.

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+]$$

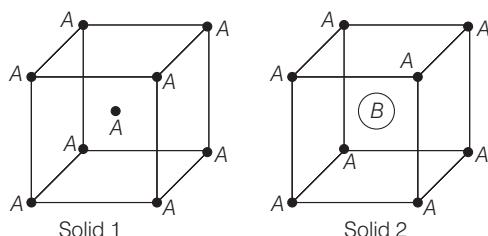
$$[\because [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]]$$

$$\Rightarrow \text{pH} = \text{p}K_a = -\log(2 \times 10^{-5}) = 5 - \log 2 = 4.7$$

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Solid State

Objective Questions I (Only one correct option)



- (a) 65% (b) 90% (c) 75% (d) 45%

12. At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of $x \text{ \AA}$. What is the approximate density of Cu (in g cm⁻³) at this temperature?

[Atomic mass of Cu = 63.55 u] (2019 Main, 9 Jan II)

- (a) $\frac{211}{x^3}$ (b) $\frac{205}{x^3}$
 (c) $\frac{105}{x^3}$ (d) $\frac{422}{x^3}$

13. The one that is extensively used as a piezoelectric material is (2019 Main, 9 Jan I)

- (a) quartz (b) tridymite
 (c) amorphous silica (d) mica

14. Which type of ‘defect’ has the presence of cations in the interstitial sites? (2018 Main)

- (a) Schottky defect (b) Vacancy defect
 (c) Frenkel defect (d) Metal deficiency defect

15. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is ‘ a ’, the closest approach between two atoms in metallic crystal will be (2017 Main)

- (a) $2a$ (b) $2\sqrt{2}a$ (c) $\sqrt{2}a$ (d) $\frac{a}{\sqrt{2}}$

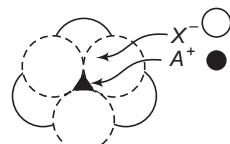
16. Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately (2015 Main)

- (a) 1.86 Å (b) 3.22 Å
 (c) 5.72 Å (d) 0.93 Å

17. CsCl crystallises in body centred cubic lattice. If ‘ a ’ its edge length, then which of the following expressions is correct? (2014 Main)

- (a) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 3a$ (b) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{3a}{2}$
 (c) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \sqrt{3}a$

18. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is (2013 Adv.)



- (a) 104 pm (b) 125 pm
 (c) 183 pm (d) 57 pm

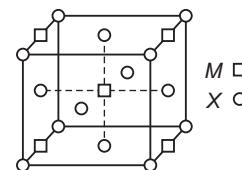
19. Experimentally it was found that a metal oxide has formula $M_{0.98}\text{O}$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be

- (a) 7.01% (b) 4.08% (2013 Main)
 (c) 6.05% (d) 5.08%

20. Which of the following exists as covalent crystals in the solid state? (2013 Main)

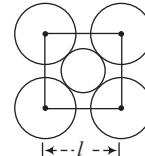
- (a) Iodine (b) Silicon
 (c) Sulphur (d) Phosphorus

21. A compound M_pX_q has cubic close packing (ccp) arrangement of X . Its unit cell structure is shown below. The empirical formula of the compound, is (2012)



- (a) MX (b) MX_2 (c) M_2X (d) M_5X_{14}

22. The packing efficiency of the two-dimensional square unit cell shown below is (2010)



- (a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54%

23. Which of the following fcc structure contains cations in alternate tetrahedral voids? (2005, 1M)

- (a) NaCl (b) ZnS (c) Na_2O (d) CaF_2

24. A substance A_xB_y crystallises in a face centred cubic (fcc) lattice in which atoms A occupy each corner of the cube and atoms B occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y (2002, 1M)

- (a) AB_3 (b) A_4B_3 (c) A_3B
 (d) composition cannot be specified

25. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is (2001, S, 1M)

- (a) AB_2 (b) A_2B (c) A_4B_3 (d) A_3B_4

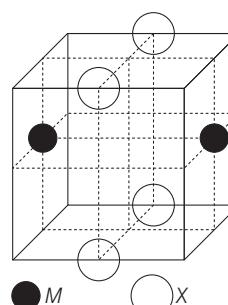
26. The coordination number of a metal crystallising in a hexagonal close-packed structure is (1999, 2M)

- (a) 12 (b) 4 (c) 8 (d) 6

Objective Questions II

(One or more than one correct option)

27. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s). (2020 Adv.)



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Numerical Answer Type Question

32. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instruction given below. Neglect the charge balance. (2018 Adv.)

 - (a) Remove all the anions (X) except the central one
 - (b) Replace all the face centered cations (M) by anions (X)
 - (c) Remove all the corner cations (M)
 - (d) Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{Number of anions}}{\text{Number of cations}} \right)$ in Z is _____

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct Statement II is correct Statement II is the correct explanation of Statement I
 - (b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I
 - (c) Statement I is correct Statement II is incorrect
 - (d) Statement I is incorrect Statement II is correct

- 33. Statement I** In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.

Statement II Equal numbers of cation and anion vacancies are present. (2001, 1M)

Passage Based Questions

Passage

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (hcp), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer.

Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be ' r '.

- 34.** The number of atoms in one of this hcp unit cell is
(2008, 3 × 4M = 12M)
(a) 4 (b) 6 (c) 12 (d) 17

35. The volume of this hcp unit cell is
(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$ (c) $12\sqrt{2}r^3$ (d) $\frac{64r^3}{3\sqrt{3}}$

36. The empty space in this hcp unit cell is
(a) 74 % (b) 47.6 % (c) 32 % (d) 26 %

Match the Column

- 37.** Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. (2007, 6M)

Column I	Column II
A. Simple cubic and face centred cubic	p. have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$
B. Cubic and rhombohedral	q. are two crystal systems
C. Cubic and tetragonal	r. have only two crystallographic angles of 90°
D. Hexagonal and monoclinic	s. belong to same crystal system

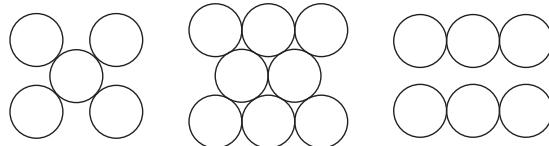
Integer Answer Type Questions

38. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3} , then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is (2017 Adv.)
39. The number of hexagonal faces that are present in a truncated octahedron is (2011)
40. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3} . The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is (2010)

Subjective Questions

41. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 \AA which crystallises in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm. (2006, 3M)
42. An element crystallises in fcc lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure. (2005, 2M)
43. The crystal AB (rock salt structure) has molecular weight $6.023y \text{ u}$. Where, y is an arbitrary number in u. If the minimum distance between cation and anion is $y^{1/3} \text{ nm}$ and the observed density is 20 kg/m^3 . Find the (i) density in kg/m^3 and (ii) type of defect. (2004, 2M)

44. (i) Marbles of diameter 10 mm are to be put in a square area of side 40 mm so that their centres are within this area.
(ii) Find the maximum number of marbles per unit area and deduce an expression for calculating it. (2003, 4M)
45. The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structures and identify these planes in your diagram. (2000)



46. A metal crystallises into two cubic phases, face centred cubic (fcc) and body centred cubic (bcc), whose unit cell lengths are 3.5 and 3.0 \AA , respectively. Calculate the ratio of densities of fcc and bcc. (1999, 3M)
47. Chromium metal crystallises with a body centred cubic lattice. The length of the unit edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3 ? (1997, 3M)
48. A metallic element crystallises into a lattice containing a sequence of layers of $ABABAB\dots$. Any packing of layers leaves out voids in the lattice. What percentage of this lattice is empty space? (1996, 3M)
49. Sodium crystallises in a bcc cubic lattice with the cell edge, $a = 4.29 \text{ \AA}$. What is the radius of sodium atom? (1994, 2M)

Answers

- | | | | | | | | | |
|--|------------------------------|------------|----------------|--------------|--------------|---------|---------|-----------|
| 1. (a) | 2. (d) | 3. (b) | 4. (c) | 5. (b) | 6. (d) | 7. (b) | 8. (d) | 9. (a) |
| 10. (c) | 11. (d) | 12. (d) | 13. (a) | 14. (c) | 15. (d) | 16. (a) | 17. (c) | 18. (a) |
| 19. (b) | 20. (b) | 21. (b) | 22. (d) | 23. (b) | 24. (a) | 25. (d) | 26. (a) | 27. (a,c) |
| 28. (b,c,d) | 29. (a) | 30. (b,c) | 31. (a,c,d) | 32. (c) | 33. (a) | 34. (b) | 35. (a) | 36. (d) |
| 37. A \rightarrow p, s; B \rightarrow q; C \rightarrow q; D \rightarrow q, r | 38. (2) | 39. (8) | 40. (7) | 41. (217 pm) | 42. (117 pm) | | | |
| 46. (1.26) | 47. (7.3 g/cm ³) | 48. (0.74) | 49. (1.86 \AA) | | | | | |

Hints & Solutions

1. Number of O^{2-} ions in ccp = 4
Total charge on oxide = -8
Number of tetrahedral voids = 8
Number of voids = 4
Number of cation M_1 occupies 50% of octahedral voids,

$$\frac{50}{100} \times 4 = 2$$

Number of cation M_2 occupies 12.5% of tetrahedral voids of oxide lattice,

$$\frac{12.5}{100} \times 8 = 1$$

So, formula is $(M_1)_2(M_2)O_4$.
This must be neutral. Both metals must have + 8 charge on total.
From given options :
{Oxidation number of $M_1 = + 2$
{Oxidation number of $M_2 = + 4$
 $\therefore (2 \times + 2) + (1 \times + 4) = + 8$
Hence, correct option is (a).

2. We know that,

$$d = \frac{Z \times M}{a^3 \times N_A}$$

Given, density $d = 6.17 \text{ g}$

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edge length $a = 300 \text{ pm} = 3 \times 10^{-8} \text{ cm}$,

$$N_A = 6 \times 10^{23} \text{ mol}^{-1}$$

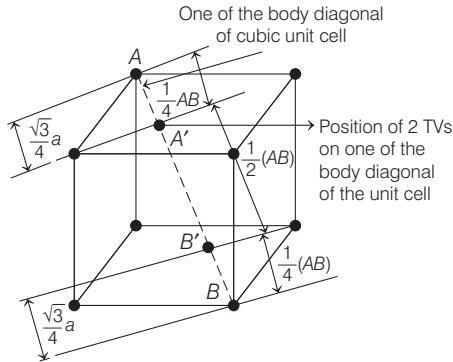
$$\therefore 6.17 = \frac{2 \times M}{(3 \times 10^{-8})^3 \times 6 \times 10^{23}} \quad (\text{For bcc, } Z = 2)$$

$$\Rightarrow M = 50 \text{ g/mol}$$

Hence, number of molecules present in 200 g of X_2 is

$$N = \frac{w}{M} \times N_A = \frac{200}{50} \times N_A = 4N_A$$

3. The ratio of number of atoms present in simple cubic, body centred cubic and face centered cubic structure are $1 : 2 : 4$ respectively.
4. In fcc unit cell, two tetrahedral voids are formed on each of the four non-parallel body diagonals of the cube at a distance of $\sqrt{3}a/4$ from every corner along the body diagonal.



The angle between body diagonal and an edge is $\cos^{-1}(1/\sqrt{3})$. So, the projection of the line on an edge is $a/4$. Similarly, other tetrahedral void also will be $a/4$ away. So, the distance between

$$\text{these two is } \left[a - \frac{a}{4} \right] - \frac{a}{4} = \frac{a}{2}.$$

5.

Key Idea Packing efficiency

$$= \frac{\text{Volume occupied by sphere}}{\text{Volume of cube}} \times 100$$

Given,

$$r_B = 2r_A$$

$$a_2 = a_1 + \frac{50}{100}a_1 = 1.5a_1$$

For bcc lattice

$$4r_A = \sqrt{3}a_1$$

$$r_A = \frac{\sqrt{3}a_1}{4} \Rightarrow a_1 = \frac{4r_A}{\sqrt{3}}$$

$$\therefore a_2 = 1.5 \left(\frac{4r_A}{\sqrt{3}} \right) = \frac{3}{2} \left(\frac{4r_A}{\sqrt{3}} \right)$$

$$a_2 = 2\sqrt{3}r_A$$

$$\text{Packing efficiency} = \frac{\frac{4}{3}\pi r_A^3 \times z_A + \frac{4}{3}\pi r_B^3 \times z_B}{a_2^3}$$

[As the atoms A are present at the edges only $z_A = 1 \times 8 = 1$, atom B is present only at the body centre $z_B = 1$]

$$\therefore \text{PE}_2 = \frac{\left(\frac{4}{3}\pi r_A^3 \times 1 \right) + \left(\frac{4}{3}\pi r_B^3 \times 1 \right)}{a_2^3}$$

$$= \frac{\frac{4}{3}\pi r_A^3 + \frac{4}{3}\pi (2r_A)^3}{(2\sqrt{3}r_A)^3} = \frac{\frac{4}{3}\pi r_A^3 \times 9}{8 \times 3\sqrt{3}r_A^3} = \frac{\pi}{2\sqrt{3}}$$

$$= 90.72\% \approx 90\%$$

6. Interstitial compounds are formed when a neutral atom with a small radius occupies in an interstitial hole (tetrahedral or octahedral voids) in a transition metal's hcp or ccp lattices (host lattice). Examples of small atoms (guest atom) are H, B, C and N.

Interstitial compounds are non-stoichiometric (Birtholide) in composition. They are very hard with very high melting points. The electrical conductivity of interstitial compounds are comparable to that of the pure metal. These are chemically unreactive in nature.

7. The number of element ' B ' in the crystal structure = $4N$

Number of tetrahedral voids = $2N$

Number of octahedral voids = N

$$\therefore \text{Number of 'A' in the crystal} = \frac{N}{2} = \frac{4}{2} = 2$$

Number of oxygen (O) atoms = $2N = 2 \times 4 = 8$

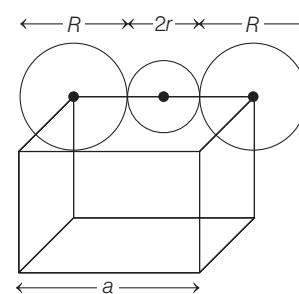
\therefore The structure of bimetallic oxide = $A_2B_4O_8 = AB_2O_4$

8. For body centred cubic bcc structure,

$$\text{radius } (R) = \frac{\sqrt{3}}{4}a \quad \dots(\text{i})$$

Where, a = edge length

According to question, the structure of cubic unit cell can be shown as follows:



$$\therefore a = 2(R + r) \quad \dots(\text{ii})$$

On substituting the value of R from Eq. (i) to Eq. (ii), we get

$$\frac{a}{2} = \frac{\sqrt{3}}{4}a + r$$

$$r = \frac{a}{2} - \frac{\sqrt{3}}{4}a = \frac{2a - \sqrt{3}a}{4}$$

$$r = \frac{a(2 - \sqrt{3})}{4}$$

$$r = 0.067a$$

9. Density of a crystal

$$d = \frac{M \times Z}{N_A \times a^3} \Rightarrow M = \frac{d \times N_A \times a^3}{Z}$$

Given, $d = 9 \times 10^3 \text{ kg m}^{-3}$

M = Molar mass of the solid

$Z = 4$ (for fcc crystal)

N_A = Avogadro's constant = $6 \times 10^{23} \text{ mol}^{-1}$

a = Edge length of the unit cell

$$= 200\sqrt{2} \text{ pm} = 200\sqrt{2} \times 10^{-12} \text{ m}$$

On substituting all the given values, we get

$$= \frac{(9 \times 10^3) \text{ kg m}^{-3} \times (6 \times 10^{23}) \text{ mol}^{-1} \times (200\sqrt{2} \times 10^{-12})^3 \text{ m}^3}{4}$$

$$= 0.0305 \text{ kg mol}^{-1}$$

10. Total effective number of atoms in hcp unit lattice = Number of octahedral voids in hcp = 6

∴ Number of tetrahedral voids (TV) in hcp

$$= 2 \times \text{Number of atoms in hcp lattice}$$

$$= 2 \times 6 = 12$$

As, formula of the lattice is A_2B_3 .

Suppose,

$$\begin{array}{ll} A & B \\ \left(\frac{1}{3} \times \text{TV}\right) & (\text{hcp}) \\ \Rightarrow & \frac{1}{3} \times 12 & 6 \\ \Rightarrow & \frac{2}{3} & 1 \\ \Rightarrow & 2 & 3 \end{array}$$

So, $A = \frac{1}{3}$ tetrahedral voids, B = hcp lattice

11. Triclinic primitive unit cell has dimensions as, $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^\circ$.

Among the seven basic or primitive crystalline systems, the triclinic system is most unsymmetrical. In other cases, edge length and axial angles are given as follows :

Hexagonal : $a = b \neq c$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Monoclinic : $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$

Tetragonal : $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

12. For fcc, rank of the unit cell (Z) = 4

Mass of one Cu-atom, $M = 63.55 \text{ u}$

Avogadro's number, $N_A = 6.023 \times 10^{23} \text{ atom}$

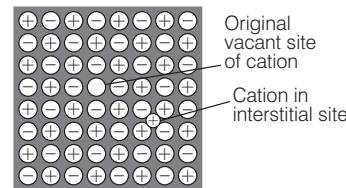
Edge length, $a = x \text{ \AA} = x \times 10^{-8} \text{ cm}$

$$\text{density } (d) = \frac{Z \times M}{N_A \times a^3}$$

$$= \frac{4 \times 63.55}{6.023 \times 10^{23} \times (x \times 10^{-8})^3} = \frac{422.048}{x^3} \text{ g cm}^{-3}$$

13. Piezoelectric materials are those materials that produce an electric current when they are placed under mechanical stress. Crystalline solids can be used as piezoelectric material hence, quartz is a correct answer.

14. It is the "Frenkel defect" in which cations leave their original site and occupy interstitial site as shown below.



15. For fcc arrangement, $4r = \sqrt{2}a$

where, r = radius and a = edge length

$$\therefore \text{Closest distance} = 2r = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$$

16. For bcc unit cell, $\sqrt{3}a = 4a$

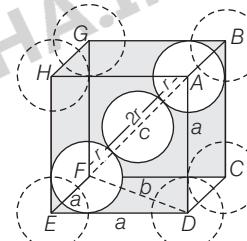
$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 4.29 \text{ \AA} = 1.85 \text{ \AA}$$

$$r = 1.85 \text{ \AA} \approx 1.86 \text{ \AA}$$

17. In CsCl, Cl^- lies at corners of simple cube and Cs^+ at the body centre. Hence, along the body diagonal, Cs^+ and Cl^- touch each other so $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 2r$

Calculation of r

In ΔADF ,



Body centred cubic unit cell

$$FD = b = \sqrt{a^2 + a^2} = \sqrt{2}a$$

In ΔAFD ,

$$c^2 = a^2 + b^2 = a^2 + (\sqrt{2}a)^2 = a^2 + 2a^2$$

$$c^2 = 3a^2 \Rightarrow c = \sqrt{3}a$$

As ΔAFD is an equilateral triangle.

$$\therefore \sqrt{3}a = 4r \quad [\because C = 3r + r + r]$$

$$\Rightarrow r = \frac{\sqrt{3}a}{4}$$

$$\text{Hence, } r_{\text{Cs}^+} + r_{\text{Cl}^-} = 2r = 2 \times \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{2}a$$

18. PLAN Given arrangement represents octahedral void and for this

$$\frac{r_+ (\text{cation})}{r_- (\text{anion})} = 0.414$$

$$\frac{r(A^+)}{r(X^-)} = 0.414$$

$$r(A^+) = 0.414 \times r(X^-) = 0.414 \times 250 \text{ pm}$$

$$= 103.5 \text{ pm} \approx 104 \text{ pm}$$

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19. From the valency of M^{2+} and M^{3+} , it is clear that three M^{2+} ions will be replaced by M^{3+} causing a loss of one M^{3+} ion. Total loss of them from one molecule of $MO = 1 - 0.98 = 0.02$

Total M^{3+} present in one molecule of

$$MO = 2 \times 0.02 = 0.04$$

That M^{2+} and $M^{3+} = 0.98$

$$\text{Thus, \% of } M^{3+} = \frac{0.04 \times 100}{0.98} = 4.08\%$$

20. Silicon exists as covalent crystal in solid state. (Network like structure, as seen in diamond).

21. Contribution of atom from the edge centre is $1/4$. Therefore, number of

$$M = \frac{1}{4} \times 4 \text{ (from edge centre)} + 1 \text{ (from body centre)} = 2$$

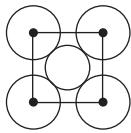
$$\text{Number of } X = \frac{1}{8} \times 8 \text{ (from corners)} + \frac{1}{2} \times 6 \text{ (from face centre)} = 4$$

$$\Rightarrow \text{Empirical formula} = M_2X_4 = MX_2$$

22. Contribution of circle from corner of square = $\frac{1}{4}$

\Rightarrow Effective number of circle per square

$$= \frac{1}{4} \times 4 + 1 \text{ (at centre)} = 2$$



\Rightarrow Area occupied by circle = $2\pi r^2$, r = radius.

Also, diagonal of square $4r = \sqrt{2} L$, where L = side of square.

\Rightarrow Packing fraction = $\frac{\text{Area occupied by circles}}{\text{Area of square}}$

$$= \frac{2\pi r^2}{L^2} = \frac{2\pi r^2}{8r^2} = \frac{\pi}{4} = 0.785$$

\Rightarrow % packing efficiency = 78.5%.

23. In ZnS, S^{2-} (sulphide ions) are present at fcc positions giving four sulphide ions per unit cell. To comply with 1 : 1 stoichiometry, four Zn^{2+} ions must be present in four alternate tetrahedral voids out of eight tetrahedral voids present.

In NaCl, Na^+ ions are present in octahedral voids while in Na_2O , Na^+ ions are present in all its tetrahedral voids giving the desired 2 : 1 stoichiometry. In CaF_2 , Ca^{2+} ions occupies fcc positions and all the tetrahedral voids are occupied by fluoride ions.

24. In cubic system, a corner contribute $\frac{1}{8}$ th part of atom to one unit cell and a face centre contribute $\frac{1}{2}$ part of atom to one unit cell.

Therefore,

$$\text{Number of } A \text{ per unit cell} = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } B \text{ per unit cell} = \frac{1}{2} \times 6 = 3$$

$$\Rightarrow \text{Formula} = AB_3$$

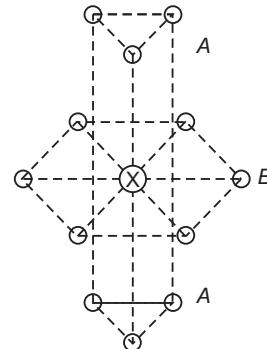
25. In NaCl, Na^+ occupies body centre and edge centres while Cl^- occupies corners and face centres, giving four Na^+ and four Cl^- per unit cell. In the present case A represent Cl^- and B represents Na^+ . Two face centres lies on one axis.

$$\Rightarrow \text{Number of } A \text{ removed} = 2 \times \frac{1}{2} = 1$$

Number of B is removed because it is not present on face centres.
 $\Rightarrow A$ remaining = 4 - 1 = 3, B remaining = 4,

$$\text{Formula} = A_3B_4$$

26. Three consecutive layers of atoms in hexagonal close packed lattice is shown below:



Atom X is in contact of 12 like atoms, 6 from layer B and 3 from top and bottom layers A each.

27. (a) The empirical formula of the compound:

$$\text{Contribution of } M \text{ and } X: M \left(2 \times \frac{1}{2}\right) X \left(4 \times \frac{1}{4}\right) \Rightarrow MX$$

- (b) Coordination number of both M and X is 8.

$$(c) \text{Distance between } M \text{ and } X = \sqrt{\frac{a^2}{4} + \frac{a^2}{2}} = \sqrt{\frac{3}{4}}a = \frac{\sqrt{3}}{2}a \\ \Rightarrow 0.866a$$

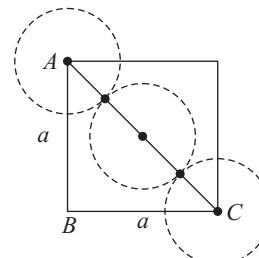
- (d) $r_M : r_X = (\sqrt{3} - 1) : 1 \Rightarrow 0.732 : 1$, thus statement (d) is incorrect.

28. (a) Nearest neighbour in the topmost layer of ccp structure is 9 thus, incorrect.

- (b) Packing efficiency is 74% thus, correct.

- (c) Tetrahedral voids = 2

Octahedral voids = 1 per atom thus, correct.



$$(d) \text{Edge length, } a = \frac{4}{\sqrt{2}}r = 2\sqrt{2}r$$

thus, correct

Explanation Edge length = a

Radius = r

$$AC^2 = AB^2 + BC^2$$

$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$4r = \sqrt{2}a$$

$$\Rightarrow r = \frac{\sqrt{2}}{4} a = \frac{a}{2\sqrt{2}}$$

$$\Rightarrow a = 2\sqrt{2} r$$

In ccp structure, number of spheres is 4.

$$\text{Hence, volume of 4 spheres} = 4 \left(\frac{4}{3} \pi r^3 \right)$$

$$\text{Total volume of unit cell} = a^3 = (2\sqrt{2}r)^3$$

% of packing efficiency

$$= \frac{\text{Volume of 4 spheres}}{\text{Volume of unit cell}}$$

$$= \frac{4 \left(\frac{4}{3} \pi r^3 \right)}{(2\sqrt{2}r)^3} \times 100$$

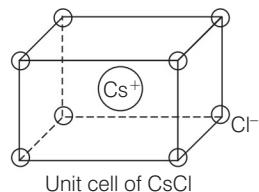
$$= 74.05\% \approx 74\%$$

29. Oxide ions are at ccp positions, hence $4O^{2-}$ ions. Also, there are four octahedral voids and eight tetrahedral voids. Since 'm' fraction of octahedral voids contain Al^{3+} and 'n' fraction of tetrahedral voids contain Mg^{2+} ions, to maintain electroneutrality $2(2Al^{3+}) = +6$ charge) and ($Mg^{2+} = +2$ charge), will make unit cell neutral

$$\text{Hence: } m = \frac{2}{4} = \frac{1}{2}, n = \frac{1}{8}$$

30. (a) Wrong statement. A small difference in sizes of cation and anion favour Schottky defect while Frenkel defect is favoured by large difference in sizes of cation and anion.
 (b) Correct statement. In Frenkel defect the smaller atom or ion gets dislocated from its normal lattice positions and occupies the interstitial space.
 (c) **Correct Statement** In F-centre defect, some anions leave the lattice and the vacant sites hold the electrons trapped in it maintaining the overall electroneutrality of solid.
 (d) Wrong statement : In Schottky defect, some of the atoms or ions remaining absent from their normal lattice points without distorting the original unit cell dimension. This lowers the density of solid.

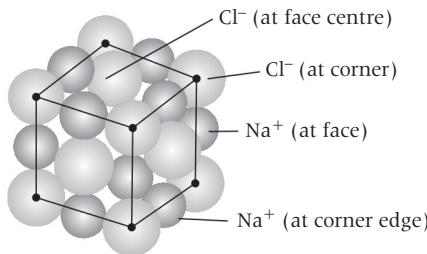
31. (a) The unit cell of CsCl has bcc arrangement of ions in which each ion has eight oppositely charged ions around it in the nearest neighbours as shown below :



- (b) In bcc, coordination number of atom is 8.
 (c) In an unit cell, a corner is shared in eight unit cells and a face centre is shared between two adjacent unit cells.
 (d) In NaCl unit cell; $2(r_{Na^+} + r_{Cl^-}) = a$
 $\Rightarrow a = 2(95 + 181) = 552 \text{ pm}$

Hence, a, c, d are correct.

32. The unit cell of initial structure of ionic solid MX looks like



In NaCl type of solids cations (Na^+) occupy the octahedral voids while anions (Cl^-) occupy the face centre positions.

However, as per the demand of problem the position of cations and anions are swapped.

We also know that (for 1 unit cell)

(A) Total number of atoms at FCC = 4

(B) Total number of octahedral voids = 4

(as no. of atoms at FCC = No. of octahedral voids)

Now taking the conditions one by one

- (i) If we remove all the anions except the central one than number of left anions.

$$= 4 - 3 = 1$$

- (ii) If we replace all the face centred cations by anions than effective number of cations will be $= 4 - 3 = 1$

Likewise effective number of anions will be $= 1 + 3 = 4$

- (iii) If we remove all the corner cations then effective number of cations will be $1 - 1 = 0$

- (iv) If we replace central anion with cation then effective number of cations will be $0 + 1 = 1$

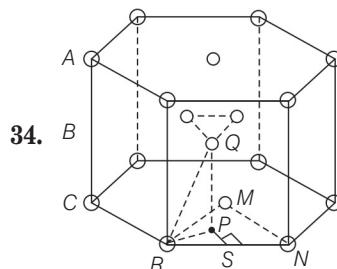
Likewise effective number of anions will be $4 - 1 = 3$

Thus, as the final outcome, total number of cations present in Z after fulfilling all the four sequential instructions = 1

Likewise, total number of anions = 3

$$\text{Hence, the value of } \frac{\text{Number of anions}}{\text{Number of cations}} = \frac{3}{1} = 3$$

33. In ionic solid MX (1 : 1 solid) same number of M^{n+} and X^{n-} ions are lost in Schottky defect to maintain electroneutrality of solid.



A hcp unit cell

Contribution of atoms from corner = $1/6$

Contribution from face centre = $1/2$

$$\Rightarrow \text{Total number of atoms per unit cell} = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 = 6$$

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35. In close packed arrangement, side of the base = $2r$

$$\Rightarrow RS = r$$

Also MNR is equilateral triangle, $\angle PRS = 30^\circ$

$$\text{In triangle } PRS, \cos 30^\circ = \frac{RS}{PR} = \frac{\sqrt{3}}{2}$$

$$\Rightarrow PR = \frac{2}{\sqrt{3}} RS = \frac{2}{\sqrt{3}} r$$

$$\text{In right angle triangle } PQR : PQ = \sqrt{QR^2 - PR^2} = 2\sqrt{\frac{2}{3}} r$$

$$\Rightarrow \text{Height of hexagon} = 2PQ = 4\sqrt{\frac{2}{3}} r$$

$$\Rightarrow \text{Volume} = \text{Area of base} \times \text{height} = 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4\sqrt{\frac{2}{3}} r \\ = 24\sqrt{2} r^3$$

36. Packing fraction = $\frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$

$$= 6 \times \frac{4}{3} \pi r^3 \times \frac{1}{24\sqrt{2} r^3} = 0.74$$

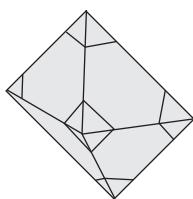
$$\Rightarrow \text{Fraction of empty space} = 1 - 0.74 = 0.26 = 26\%$$

37. A. Simple cubic and face centred cubic both have cell parameters $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. Also both of them belongs to same, cubic, crystal system.
 B. The cubic and rhombohedral crystal system belongs to different crystal system.
 C. Cubic and tetragonal are two different types of crystal systems having different cell parameters.
 D. Hexagonal and monoclinic are two different crystal system and both have two of their crystallographic angles of 90° .

38. Density (ρ) = $8 = \frac{4 \times M}{N_A (4 \times 10^{-8} \text{ cm})^3}$

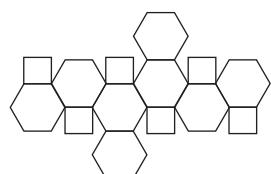
$$\Rightarrow M = 128 \times 10^{-24} N_A \Rightarrow \text{No. of atoms} = \frac{256}{M} \times N_A \\ = \frac{256}{128 \times 10^{-24} N_A} \times N_A = 2 \times 10^{24}$$

39. The truncated octahedron is the 14-faced Archimedean solid, with 14 total faces : 6 squares and 8 regular hexagons. The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron as :



Truncated octahedron

Truncated octahedron unfolded in two-dimension



40. Ag crystallises in fcc unit cell with 4 atoms per unit cell.

$$\rho = \frac{4 \times 108}{6.023 \times 10^{23} \times a^3} = 10.5 \text{ g cm}^{-3}.$$

$$\Rightarrow a^3 (\text{Volume of unit cell}) = 6.83 \times 10^{-23} \text{ cm}^3$$

$$\Rightarrow a = 4 \times 10^{-8} \text{ cm} = 4 \times 10^{-10} \text{ m}$$

$$\Rightarrow \text{Surface area of unit cell} = a^2 = 1.6 \times 10^{-19} \text{ m}^2$$

$$\Rightarrow \text{Number of unit cells on } 10^{-12} \text{ m}^2 \text{ surface}$$

$$= \frac{10^{-12}}{1.6 \times 10^{-19}} = 6.25 \times 10^6$$

\therefore There are two atoms (effectively) on one face of unit cell

$$\text{Number of atoms on } 10^{-12} \text{ m}^2 \text{ surface} = 2 \times \text{number of unit cell} \\ = 1.25 \times 10^7. \quad [\because y \times 10^x]$$

$$\Rightarrow x = 7 \Rightarrow y = 1.25$$

41. From the given information, the number of atoms per unit cell and therefore, type of unit cell can be known as

$$\rho = \frac{NM}{N_A a^3}$$

$$\Rightarrow N = \frac{\rho N_A a^3}{M} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8} \text{ cm})^3}{75} = 2 \text{ (bcc)}$$

$$\Rightarrow \text{In bcc, } 4r = \sqrt{3}a$$

$$\Rightarrow r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 5 \times 10^{-10} \text{ m} \\ = 2.17 \times 10^{-10} \text{ m} = 217 \text{ pm}$$

42. In a cubic crystal system, there are two types of voids known as octahedral and tetrahedral voids. If r_1 is the radius of void and r_2 is the radius of atom creating these voids then

$$\left(\frac{r_1}{r_2} \right)_{\text{octa}} = 0.414$$

$$\text{and } \left(\frac{r_1}{r_2} \right)_{\text{tetra}} = 0.225$$

The above radius ratio values indicate that octahedral void has larger radius, hence for maximum diameter of atom to be present in interstitial space :

$$r_1 = 0.414 r_2$$

$$\text{Also in fcc, } 4r_2 = \sqrt{2}a$$

$$\Rightarrow \text{Diameter required } (2r_1) = (2r_2) \times 0.414$$

$$= \frac{a}{\sqrt{2}} \times 0.414$$

$$= \frac{400 \times 0.414}{\sqrt{2}} = 117 \text{ pm}$$

43. (i) In rock salt like crystal AB, there are four AB units per unit cell. Therefore, density (d) is

$$d = \frac{4 \times 6.023 y}{6.023 \times 10^{23} \times 8y \times 10^{-27}}$$

$$[\because a = 2y^{1/3} \text{ nm} = 2y^{1/3} \times 10^{-9} \text{ m}]$$

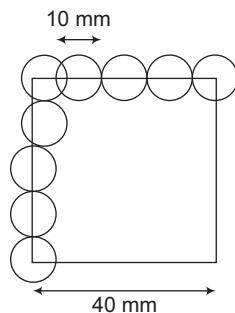
$$= 5 \times 10^3 \text{ g/m}^3 = 5 \text{ kg/m}^3$$

- (ii) Since, observed density is greater than expected, theoretical density, there must be some excess metal occupying interstitial spaces. This type of defect is known as **metal excess defect**.

44. (i) Side of square = 40 mm

Diameter of marble = 10 mm

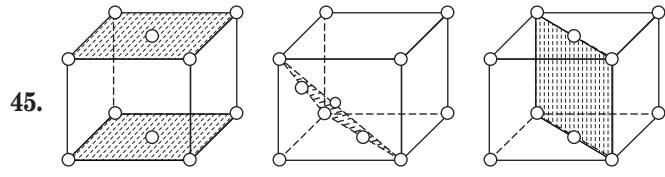
Number of marble spheres along an edge of square with their centres within the square = 5 (shown in diagram)



Maximum number of marbles per unit area = $5 \times 5 = 25$

- (ii) If x mm is the side of square and d is diameter of marble then maximum number of marbles on square area with centres within square area can be known by the following general formula :

$$N = \left(\frac{x}{d} + 1 \right)^2$$



46. Density $\propto \frac{N}{a^3}$

$$\Rightarrow \frac{d_1}{d_2} = \frac{N_1}{N_2} \left(\frac{a_2}{a_1} \right)^3 = \frac{4}{2} \left(\frac{3}{3.5} \right)^3 = 1.26$$

47. In bcc unit cell, $4r = \sqrt{3}a$

$$\Rightarrow r (\text{Cr}) = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 287 \text{ pm} = 124.3 \text{ pm}$$

$$\text{Density of solid} = \frac{NM}{N_A \cdot a^3}$$

N = Number of atoms per unit cell, M = Molar mass

a^3 = Volume of cubic unit cell, N_A = Avogadro's number

$$= \frac{2 \times 52 \text{ g}}{6.023 \times 10^{23}} \times \left(\frac{1}{2.87 \times 10^{-8} \text{ cm}} \right)^3 = 7.3 \text{ g/cm}^3$$

48. The given arrangement : ABABAB..... represents hexagonal close-packed unit cell in which there are six atoms per unit cell. Also, volume of unit cell = $24\sqrt{2}r^3$.

$$\Rightarrow \text{Packing fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}} \\ = 6 \times \frac{4}{3} \pi r^3 \times \frac{1}{24\sqrt{2}r^3} = 0.74$$

\Rightarrow Percent empty space = $100(1 - 0.74) = 26\%$

49. In bcc arrangement of atoms : $4r = \sqrt{3}a$, atoms on body diagonal remain in contact

$$\Rightarrow r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.86 \text{ \AA}$$

9

Solutions and Colligative Properties

Topic 1 Solution and Vapour Pressure of Liquid Solutions

Objective Questions I (Only one correct option)

1. Henry's constant (in kbar) for four gases α , β , γ and δ in water at 298 K is given below :

	α	β	γ	δ
K_H	50	2	2×10^{-5}	0.5

(density of water = 10^3 kg m $^{-3}$ at 298 K) This table implies that

(2020 Main, 3 Sep I)

- (a) α has the highest solubility in water at a given pressure
 - (b) solubility of γ at 308 K is lower than at 298 K
 - (c) The pressure of a 55.5 molal solution of γ is 1 bar
 - (d) The pressure of a 55.5 molal solution of δ is 250 bar
2. The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg $^{-1}$) of the aqueous solution is
- (2019 Main, 12 April I)
- (a) 13.88×10^{-2}
 - (b) 13.88×10^{-1}
 - (c) 13.88
 - (d) 13.88×10^{-3}

3. What would be the molality of 20% (mass/mass) aqueous solution of KI? (Molar mass of KI = 166 g mol $^{-1}$)
- (2019 Main, 9 April I)
- (a) 1.48
 - (b) 1.51
 - (c) 1.35
 - (d) 1.08

4. Liquid M and liquid N form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is
- (2019 Main, 9 April I)

x_M = mole fraction of M in solution;

x_N = mole fraction of N in solution;

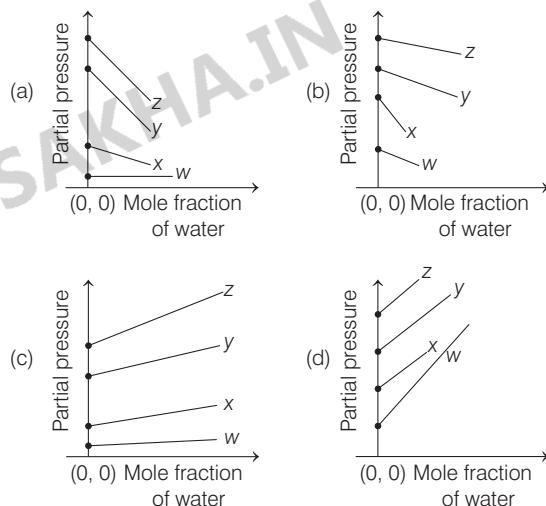
y_M = mole fraction of M in vapour phase;

y_N = mole fraction of N in vapour phase

- (a) $\frac{x_M}{x_N} > \frac{y_M}{y_N}$
- (b) $\frac{x_M}{x_N} = \frac{y_M}{y_N}$
- (c) $\frac{x_M}{x_N} < \frac{y_M}{y_N}$
- (d) $(x_M - y_M) < (x_N - y_N)$

5. For the solution of the gases w , x , y and z in water at 298 K, the Henry's law constants (K_H) are 0.5, 2, 35 and 40 K bar, respectively. The correct plot for the given data is

(2019 Main, 8 April II)



6. The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are

(2019 Main, 8 April I)

- (a) 450 mmHg, 0.4, 0.6
- (b) 500 mmHg, 0.5, 0.5
- (c) 450 mmHg, 0.5, 0.5
- (d) 500 mmHg, 0.4, 0.6

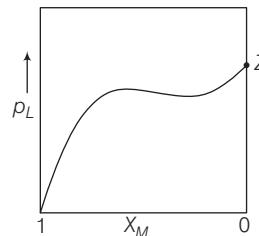
7. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of A at this temperature is

(2019 Main, 10 Jan I)

Objective Questions II

(One or more than one correct option)

15. For a solution formed by mixing liquids L and M , the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M , respectively, in the solution. The correct statement(s) applicable to this system is (are) (2017 Adv.)



- (a) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

(b) Attractive intermolecular interactions between L - L in pure liquid L and M - M in pure liquid M are stronger than those between L - M when mixed in solution

(c) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$

(d) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$

16. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are) (2016 Adv.)

(a) carbon tetrachloride + methanol

(b) carbon disulphide + acetone

(c) benzene + toluene

Numerical Answer Type Questions

- Numerical Answer Type questions**

17. Liquids A and B form ideal solution for all compositions of A and B at 25°C . Two such solutions with 0.25 and 0.50 mole fractions of A have the total vapour pressure of 0.3 and 0.4 bar, respectively. What is the vapour pressure of pure liquid B in bar? (2020 Adv.)

18. The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is 1.2 g cm^{-3} , then molarity of urea solution is (Given data : Molar masses of urea and water are 60 g mol^{-1} and 18 g mol^{-1} , respectively) (2019 Adv.)

19. Liquids A and B form ideal solution over the entire range of composition. At temperature T , equimolar binary solution of liquids A and B has vapour pressure 45 torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B , respectively, has vapour pressure of 22.5 torr. The value of x_A / x_B in the new solution is _____.
(Given that the vapour pressure of pure liquid A is 20 Torr at temperature T) (2018 Adv.)

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True/False

- 20.** Following statement is true only under some specific conditions. Write the condition for it.
“Two volatile and miscible liquids can be separated by fractional distillation into pure components.” (1994)

Subjective Questions

- 21.** The vapour pressure of two miscible liquids *A* and *B* are 300 and 500 mm of Hg respectively. In a flask 10 moles of *A* is mixed with 12 moles of *B*. However, as soon as *B* is added, *A* starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 min, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. **(2001, 4M)**

22. The molar volume of liquid benzene (density = 0.877 g/mL) increases by a factor of 2750 as it vaporises at 20° C and that of liquid toluene (density = 0.867 g mL⁻¹) increases by a factor of 7720 at 20° C. A solution of benzene and toluene at 20° C has a vapour pressure of 45.0 torr. Find the mole fraction of benzene in the vapour above the solution. **(1996, 3M)**

23. What weight of the non-volatile solute urea ($\text{NH}_2-\text{CO}-\text{NH}_2$) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? **(1993, 3M)**

24. The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100° C is 70%. If the vapour-pressure of water at 100° C is 760mm, calculate the vapour pressure of the solution. **(1991, 4M)**

25. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of

27. The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by the mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. **(1986, 4M)**

28. An organic compound ($\text{C}_x\text{H}_{2y}\text{O}_y$) was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O . The hot gases when cooled to 0° C and 1 atm pressure, measured 2.24 L. The water collected during cooling weight 0.9 g. The vapour pressure of pure water at 20° C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound. **(1983, 5M)**

29. Two liquids *A* and *B* form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of *A* and 3 moles of *B* is 550 mm of Hg. At the same temperature, if one more mole of *B* is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of *A* and *B* in their pure states. **(1982, 4M)**

30. The vapour pressure of pure benzene is 639.70 mm of Hg and the vapour pressure of solution of a solute in benzene at the same temperature is 631.9 mm of Hg. Calculate the molality of the solution. **(1981, 3M)**

31. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/mL? To what volume should 100 mL of this solution be diluted in order to prepare a 1.5 N solution? **(1978, 2M)**

Topic 2 Colligative Properties

Objective Questions I (Only one correct option)

the solution is 600 mm Hg. What is the molecular weight of the solid substance? (1990, 3M)

- 26.** The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solute. **(1989, 3M)**

27. The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by the mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. **(1986, 4M)**

28. An organic compound ($C_xH_{2y}O_z$) was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O . The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 L. The water collected during cooling weight 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound. **(1983, 5M)**

29. Two liquids *A* and *B* form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of *A* and 3 moles of *B* is 550 mm of Hg. At the same temperature, if one more mole of *B* is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of *A* and *B* in their pure states. **(1982, 4M)**

30. The vapour pressure of pure benzene is 639.70 mm of Hg and the vapour pressure of solution of a solute in benzene at the same temperature is 631.9 mm of Hg. Calculate the molality of the solution. **(1981, 3M)**

31. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/mL? To what volume should 100 mL of this solution be diluted in order to prepare a 1.5 N solution? **(1978, 2M)**

constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points, $\frac{\Delta T_b(A)}{\Delta T_b(B)}$, is

- (a) 5 : 1 (b) 10 : 1 (c) 1 : 5 (d) 1 : 0.2

3. At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be
 (Molar mass of urea = 60 g mol⁻¹) (2019 Main, 10 April I)

(a) 0.027 mmHg (b) 0.031 mmHg
 (c) 0.017 mmHg (d) 0.028 mmHg

4. Molal depression constant for a solvent is $4.0 \text{ K kg mol}^{-1}$. The depression in the freezing point of the solvent for 0.03 mol kg^{-1} solution of K_2SO_4 is
 (Assume complete dissociation of the electrolyte)

(2019 Main, 9 April II)

- (a) 0.18 K (b) 0.36 K (c) 0.12 K (d) 0.24 K

5. The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M BaCl_2 in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L^{-1}) in solution is
 (2019 Main, 9 April I)

- (a) 4×10^{-2} (b) 16×10^{-4}
 (c) 4×10^{-4} (d) 6×10^{-2}

6. Molecules of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) dimerise in benzene. ‘ w ’ g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K . If the percentage association of the acid to form dimer in the solution is 80 , then w is

(Given that $K_f = 5 \text{ K kg mol}^{-1}$, molar mass of benzoic acid = 122 g mol^{-1})
 (2019 Main, 12 Jan II)

- (a) 1.8 g (b) 1.0 g (c) 2.4 g (d) 1.5 g

7. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y . If molecular weight of X is A , then molecular weight of Y is
 (2019 Main, 12 Jan I)

- (a) $4A$ (b) $2A$ (c) $3A$ (d) A

8. K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is
 (2019 Main, 11 Jan II)

- (a) 1.6 (b) 1.8 (c) 2.2 (d) 2.0

9. The freezing point of a diluted milk sample is found to be -0.2° C , while it should have been -0.5° C for pure milk. How much water has been added to pure milk to make the diluted sample?
 (2019 Main, 11 Jan I)

- (a) 2 cups of water to 3 cups of pure milk
 (b) 1 cup of water to 3 cups of pure milk
 (c) 3 cups of water to 2 cups of pure milk
 (d) 1 cup of water to 2 cups of pure milk

10. Elevation in the boiling point for 1 molal solution of glucose is 2 K . The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K . The relation between K_b and K_f is
 (2019 Main, 10 Jan II)

- (a) $K_b = 1.5 K_f$ (b) $K_b = 0.5 K_f$
 (c) $K_b = K_f$ (d) $K_b = 2K_f$

11. A solution contains 62 g of ethylene glycol in 250 g of water is cooled upto -10° C . If K_f for water is $1.86 \text{ K kg mol}^{-1}$, then amount of water (in g) separated as ice is
 (2019 Main, 9 Jan II)

- (a) 32 (b) 48 (c) 64 (d) 16

12. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point? (2018 Main)

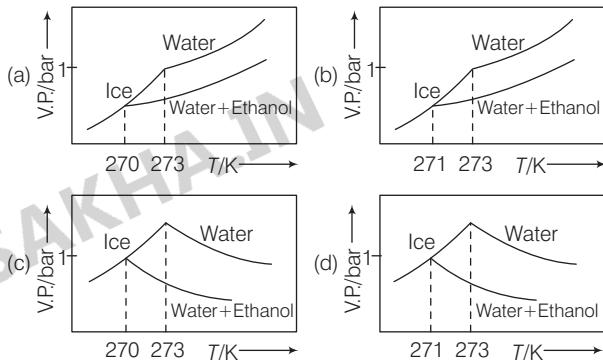
- (a) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ (b) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (c) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (d) $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

13. The freezing point of benzene decreases by 0.45° C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be
 (K_f for benzene = $5.12 \text{ K kg mol}^{-1}$)
 (2017 Main)

- (a) 64.6% (b) 80.4% (c) 74.6% (d) 94.6%

14. Pure water freezes at 273 K and 1 bar . The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1} . The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is 46 g mol^{-1}]
 (2017 Adv.)

Among the following, the option representing change in the freezing point is



15. Consider separate solution of $0.500 \text{ M C}_2\text{H}_5\text{OH}(aq)$, $0.100 \text{ M Mg}_3(\text{PO}_4)_2(aq)$, $0.250 \text{ M KBr}(aq)$ and $0.125 \text{ M Na}_3\text{PO}_4(aq)$ at 25° C . Which statement is true about these solution, assuming all salts to be strong electrolytes?

- (a) They all have the same osmotic pressure (2014 Main)
 (b) $0.100 \text{ M Mg}_3(\text{PO}_4)_2(aq)$ has the highest osmotic pressure
 (c) $0.125 \text{ M Na}_3\text{PO}_4(aq)$ has the highest osmotic pressure
 (d) $0.500 \text{ M C}_2\text{H}_5\text{OH}(aq)$ has the highest osmotic pressure

16. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2° C . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76 \text{ K kg mol}^{-1}$).
 (2012)

- (a) 724 (b) 740 (c) 736 (d) 718

17. The freezing point ($\text{in }^\circ \text{C}$) of solution containing 0.1 g of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (mol. wt. 329) in 100 g of water ($K_f = 1.86 \text{ K kg mol}^{-1}$) is
 (2011)

- (a) -2.3×10^{-2} (b) -5.7×10^{-2}
 (c) -5.7×10^{-3} (d) -1.2×10^{-2}

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18. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72 \text{ K kg mol}^{-1}$), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is (2007, 3M)
- (a) 0.5 (b) 1 (c) 2 (d) 3
19. The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is. [Some useful data, $K_b = 0.52 \text{ K kg mol}^{-1}$, molecular weight of $CuCl_2 = 134.4 \text{ g}$.] (2005, 1M)
- (a) 0.05 (b) 0.1 (c) 0.16 (d) 0.21
20. 0.004 M Na_2SO_4 is isotonic with 0.01 M glucose. Degree of dissociation of Na_2SO_4 is (2004, S, 1M)
- (a) 75% (b) 50% (c) 25% (d) 85%
21. During depression of freezing point in a solution the following are in equilibrium (2003)
- (a) liquid solvent, solid solvent
 (b) liquid solvent, solid solute
 (c) liquid solute, solid solute
 (d) liquid solute, solid solvent
22. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to (1996, 1M)
- (a) ionisation of benzoic acid
 (b) dimerisation of benzoic acid
 (c) trimerisation of benzoic acid
 (d) solvation of benzoic acid
23. The freezing point of equimolar aqueous solutions will be highest for (1990, 1M)
- (a) $C_6H_5NH_3Cl$ (aniline hydrochloride)
 (b) $Ca(NO_3)_2$
 (c) $La(NO_3)_3$
 (d) $C_6H_{12}O_6$ (glucose)
24. Which of the following 0.1 M aqueous solution will have the lowest freezing point? (1989, 1M)
- (a) Potassium sulphate (b) Sodium chloride
 (c) Urea (d) Glucose
25. When mercuric iodide is added to the aqueous solution of potassium iodide (1987, 2M)
- (a) freezing point is raised
 (b) freezing point is lowered
 (c) freezing point does not change
 (d) boiling point does not change

Objective Questions II

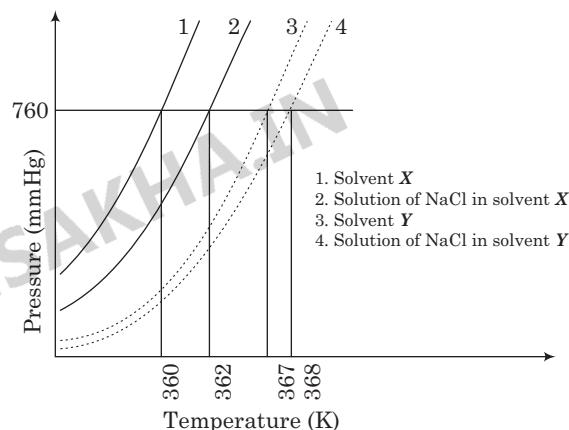
(One or more than one correct option)

26. In the depression of freezing point experiment, it is found that the (1999, 3M)
- (a) vapour pressure of the solution is less than that of pure solvent
 (b) vapour pressure of the solution is more than that of pure solvent
 (c) only solute molecules solidify at the freezing point
 (d) only solvent molecules solidify at the freezing point

Numerical Answer Type Questions

27. The osmotic pressure of a solution of $NaCl$ is 0.10 atm and that of a glucose solution is 0.20 atm. The osmotic pressure of a solution formed by mixing 1 L of the sodium chloride solution with 2 L of the glucose solution is $x \times 10^{-3}$ atm. x is (nearest integer). (2020 Main, 4 Sep II)
28. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapour pressure decreases from 650 mmHg to 640 mmHg. The depression of freezing point of benzene (in K) upon addition of the solute is (Given data : Molar mass and the molal freezing point depression constant of benzene are 78 g mol^{-1} and $5.12 \text{ K kg mol}^{-1}$, respectively). (2019 Adv.)

29. The plot given below shows $p-T$ curves (where p is the pressure and T is the temperature) for two solvents X and Y and isomolal solution of $NaCl$ in these solvents. $NaCl$ completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y . Solute S is known to undergo dimerisation in these solvents. If the degree of dimerisation is 0.7 in solvent Y , the degree of dimerisation in solvent X is _____. (2018 Adv.)

Subjective Questions

30. 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of $K_f = 14$. If the depression in freezing point is 7 K, then find the percentage of phenol that dimerises. (2006, 2M)
31. 1.22 g C_6H_5COOH is added into two solvents and data of ΔT_b and K_b are given as :
- (i) In 100 g CH_3COCH_3 , $\Delta T_b = 0.17$, $K_b = 1.7 \text{ K kg/mol}$
 - (ii) In 100 g benzene, $\Delta T_b = 0.13$ and $K_b = 2.6 \text{ K kg/mol}$
- Find out the molecular weight of C_6H_5COOH in both the cases and interpret the result. (2004, 2M)

Answers

Topic 1

1. (d) 2. (c) 3. (b) 4. (a)
 5. (a) 6. (d) 7. (b) 8. (b)
 9. (b) 10. (b) 11. (a) 12. (b)
 13. (b) 14. (c) 15. (b, d) 16. (a, b)
 17. (0.2) 18. (2.98 M) 19. (19) 20. (T)
 22. (0.72) 23. (18.5) 24. (746.32 mm)
 25. (65.25) 26. (0.75) 27. (0.657) 30. (0.158)
 31. (180.40 mL)

Topic 2

1. (c) 2. (c) 3. (c) 4. (b)
 5. (d) 6. (c) 7. (c) 8. (b)
 9. (c) 10. (d) 11. (c) 12. (d)
 13. (d) 14. (b) 15. (a) 16. (a)
 17. (a) 18. (a) 19. (c) 20. (a)
 21. (a) 22. (b) 23. (d) 24. (a)
 25. (a) 26. (a,d) 27. (167.00) 28. (1.02)
 29. (0.05) 30. (75%) 32. (0.23°C) 35. (23.44 mm)
 36. (156 g/mol) 37. (d) 38. (a) 39. (b)
 40. (K_f) 42. (2)

Hints & Solutions

Topic 1 Solution and Vapour Pressure of Liquid Solutions

1. Henry's equation for solubility (S) of a gas (β) in a liquid is expressed in terms of mole-fraction of the gas (χ_B) at a given temperature,

$$p = K_H \times \chi_B = K_H \times S$$

So, solubility of gas, $S \propto \frac{1}{K_H}$ at T (K) and given pressure.

Order of solubility of the gases (high the value of K_H , lower is the solubility):

$$\gamma > \delta > \beta > \alpha$$

So, option (a) is not correct.

Again, $K_H \propto$ temperature, i.e. solubility of the gas will decrease with increase in temperature also.

But this conclusion cannot be drawn from table.

So, option (b) is not correct.

We know, mole-fraction of a solute (B) in a binary aqueous solution,

$$\chi_B = \frac{18m}{1000 + 18m} \quad [\because m = \text{molality}]$$

For γ at $m = 55.5$ molal

$$p = K_H^\gamma \times m = (2 \times 10^{-5}) \times \left(\frac{18 \times 55.5}{1000 + 18 \times 55.5} \right) \\ = 1.81 \times 10^{-5} \text{ K bar} = 1.8 \times 10^{-2} \text{ bar}$$

So, option (c) is not correct.

For δ at $m = 55.5$ molal

$$p = K_H^\delta = (0.5) \times \left(\frac{18 \times 55.5}{1000 + 18 \times 55.5} \right) \\ = 0.2498 \text{ k bar} \approx 250 \text{ bar}$$

So, option (d) is correct.

2. **Key Idea** Molality (m) = $\frac{\text{Mass of solute } (w_2) \times 1000}{\text{Molar mass of solute } (M_2) \times \text{mass of solvent } (w_1)}$

$$m = \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\text{and also, } m = n_2 \times \frac{1000}{n_1 \times M_1}$$

$X_{\text{solvent}} = 0.8$ (Given) It means that $n_{\text{solvent}} (n_1) = 0.8$ and $n_{\text{solute}} (n_2) = 0.2$

Using formula $m = n_2 \times \frac{1000}{n_1 \times M_1} = 0.2 \times \frac{1000}{0.8 \times 18} = 13.88 \text{ mol kg}^{-1}$

3. **Key Idea** Molality is defined as number of moles of solute per kg of solvent.

$$m = \frac{w_2}{Mw_2} \times \frac{1000}{w_1}$$

w_2 = mass of solute, Mw_2 = molecular mass of solute

w_1 = mass of solvent.

The molality of 20% (mass/mass) aqueous solution of KI can be calculated by following formula.

$$m = \frac{w_2 \times 1000}{Mw_2 \times w_1}$$

20% aqueous solution of KI means that 20 gm of KI is present in 80 gm solvent.

$$m = \frac{20}{166} \times \frac{1000}{80} = 1.506 \approx 1.51 \text{ mol/kg}$$

4. **Key Idea** For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. This is known as Raoult's law.

Liquid M and N form an ideal solution. Vapour pressures of pure liquids M and N are 450 and 700 mm Hg respectively.

$$\therefore p^\circ_N > p^\circ_M$$

So, by using Raoult's law

$$y_N > x_N \quad \dots(i)$$

and

$$x_M > y_M \quad \dots(ii)$$

Multiplying (i) and (ii) we get

$$y_N x_M > y_M x_N$$

$$\therefore \frac{x_M}{x_N} > \frac{y_M}{y_N}$$

Thus, correct relation is (a).

5. According to Henry's law (at constant temperature)

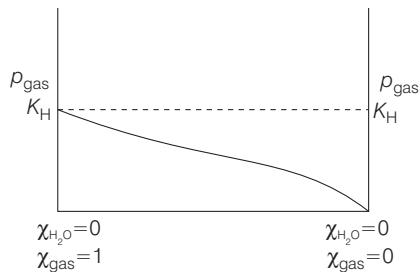
$$p_{\text{gas}} = K_H \times \chi_{\text{gas(solute)}} = K_H \times [1 - \chi_{\text{H}_2\text{O(solvent)}}]$$

$$p_{\text{gas}} = K_H - K_H \chi_{\text{H}_2\text{O}}$$

p_{gas} = partial pressure of the gas above its solution with a liquid (solvent) say water.

χ_{gas} = mole fraction of the gas (solute) in the solution.

$\chi_{\text{H}_2\text{O}}$ = mole fraction of water (solvent).



[i.e. $p_{\text{gas}} = K_H$] Higher the value of K_H , higher will be the partial pressure of the gas (p_{gas}), at a given temperature. The plot of p_{gas} vs $\chi_{\text{H}_2\text{O}}$ gives a (-ve) slope.

$$p_{\text{gas}} = K_H - K_H \times \chi_{\text{H}_2\text{O}}$$

Comparing the above equation with the equation of straight line $y = mx + c$

$$\text{Slope} = -K_H, \text{ intercept} = K_H$$

So, (i) Higher the value of K_H , more (-ve) will be the slope and it is for z ($K_H = 40$ Kbar)

(ii) Higher the value of K_H , higher with the value of intercept, i.e. partial pressure and it is also for z.

6. (d) According to Dalton's law of partial pressure

$$P_{\text{total}} = P_A + P_B = P_A^\circ \chi_A + P_B^\circ \chi_B \quad \dots(i)$$

Given, $P_A^\circ = 400$ mm Hg, $P_B^\circ = 600$ mm Hg

$$\chi_B = 0.5, \chi_A + \chi_B = 1 \therefore \chi_A = 0.5$$

On substituting the given values in Eq. (i). We get,

$$P_{\text{total}} = 400 \times 0.5 + 600 \times 0.5 = 500 \text{ mm Hg}$$

Mole fraction of A in vapour phase,

$$Y_A = \frac{P_A}{P_{\text{total}}} = \frac{P_A^\circ \chi_A}{P_{\text{total}}} = \frac{0.5 \times 400}{500} = 0.4$$

Mole of B in vapour phase,

$$Y_A + Y_B = 1$$

$$Y_B = 1 - 0.4 = 0.6$$

7. For ideal solution,

$$p = x'_A P_A^\circ + x'_B P_B^\circ$$

$$\therefore x'_A = 0.4, x'_B = 0.6$$

$$P_A^\circ = 7 \times 10^3 \text{ Pa}, P_B^\circ = 12 \times 10^3 \text{ Pa}$$

On substituting the given values in Eq. (i),
we get

$$\begin{aligned} p &= 0.4 \times 7 \times 10^3 + 0.6 \times 12 \times 10^3 \\ &= 10 \times 10^3 \text{ Pa} = 1 \times 10^4 \text{ Pa} \end{aligned}$$

In vapour phase,

$$x_A = \frac{P_A}{P} = \frac{x'_A P_A^\circ}{P} = \frac{0.4 \times 7 \times 10^3}{1 \times 10^4} = 0.28$$

$$\therefore x_B = 1 - 0.28 = 0.72 \quad [\because x_A + x_B = 1]$$

8. At constant temperature, solubility of a gas (S) varies inversely with Henry's law constant (K_H)

$$K_H = \frac{\text{Pressure}}{\text{Solubility of a gas in a liquid}} = \frac{P}{S}$$

Thus, higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

9. Key Idea Vapour pressure of water (p°) = 760 torr

$$\begin{aligned} \text{Number of moles of glucose} &= \frac{\text{Mass (g)}}{\text{Molecular mass (g mol}^{-1})} \\ &= \frac{18 \text{ g}}{180 \text{ g mol}^{-1}} = 0.1 \text{ mol} \end{aligned}$$

Molar mass of water = 18 g/mol

Mass of water (given) = 178.2 g

Number of moles of water

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{178.2 \text{ g}}{18 \text{ g/mol}} = 9.9 \text{ mol}$$

Total number of moles = (0.1 + 9.9) moles = 10 moles

Now, mole fraction of glucose in solution = Change in pressure with respect to initial pressure

$$\text{i.e. } \frac{\Delta p}{p^\circ} = \frac{0.1}{10} \quad \text{or} \quad \Delta p = 0.01 p^\circ = 0.01 \times 760 = 7.6 \text{ torr}$$

∴ Vapour pressure of solution = (760 - 7.6) torr = 752.4 torr

10. Given, $p^\circ = 185$ Torr at 20°C

$$P_s = 183 \text{ Torr at } 20^\circ\text{C}$$

Mass of non-volatile substance, $m = 1.2 \text{ g}$

Mass of acetone taken = 100 g

$$M = ?$$

$$\text{As, we have } \frac{P^\circ - P_s}{P_s} = \frac{n}{N}$$

Putting the values, we get,

$$\frac{185 - 183}{183} = \frac{\frac{1.2}{M}}{\frac{100}{58}} \Rightarrow \frac{2}{183} = \frac{1.2 \times 58}{100 \times M}$$

$$\therefore M = \frac{183 \times 1.2 \times 58}{2 \times 100}$$

$$M = 63.684 = 64 \text{ g/mol}$$

11. Give, $K_H = 1 \times 10^5 \text{ atm}$, $\chi_{\text{N}_2} = 0.8$

$$n_{\text{H}_2\text{O}} = 10 \text{ moles}, P_{\text{total}} = 5 \text{ atm}$$

$$P_{\text{N}_2} = P_{\text{total}} \times \chi_{\text{N}_2} = 5 \times 0.8 = 4 \text{ atm}$$

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According to Henry's law,

$$P_{N_2} = K_H \times \chi_{N_2}$$

$$4 = 10^5 \times \chi_{N_2}$$

$$\chi_{N_2} = 4 \times 10^{-5}$$

$$\frac{n_{N_2}}{n_{N_2} + n_{H_2O}} = 4 \times 10^{-5}$$

$$\frac{n_{N_2}}{n_{N_2} + 10} = 4 \times 10^{-5}$$

$$n_{N_2} = 4 \times 10^{-4}$$

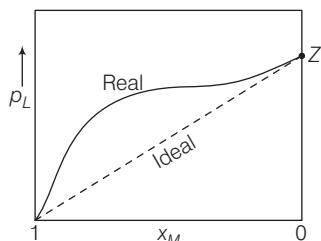
12. Molality = moles of solute present in 1.0 kg of solvent.

13. The relative lowering of vapour pressure :

$$\frac{-\Delta p}{p^\circ} = \chi_2 \quad (\text{mole fraction of solute})$$

14. In case of positive deviation from Raoult's law, the observed vapour pressure is greater than the ideal vapour pressure and boiling point of azeotrope becomes lower than either of pure liquid.

15. The graph shown indicates that there is positive deviation because the observed vapour pressure of L is greater than the ideal pressure



Since, deviation is positive, the intermolecular force between L and M is smaller than the same in pure L and pure M .

Also as $x_L \rightarrow 1, x_M \rightarrow 0$, the real curve approaching ideal curve where Raoult's law will be obeyed.

16. When intermolecular attraction between two components A and B in the mixture is same as between A and A or B and B , hence it is a case of ideal solution.

When intermolecular attraction between A and B in a mixture is smaller than that between A and A or B and B , then mixture is more vaporised, bp is lowered. It is a case of positive deviation from Raoult's law.

When intermolecular attraction between A and B is higher than that between A and A or B and B , then mixture is less vaporised, bp is increased. It is a case of negative deviation.

(a) Methanol molecules (CH_3OH) are hydrogen bonded. In a mixture of CCl_4 and CH_3OH , extent of H-bonding is decreased. Mixture is more vaporised thus, positive deviation from Raoult's law.

(b) Acetone molecules have higher intermolecular attraction due to dipole-dipole interaction. With CS_2 , this interaction is decreased thus, positive deviation.

(c) Mixture of benzene and toluene forms ideal solution.

(d) Phenol and aniline have higher interaction due to intermolecular H-bonding. Hence, negative deviation.

17. Using Raoult's law equation for a mixture of volatile liquids.

$$P_T = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$0.3 = 0.25 \chi p_A^\circ + 0.75 \chi p_B^\circ \quad \dots \text{(i)}$$

$$0.4 = 0.5 \chi p_A^\circ + 0.5 \chi p_B^\circ \quad \dots \text{(ii)}$$

By solving equation (i) and (ii)

$$p_A^\circ = 0.6 \text{ bar and } p_B^\circ = 0.2 \text{ bar}$$

Thus, the vapour pressure of pure liquid B in bar is 0.2.

18. Key Idea Molarity (M) = $\frac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (in mL)}}$

$$\text{Also, volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\text{Given, mole fraction of urea } (\chi_{\text{urea}}) = 0.05$$

$$\text{Mass of water} = 900 \text{ g}$$

$$\text{Density} = 1.2 \text{ g/cm}^3$$

$$\chi_{\text{urea}} = \frac{n_{\text{urea}}}{n_{\text{urea}} + 50} \quad [\because \text{Moles of water} = \frac{900}{18} = 50]$$

$$0.05 = \frac{n_{\text{urea}}}{n_{\text{urea}} + 50} \Rightarrow 19n_{\text{urea}} = 50$$

$$n_{\text{urea}} = 2.6315 \text{ moles}$$

$$w_{\text{urea}} = n_{\text{urea}} \times (M \cdot \text{wt})_{\text{urea}} = (2.6315 \times 60) \text{ g}$$

$$V = \frac{2.6315 \times 60 + 900}{1.2} \left[\because \text{Density} = \frac{\text{Mass of solution}}{\text{Volume of solution}} \right]$$

$$= 881.57 \text{ mL}$$

Now, molarity

$$= \frac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (mL)}}$$

$$= \frac{2.6315 \times 1000}{881.57} = 2.98 \text{ M}$$

19. Key Idea Use the formula

$$P_{\text{Total}} = p_A^\circ \times \chi_A + p_B^\circ \times \chi_B$$

$$\text{and for equimolar solutions } \chi_A = \chi_B = \frac{1}{2}$$

$$\text{Given, } P_{\text{Total}} = 45 \text{ torr for equimolar solution}$$

$$p_A^\circ = 20 \text{ torr}$$

$$\text{So, } 45 = p_A^\circ \times \frac{1}{2} + p_B^\circ \times \frac{1}{2} = \frac{1}{2} (p_A^\circ + p_B^\circ)$$

$$\text{or } p_A^\circ + p_B^\circ = 90 \text{ torr} \quad \dots \text{(i)}$$

$$\text{But we know } p_A^\circ = 20 \text{ torr}$$

$$\text{so, } p_B^\circ = 90 - 20 = 70 \text{ torr} \quad (\text{From Eq. (i)})$$

Now, for the new solution from the same formula

$$\text{Given, } P_{\text{Total}} = 22.5 \text{ torr}$$

$$\text{So, } 22.5 = 20\chi_A + 70(1-\chi_A) \quad (\text{As } \chi_A + \chi_B = 1)$$

$$\text{or } 22.5 = 70 - 50\chi_A$$

$$\text{So, } \chi_A = \frac{70 - 22.5}{50} = 0.95$$

$$\text{Thus } \chi_B = 1 - 0.95 = 0.05 \quad (\text{as } \chi_A + \chi_B = 1)$$

Hence, the ratio

$$\frac{\chi_A}{\chi_B} = \frac{0.95}{0.05} = 19$$

20. It will be true only if boiling points of two liquids are significantly different.

21. Let after 100 min, x moles of A are remaining unpolymerised moles of $B = 12$

Moles of non-volatile solute = 0.525

$$\Rightarrow \text{Mole fraction of } A = \frac{x}{x + 12 + 0.525}$$

$$\text{Mole fraction of } B = \frac{12}{x + 12 + 0.525}$$

$$\Rightarrow 400 = \left(\frac{x}{x + 12.525} \right) \times 300 + \left(\frac{12}{x + 12.525} \right) \times 500$$

$$\Rightarrow x = 9.9$$

\Rightarrow Moles of A polymerised in 100 min = $10 - 9.9 = 0.10$

$$\Rightarrow k = \frac{1}{t} \ln \frac{10}{9.9} = \frac{1}{100} \ln \frac{10}{9.9} \text{ min}^{-1}$$

$$= 1.005 \times 10^{-4} \text{ min}^{-1}$$

22. Volume of 1.0 mole liquid benzene = $\frac{78}{0.877}$ mL = 88.94 mL

\Rightarrow Molar volume of benzene vapour at 20°C

$$= \frac{88.94 \times 2750}{1000} \text{ L} = 244.58 \text{ L}$$

$$\Rightarrow \text{VP of pure benzene at } 20^\circ\text{C} = \frac{0.082 \times 293}{244.58} \times 760 \text{ mm}$$

$$= 74.65 \text{ mm}$$

Similarly; molar volume of toluene vapour

$$= \frac{92}{0.867} \times \frac{7720}{1000} \text{ L} = 819.2 \text{ L}$$

$$\Rightarrow \text{VP of pure toluene} = \frac{0.082 \times 293}{819.2} \times 760 \text{ mm} = 22.3 \text{ mm}$$

Now, let mole fraction of benzene in the liquid phase = χ

$$\Rightarrow 4.65\chi + 22.3(1-\chi) = 45$$

$$\Rightarrow \chi = 0.43$$

\Rightarrow Mole fraction of benzene in vapour phase

$$= \frac{\text{Partial vapour pressure of benzene}}{\text{Total vapour pressure}}$$

$$= \frac{74.65 \times 0.43}{45} = 0.72$$

23. Vapour pressure of solution = $0.75 \times \text{VP of water}$

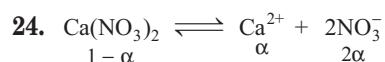
$$\Rightarrow 75 = 100\chi_1 : \chi_1 = \text{mole fraction of solute}$$

$$\Rightarrow \chi_1 = \frac{3}{4} \text{ and } \chi_2 = 1 - \chi_1 = \frac{1}{4}$$

$$\Rightarrow \frac{\chi_2}{\chi_1} = \frac{n_2}{n_1} = \frac{1}{3} \Rightarrow n_2 = \frac{n_1}{3} = \frac{100}{18 \times 3} = 1.85$$

\Rightarrow Weight of urea = $1.85 \times 60 = 111 \text{ g}$

$$\text{Molality} = \frac{n_2}{n_1} \times \frac{1000}{M_1} = \frac{1}{3} \times \frac{1000}{18} = 18.5$$



$$i = 1 + 2\alpha \text{ where, } \alpha = 0.7 \Rightarrow i = 1 + 2 \times 0.7 = 2.4$$

$$\Rightarrow \text{Mole fraction of solvent} = \frac{n_1}{n_1 + n_2}$$

$$= \frac{\left(\frac{100}{18} \right)}{\left(\frac{100}{18} \right) + 2.4 \times \frac{7}{164}} = 0.982$$

$$\Rightarrow p = p_0\chi_1 = 760 \times 0.982$$

$$(\text{VP of H}_2\text{O at } 100^\circ\text{C} = 760 \text{ mm of Hg})$$

$$= 746.32 \text{ mm}$$

25. According to Raoult's law :

$$p = p_0\chi_1$$

$$\Rightarrow 600 = 640 \left(\frac{n_1}{n_1 + n_2} \right)$$

$$\Rightarrow \frac{n_2}{n_1} = \frac{64}{60} - 1 = \frac{1}{15}$$

$$\Rightarrow n_2 = \frac{39}{78} \times \frac{1}{15} = 0.033$$

$$\Rightarrow \frac{2.175}{M} = 0.033$$

$$\Rightarrow M = 65.25$$

26. At 373 K (bp) of H_2O , Vapour pressure = 760 mm
VP of solution at 373 K = 750 mm

$$\Rightarrow p = p_0\chi_1 \text{ or } 750 = 760 \chi_1$$

$$\Rightarrow \chi_1 = \frac{75}{76} = \text{mole fraction of H}_2\text{O}$$

$$\Rightarrow \chi_2 = 1 - \frac{75}{76} = \frac{1}{76} = \text{mole fraction of solute}$$

$$\text{Now } \frac{n_2}{n_1 + n_2} = \frac{1}{76}$$

$$\Rightarrow \frac{n_1}{n_2} = 75$$

$$\Rightarrow \text{Molality} = \frac{n_2}{n_1 M_1} \times 1000 = \frac{1000}{75 \times 18} = 0.74 \text{ molal}$$

$$27. \text{Moles of ethanol} = \frac{60}{46} = 1.3$$

$$\text{Moles of methanol} = \frac{40}{32} = 1.25$$

$$\Rightarrow \text{Mole fraction of ethanol} = \frac{1.3}{1.3 + 1.25} = 0.51$$

$$\Rightarrow \text{Vapour pressure of solution} = p_{\text{ethanol}} + p_{\text{methanol}}$$

$$= 0.51 \times 44.5 + 0.49 \times 88.7$$

$$= 66.16 \text{ mm}$$

Mole fraction of methanol in vapour phase

$$= \frac{p_{\text{methanol}}}{\text{Total vapour pressure}} = \frac{43.463}{66.16} = 0.657$$

28. From lowering of vapour pressure information :

$$\frac{0.104}{17.5} = \chi_2 = \frac{n_2}{n_1 + n_2}$$

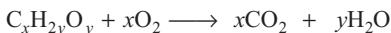
$$\Rightarrow \frac{n_1}{n_2} + 1 = 168.27$$

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$$\Rightarrow \frac{n_1}{n_2} = 167.27 \Rightarrow \frac{1000}{18} \times \frac{M}{50} = 167.27$$

$$\Rightarrow M = 150 \text{ g/mol}$$

Also, the combustion reaction is :



$\therefore 18y$ g of H_2O is produced from 1.0 mole of compound.

$$\therefore 0.9 \text{ g of } \text{H}_2\text{O} \text{ will be produced from } \frac{0.9}{18y} = \frac{1}{20y} \text{ mol}$$

$$\Rightarrow \text{At the end, moles of O}_2 \text{ left} = \frac{x}{20y}$$

$$\text{moles of CO}_2 \text{ formed} = \frac{x}{20y}$$

$$\Rightarrow \text{Total moles of gases at STP} = \frac{2x}{20y} = \frac{2.24}{22.4}$$

$$\Rightarrow x = y$$

$$\Rightarrow \text{Molar mass; } 150 = 12x + 2x + 16x = 30x$$

$$\Rightarrow x = \frac{150}{30} = 5$$

$$\Rightarrow \text{Formula} = \text{C}_5\text{H}_{10}\text{O}_5$$

29. When 1.0 mole of A is mixed with 3 moles of B.

$$550 = 0.25 p_A^\circ + 0.75 p_B^\circ \quad \dots(i)$$

- When 1.0 mole of A is mixed with 4 moles of B.

$$560 = 0.20 p_A^\circ + 0.80 p_B^\circ \quad \dots(ii)$$

Now, solving (i) and (ii) $p_A^\circ = 400 \text{ mm}$

$$p_B^\circ = 600 \text{ mm.}$$

30. According to Raoult's law :

$$p = p_0 \chi_1 \Rightarrow 631.9 = 639.7 \chi_1$$

$$\Rightarrow \chi_1 = 0.9878 \Rightarrow \chi_2 = 0.0122$$

$$\Rightarrow \text{Molality} = \frac{0.0122}{0.9878 \times 78} \times 1000 = 0.158$$

31. Let us consider 1.0 L of solution.

$$\text{Weight of solution} = 1000 \times 1.02 = 1020 \text{ g}$$

$$\text{Weight of H}_2\text{SO}_4 = 1020 \times \frac{13}{100} = 132.60 \text{ g}$$

$$\text{Weight of H}_2\text{O} = 1020 - 132.60 = 887.40 \text{ g}$$

$$\Rightarrow \text{Molarity} = \frac{132.60}{98} = 1.353 \text{ M}$$

$$\text{Molality} = \frac{132.60}{98} \times \frac{1000}{887.40} = 1.525 \text{ m}$$

$$\text{Normality} = 2 \times M = 2.706$$

$$\Rightarrow 2.706 \times 100 = 1.5 \text{ V} \Rightarrow V = 180.40 \text{ mL}$$

Topic 2 Colligative Properties

1. **Key Idea** Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature (T).

Thus, $\pi \propto C$, $\pi = CRT$ (for dilute solution)

$$\pi = \frac{n}{V} RT$$

For the relation, $\pi = CRT = \frac{n}{V} RT$

Given, mass of urea = 0.6 g

Molar mass of urea = 60 g mol⁻¹

Mass of glucose = 1.8 g

Molar mass of glucose = 180 g mol⁻¹

$$\pi = \frac{[n_2 (\text{urea}) + n_2 (\text{glucose})]}{V} RT$$

$$= \frac{\left(\frac{0.6}{60} + \frac{1.8}{180} \right)}{100} \times 1000 \times 0.0821 \times 300$$

$$= (0.01 + 0.01) \times 10 \times 0.0821 \times 300$$

$$\pi = 4.92 \text{ atm}$$

2. The expression of elevation of boiling point,

$$\Delta T_b = K_b \times m \times i = k_b \times \frac{w_2 \times 1000}{M_2 \times w_1} \times i$$

where, m = molality

i = van't Hoff factor = 1 (for non-electrolyte/non-associable)

w_2 = mass of solute in g = 1 g (present in both of the solutions)

M_2 = molar mass of solute in g mol⁻¹ (same solute in both of the solutions)

w_1 = mass of solvent in g = 100 g (for both of the solvents A and B)

K_b = ebullioscopic constant

So, the expression becomes,

$$\Delta T_b \propto K_b$$

$$\Rightarrow \frac{\Delta T_b(A)}{\Delta T_b(B)} = \frac{K_b(A)}{K_b(B)} = \frac{1}{5} \quad \left[\text{Given } \frac{K_b(A)}{K_b(B)} = \frac{1}{5} \right]$$

3. **Key Idea** For dilute solution, lowering of vapour pressure (Δp) = $p^0 - p$ and relative lowering of vapour pressure = $\frac{\Delta p}{p^0}$

which is a colligative property of solutions.

$$\frac{\Delta p}{p^0} = \chi_B \times i \Rightarrow \Delta p = \chi_B \times i \times p^0$$

where, p^0 = vapour pressure of pure solvent

i = van't Hoff factor

χ_B = mole fraction of solute

Given,

p^0 = vapour pressure of pure water of 25°C = 35 mm Hg

χ_B = mole fraction of solute (urea)

$$= \frac{n_B}{n_A + n_B} = \frac{\frac{0.6}{60}}{\frac{360}{18} + \frac{0.6}{60}} = \frac{0.01}{20 + 0.01} = \frac{0.01}{20.01} = 0.0005$$

i = van't Hoff factor = 1 (for urea)

Now, according to Raoult's law

$$\Delta p = \chi_B \times i \times p^0$$

On substituting the above given values, we get

$$\Delta p = 0.0005 \times 1 \times 35 = 0.0175 \text{ mm Hg}$$

- 4.** **Key Idea** Depression in freezing point (ΔT_f) is given by
 $\Delta T_f = iK_f m$
i = vant Hoff factor
 K_f = molal depression constant
 m = molality

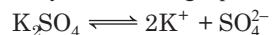
$$K_f = 4.0 \text{ K kg mol}^{-1} \quad (\text{Given})$$

$$m = 0.03 \text{ mol kg}^{-1} \quad (\text{Given})$$

$$\Delta T_f = ?$$

For K_2SO_4 , $i = 3$

It can be verified by the following equation :



Using formula

$$\Delta T_f = iK_f \times m$$

$$\Delta T_f = 3 \times 4 \times 0.03 = 0.36 \text{ K}$$

- 5.** **Key Idea** Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature, $\pi = CRT$

Concentration of $\text{BaCl}_2 = 0.01 \text{ M}$ (Given)

$$\pi_{XY} = 4\pi_{\text{BaCl}_2} \quad (\text{Given})$$

$$i \times CRT = 4 \times i \times CRT \quad \dots(\text{i})$$

For the calculation of i ,

$$XY \longrightarrow X^+ + Y^- \quad (\text{Here, } i = 2)$$

$$\text{BaCl}_2 \longrightarrow \text{Ba}^{2+} + 2\text{Cl}^- \quad (\text{Here, } i = 3)$$

Putting the values of i in (i)

$$2 \times [XY] = 4 \times 3 \times [\text{BaCl}_2]$$

$$2 \times [XY] = 12 \times 0.01$$

$$[XY] = \frac{12 \times 0.01}{2}$$

So, the concentration of $XY = 0.06 \text{ mol L}^{-1}$

$$= 6 \times 10^{-2} \text{ mol L}^{-1}$$

- 6.** Molecules of benzoic acid dimerise in benzene as:



Now, we know that depression in freezing point (ΔT_f) is given by following equation:

$$\Delta T_f = i \times K_f \times m = \frac{i \times K_f \times w_{\text{solute}} \times 1000}{Mw_{\text{solute}} \times w_{\text{solvent}}} \quad \dots(\text{i})$$

Given, w_{solute} (benzoic acid) = $w \text{ g}$

$$w_{\text{solvent}}$$
 (benzene) = 30 g

$$Mw_{\text{solute}}$$
 (benzoic acid) = 122 g mol^{-1} , $\Delta T_f = 2 \text{ K}$

$$K_f = 5 \text{ K kg mol}^{-1}$$
, $\% \alpha = 80$ or $\alpha = 0.8$



Initial	1	0
Final	$1 - \alpha$	$\alpha / 2$
	$= 1 - 0.8 = 0.2$	$0.8 / 2 = 0.4$

Total number of moles at equilibrium = $0.2 + 0.4 = 0.6$

$$i = \frac{\text{Number of moles at equilibrium}}{\text{Number of moles present initially}}$$

$$i = \frac{0.6}{1} = 0.6$$

On substituting all the given values in Eq. (i), we get

$$2 = \frac{0.6 \times 5 \times w \times 1000}{122 \times 30}, \quad w = 2.44 \text{ g}$$

Thus, weight of acid (w) is 2.4 g.

- 7.** Given, Freezing point of 4% aqueous solution of X .

= Freezing point of 12% aqueous solution of Y

$$\text{or} \quad (\Delta T_f)_X = (\Delta T_f)_Y \quad [\because \Delta T_f = T_f^\circ - T_f]$$

$$K_f \times m_X = K_f m_Y$$

where, m_X and m_Y are molality of X and Y , respectively.

$$\text{or} \quad m_X = m_Y$$

$$\text{Now, molality} = \frac{\text{Number of moles of solute (n)}}{\text{Mass of solvent (in kg)}}$$

$$n = \frac{\text{Weight}}{\text{Molecular mass}}$$

$$\frac{w_X}{M_X \times (w_{\text{solvent}})_1} = \frac{w_Y}{M_Y \times (w_{\text{solvent}})_2}$$

$$\text{Given, } w_X = 4 \text{ and } w_{(\text{solvent})_1} = 96$$

$$w_Y = 12 \text{ and } w_{(\text{solvent})_2} = 88$$

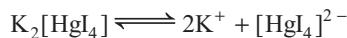
$$M_X = A$$

$$\therefore \frac{4 \times 1000}{M_X \times 96} = \frac{12 \times 1000}{M_Y \times 88}$$

$$\text{Thus, } M_Y = \frac{12 \times 1000 \times M_X \times 96}{4 \times 1000 \times 88}$$

$$= \frac{96 \times 12}{4 \times 88} \times A = 3.27A \approx 3A$$

- 8.** The ionisation of K_2HgI_4 in aqueous solution is as follows:



vant Hoff factor (i) for ionisation reaction is given as,
 $i = 1 + \alpha (n - 1)$

where,

n = number of ions,

α = degree of ionisation or dissociation

From above equation, it is clear that $n = 3$

$$i = 1 + 0.4 (3 - 1)$$

$$[\text{Given, } \% \alpha = 40\% \text{ or } \alpha = 0.4]$$

$$= 1.8$$

- 9.** We know that,

Depression in freezing points (ΔT_f)

$$T_f^\circ - T_f = K_f \times m \times i$$

where, K_f = molal depression constant

$$m = \text{molality} = \frac{w_{\text{solute}} \times 1000}{M_{\text{solute}} \times w_{\text{solvent}} \text{ (in g)}}$$

i = van't Hoff factor

For diluted milk

$$\Delta T_{f_1} = K_f \times m_1 \times i$$

$$\Rightarrow 0 - (0.2) \Rightarrow 0.2 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(\text{H}_2\text{O})} \times 1$$

For pure milk

$$\Delta T_{f_2} = K_f \times m_2 \times i$$

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$$\Rightarrow 0 - (-0.5) = 0.5 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_2(\text{H}_2\text{O})} \times 1$$

So, $\frac{0.2}{0.5} = \frac{K_f}{K_f} \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(\text{H}_2\text{O})} \times \frac{M_{\text{milk}} \times w_2(\text{H}_2\text{O})}{w_{\text{milk}} \times 1000} = \frac{w_2(\text{H}_2\text{O})}{w_1(\text{H}_2\text{O})}$

$$\Rightarrow \frac{w_2(\text{H}_2\text{O}) \text{ (in pure milk)}}{w_1(\text{H}_2\text{O}) \text{ (in diluted milk)}} = \frac{2}{5}$$

i.e. 3 cups of water has to be added to 2 cups of pure milk.

10. Elevation in boiling point (ΔT_b) = $K_b \times m \times i$

Depression is freezing point (ΔT_f) = $K_f \times m \times i$

where, m = molality

For the glucose solution (van't Hoff factor, $i = 1$),

$$\Delta T_b^{1m} = \Delta T_f^{2m} = 2K$$

$$\text{So, } K_b \times 1 \times 1 = K_f \times 2 \times 1 \Rightarrow K_b = 2K_f$$

11. Considering the expression of the depression in freezing point of a solution,

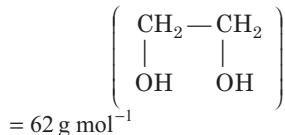
$$\Delta T_f = K_f \times m \times i$$

$$T_f^\circ - T_f = K_f \times \frac{w_B \times 1000}{M_B \times w_A (\text{in g})} \times i \quad \dots(i)$$

Here, $T_f^\circ = 0^\circ\text{C}$, $T_f = -10^\circ\text{C}$

w_B = mass of ethylene glycol = 62 g

M_B = molar mass of ethylene glycol



w_A = mass of water in g as liquid solvent,

i = van't Hoff factor = 1 (for ethylene glycol in water)

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

On substituting in Eq. (i), we get

$$0 - (-10) = 1.86 \times \frac{62 \times 1000}{62 \times w_A} \times 1$$

$$\Rightarrow w_A = \frac{1.86 \times 62 \times 1000}{10 \times 62} = 186 \text{ g}$$

So, amount of water separated as ice (solid solvent)

$$= 250 - w_A = (250 - 186)\text{g} = 64 \text{ g}$$

12. **Key idea** "Addition of solute particles to a pure solvent results to depression in its freezing point."

All the compounds given in question are ionic in nature so, consider their van't Hoff factor (i) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor (i) i.e.

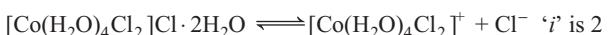
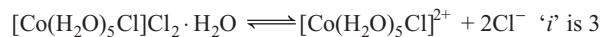
Number of solute particles \propto van't Hoff factor (i)

Thus, we can say directly

Solution with maximum freezing point will be the one in which solute with minimum van't Hoff factor is present

Now, for $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3 \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$

van't Hoff factor (i) is 4. Similarly for,



and for $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$, ' i ' is 1 as it does not show ionisation. Hence, $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

13. Let the degree of association of acetic acid (CH_3COOH) in benzene is α , then



Initial moles	1	0
Moles at equilibrium	$1 - \alpha$	$\frac{\alpha}{2}$

$$\therefore \text{Total moles} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \text{ or } i = 1 - \frac{\alpha}{2}$$

Now, depression in freezing point (ΔT_f) is given as

$$\Delta T_f = i K_f m \quad \dots(i)$$

where, K_f = molal depression constant or cryoscopic constant.
 m = molality

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} = \frac{0.2}{60} \times \frac{1000}{20}$$

Putting the values in Eq. (i)

$$\therefore 0.45 = \left[1 - \frac{\alpha}{2}\right] (5.12) \left[\frac{0.2}{60} \times \frac{1000}{20}\right]$$

$$\frac{1 - \alpha}{2} = \frac{0.45 \times 60 \times 20}{5.12 \times 0.2 \times 1000}$$

$$\Rightarrow 1 - \frac{\alpha}{2} = 0.527 \Rightarrow \frac{\alpha}{2} = 1 - 0.527$$

$$\therefore \alpha = 0.946$$

Thus, percentage of association = 94.6%

$$14. -\Delta T_f = ik_f m_2 = 1 \times 2 \times \frac{34.5}{46 \times 500} \times 1000 = 3$$

Vapour pressure curves shown in (b) is in agreement with the calculated value of $-\Delta T_f$. (a) is wrong, vapour pressure decreases on cooling.

15. **PLAN** This problem includes concept of colligative properties (osmotic pressure here) and van't Hoff factor. Calculate the effective molarity of each solution.

i.e. effective molarity = van't Hoff factor \times molarity

$$0.5 \text{ M C}_2\text{H}_5\text{OH} \text{ (aq)} \quad i = 1$$

Effective molarity = 0.5

$$0.25 \text{ M KBr} \text{ (aq)} \quad i = 2$$

Effective molarity = 0.5 M

$$0.1 \text{ M Mg}_3(\text{PO}_4)_2 \text{ (aq)} \quad i = 5$$

Effective molarity = 0.5 M

$$0.125 \text{ M Na}_3\text{PO}_4 \text{ (aq)} \quad i = 4$$

Effective molarity = 0.5 M

Molarity is same hence, all colligative properties are also same.

NOTE This question is solved by assuming that the examiner has taken $\text{Mg}_3(\text{PO}_4)_2$ to be completely soluble. However, in real it is insoluble (sparingly soluble).

16. The elevation in boiling point is

$$\Delta T_b = K_b \cdot m: m = \text{molality} = \frac{n_2}{w_1} \times 1000$$

[n_2 = Number of moles of solute, w_1 = Weight of solvent in gram]

$$\Rightarrow 2 = 0.76 \times \frac{n_2}{100} \times 1000 \Rightarrow n_2 = \frac{5}{19}$$

Also, from Raoult's law of lowering of vapour pressure :

$$\frac{-\Delta p}{p^\circ} = x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad [\because n_1 \gg n_2]$$

$$\Rightarrow -\Delta p = 760 \times \frac{5}{19} \times \frac{18}{100} = 36 \text{ mm of Hg}$$

$$\Rightarrow p = 760 - 36 = 724 \text{ mm of Hg}$$

17. van't Hoff factor (i) = 4 { $3K^+ + [Fe(CN)_6]^{3-}$ }

$$\text{Molality} = \frac{0.1}{329} \times \frac{1000}{100} = \frac{1}{329}$$

$$\Rightarrow -\Delta T_f = iK_f \cdot m \\ = 4 \times 1.86 \times \frac{1}{329} = 2.3 \times 10^{-2}$$

$$\Rightarrow T_f = -2.3 \times 10^{-2} \text{ }^\circ\text{C}$$

(As % freezing point of water is 0°C)

18. Molality = $\left(\frac{20}{172}\right) \times \frac{1000}{50} = 2.325 \text{ m}$

$$\Rightarrow -\Delta T_f = 2 = iK_f \cdot m$$

$$\Rightarrow i = \frac{2}{1.72 \times 2.325} = 0.5$$

19. Molality = $\frac{13.44}{134.1} = 0.1$

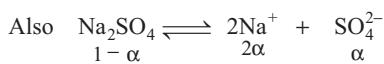
$$i = 3$$

$$\Rightarrow \Delta T_b = iK_b \cdot m = 3 \times 0.52 \times 0.1 \\ = 0.156$$

20. For isotonic solutions, they must have same concentrations of ions, Therefore,

$$0.004 i (\text{Na}_2\text{SO}_4) = 0.01$$

$$\Rightarrow i = \frac{0.01}{0.004} = 2.5$$

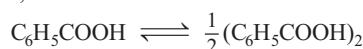


$$\Rightarrow i = 1 + 2\alpha = 2.5$$

$$\alpha = 0.75 = 75\%$$

21. During freezing, liquid solvent solidify and solid solvent remains in equilibrium with liquid solvent.

22. In benzene, benzoic acid dimerises as :



23. $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$: $i = 2$;

$$\text{Ca}(\text{NO}_3)_2 : i = 3$$

$$\text{La}(\text{NO}_3)_3 : i = 4;$$

$$\text{C}_6\text{H}_{12}\text{O}_6 : i = 1$$

Lower the value of i , smaller will be the depression in freezing point, higher will be the freezing temperature, if molalities are equal. Hence, glucose solution will have highest freezing temperature.

24. $\text{K}_2\text{SO}_4 : i = 3$

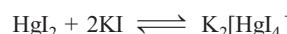
$$\text{NaCl} : i = 2$$

$$\text{Urea} : i = 1$$

$$\text{Glucose} : i = 1$$

Greater the value of i , greater the lowering in freezing point, lower will be the freezing temperature, if molarity in all cases are same. Therefore, K_2SO_4 solution has the lowest freezing point.

25. Addition of HgI_2 to KI solution establishes the following equilibrium :



The above equilibrium decreases the number of ions (4 ions on left side of reactions becomes three ions on right side), hence rises the freezing point.

26. In depression of freezing point experiment, vapour pressure of solution is less than that of pure solvent as well as only solvent molecules solidify at freezing point.

27. Osmotic pressure,

$$\pi = i \times C \times RT$$

Here, i = van't Hoff factor, T = temperature

C = concentration and R = gas constant.

For NaCl , $i = 2$

$$\text{So, } \pi_{\text{NaCl}} = i \times C_{\text{NaCl}} \times RT$$

$$0.1 = 2 \times C_{\text{NaCl}} \times RT$$

$$C_{\text{NaCl}} = \frac{0.05}{RT}$$

For glucose, $i = 1$ because it cannot ionise

$$\text{So, } \pi_{\text{glucose}} = i \times C_{\text{glucose}} \times RT$$

$$0.2 = 1 \times C_{\text{glucose}} \times RT$$

$$C_{\text{glucose}} = \frac{0.2}{RT}$$

($\because n_{\text{NaCl}}$ = numbers of moles NaCl)

$$n_{\text{NaCl}} \text{ in 1 L} = C_{\text{NaCl}} \times V_{\text{litre}}$$

$$= \frac{0.05}{RT} \quad (n_{\text{glucose}} = \text{number of moles of glucose})$$

$$n_{\text{glucose}} \text{ in 2 L} = C_{\text{glucose}} \times V_{\text{litre}} = \frac{0.4}{RT}$$

$$V_{\text{total}} = 1 + 2 = 3\text{ L}$$

$$\text{So, final conc. NaCl} = \frac{0.05}{3RT}$$

$$\text{Final conc. glucose} = \frac{0.4}{3RT}$$

$$\pi_{\text{total}} = \pi_{\text{NaCl}} + \pi_{\text{glucose}} = [i \times C_{\text{NaCl}} + C_{\text{glucose}}] RT$$

$$= \left(\frac{2 \times 0.05}{3RT} + \frac{0.4}{3RT} \right) \times RT = \frac{0.5}{3} \text{ atm}$$

$$= 0.1666 \text{ atm} = 166.6 \times 10^{-3} \text{ atm} = 167.00 \times 10^{-3} \text{ atm}$$

$$\text{So, } x = 167.00$$

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- 28.** **Key Idea** First calculate, molar mass of solute using the formula, $\frac{p^\circ - p_s}{p^\circ} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$ and then calculate ΔT_f by applying the formula; $\Delta T_f = K_f \times m$.

When 0.5 g of non-volatile solute dissolve into 39 gm of benzene then relative lowering of vapour pressure occurs. Hence, vapour pressure decreases from 650 mmHg to 640 mmHg.

Given, vapour pressure of solvent (p°) = 650 mmHg

Vapour pressure of solution (p_s) = 640 mmHg

Weight of non-volatile solute = 0.5 g

Weight of solvent (benzene) = 39 g

From relative lowering of vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{0.5}{0.5 + 39}$$

$$\frac{650 - 640}{650} = \frac{\frac{0.5}{\text{molar mass}}}{\frac{0.5}{\text{molar mass}} + \frac{39}{78}}$$

$$\frac{10}{650} = \frac{\frac{0.5}{\text{molar mass}}}{\frac{0.5}{\text{molar mass}} + 0.5}$$

$$0.5 + 0.5 \times \text{molar mass} = 65 \times 0.5$$

$$\therefore \text{Molar mass of solute} = 64 \text{ g}$$

From molal depression of freezing point,

$$\Delta T_f = K_f \times \text{molality} = \frac{K_f \times w_{\text{solute}}}{(MW)_{\text{solute}} \times w_{\text{solvent}}}$$

$$\Delta T_f = 5.12 \times \frac{0.5 \times 1000}{64 \times 39} \Rightarrow \Delta T_f = 102 \text{ K}$$

- 29.** From the graph we can note

ΔT_b for solution X i.e.,

$$\Delta T_{b(X)} = 362 - 360 = 2$$

Likewise, ΔT_b for solution Y i.e., $\Delta T_{b(Y)} = 368 - 367 = 1$

Now by using the formula

$$\Delta T_b = i \times \text{molality of solution} \times K_b$$

For solution X

$$2 = i \times m_{\text{NaCl}} \times K_{b(X)} \quad \dots(i)$$

Similarly for solution y

$$1 = i \times m_{\text{NaCl}} \times K_{b(Y)} \quad \dots(ii)$$

from Eq. (i) and (ii) above

$$\frac{K_{b(X)}}{K_{b(Y)}} = \frac{2}{1} \text{ or } 2 \quad \text{or} \quad K_{b(X)} = 2K_{b(Y)}$$

For solute S

$$2S \longrightarrow S_2 \quad (\text{given due to dimerisation})$$

Initial	α	0
Final	$(1 - \alpha)$	$\frac{\alpha}{2}$

$$\text{So, here} \quad i = \left(1 - \frac{\alpha}{2}\right)$$

$$\Delta T_{b[X](s)} = \left(1 - \frac{\alpha_1}{2}\right) K_{b(X)}$$

$$\Delta T_{b[Y](s)} = \left(1 - \frac{\alpha_2}{2}\right) K_{b(Y)}$$

Given,

$$\Delta T_{b(X)(s)} = 3\Delta T_{b(Y)(s)}$$

$$\left(1 - \frac{\alpha_1}{2}\right) K_{b(X)} = 3 \times \left(1 - \frac{\alpha_2}{2}\right) \times K_{b(Y)}$$

$$\text{or} \quad 2\left(1 - \frac{\alpha_1}{2}\right) = 3\left(1 - \frac{\alpha_2}{2}\right) \quad [\because K_{b(X)} = 2K_{b(Y)}]$$

$$\text{or} \quad 2\left(1 - \frac{\alpha_1}{2}\right) = 3\left(1 - \frac{0.7}{2}\right) \quad (\text{as given, } \alpha_2 = 0.7)$$

$$\text{or} \quad 4 - 2\alpha_1 = 6 - 2.1 \quad \text{or} \quad 2\alpha_1 = 0.1$$

$$\text{so,} \quad \alpha_1 = 0.05$$

$$\text{30. Molar mass of solute } (M_B) = \frac{1000 \times K_f \times W_B}{W_A \times \Delta T_f}$$

$$\Rightarrow M_B = \frac{1000 \times 14 \times 75.2}{1000 \times 7}$$

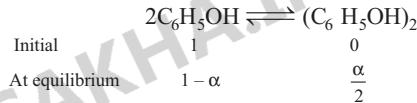
$$M_B = 150.4 \text{ g per mol}$$

Actual molar mass of phenol = 94 g/mol

Now, van't Hoff factor, $i = \frac{\text{Calculated molar mass}}{\text{Observed molar mass}}$

$$\therefore i = \frac{94}{150.4} = 0.625$$

Dimerisation of phenol can be shown as :



$$\text{Total number of moles at equilibrium, } i = 1 - \alpha + \frac{\alpha}{2}$$

$$i = 1 - \frac{\alpha}{2}$$

$$\text{But } i = 0.625, \text{ thus,} \quad 0.625 = 1 - \frac{\alpha}{2}$$

$$\alpha/2 = 1 - 0.625$$

$$\alpha = 0.75$$

Thus, the percentage of phenol that dimerises is 75%.

- 31.** (i) $\Delta T_b = K_b \cdot m_2$

$$\Rightarrow 0.17 = 1.7 \times \frac{1.22}{M} \times \frac{1000}{100} \Rightarrow M = 122$$

$$(ii) 0.13 = 2.6 \times \frac{1.22}{M} \times \frac{1000}{100} \Rightarrow M = 244$$

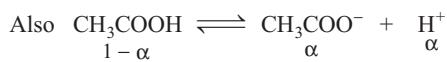
The above molar masses suggests that benzoic acid is monomeric in acetone while dimeric in benzene.

- 32.** Higher the value of K_b of a solvent suggest that there is larger polarity of solvent molecules, which in turn implies higher boiling point due to dipole-dipole interaction.

Therefore, the correct order of K_b values of the three given solvents is

Solvents	Boiling point	K_b
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.92

33. Mass of water = $500 \times 0.997 \text{ g} = 498.5 \text{ g}$



$$\Rightarrow i = 1 + \alpha = 1.23$$

$$\Rightarrow -\Delta T_f = iK_f \cdot m = 1.23 \times 1.86 \times \frac{3}{60} \times \frac{1000}{498.5} = 0.23^\circ\text{C}$$

34. (i) Empirical formula determination

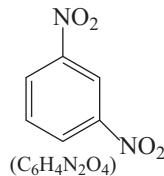
Elements	C	H	N	O
Weight %	42.86	2.40	16.67	38.07
Moles	3.57	2.40	1.19	2.38
Simplest ratio	3	2	1	2

$$\Rightarrow \text{Empirical formula} = \text{C}_3\text{H}_2\text{NO}_2$$

$$(ii) \Delta T_b = 1.84 = 2.53 \times \frac{5.5}{M} \times \frac{1000}{45}$$

$$\Rightarrow M = 168$$

\because Empirical formula weight (84) is half of molar mass, molecular formula is $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ a dinitrobenzene :



35. $-\Delta T_f = K_f \cdot m_2$

$$\Rightarrow m_2 = \frac{0.3}{1.86} = 0.1613$$

$$\text{Also, } m_2 = \frac{n_2}{n_1} \times \frac{1000}{M_1} = 0.1613$$

$$\Rightarrow \frac{n_2}{n_1} = \frac{0.1613 \times 18}{1000} = 2.9 \times 10^{-3}$$

$$\Rightarrow \frac{n_2}{n_1} + 1 = \frac{n_2 + n_1}{n_1} = 2.9 \times 10^{-3} + 1$$

$$\Rightarrow \frac{n_1}{n_1 + n_2} = \chi_1 = \frac{1}{1 + 2.9 \times 10^{-3}} = 0.997$$

$$\Rightarrow p = p_0 \chi_1 = 23.51 \times 0.997 = 23.44 \text{ mm}$$

36. $-\Delta T_f = 5.51 - 5.03 = 0.48$

$$\Rightarrow -\Delta T_f = 0.48 = K_f \cdot m$$

$$\Rightarrow 0.48 = 5.12 \times \frac{0.643}{M} \times \frac{1000}{50 \times 0.879}$$

$$\Rightarrow M = 156 \text{ g/mol}$$

37. In the given solution 'M', H_2O is solute.

$$\text{Therefore, molality of H}_2\text{O} = \frac{0.1}{0.9 \times 46} \times 1000 = 2.4$$

$$\Rightarrow -\Delta T_f = K_f^{\text{ethanol}} \times 2.4 = 2 \times 2.4 = 4.8$$

$$\Rightarrow T_f = 155.7 - 4.8 = 150.9 \text{ K}$$

38. Vapour pressure = $p(\text{H}_2\text{O}) + p(\text{ethanol})$

$$= 32.8 \times 0.1 + 40 \times 0.9 \\ = 3.28 + 36 = 39.28 \text{ mm}$$

39. Now ethanol is solute.

$$\text{Molality of solute} = \frac{0.1}{0.9 \times 18} \times 1000 = 6.17$$

$$\Rightarrow \Delta T_b = 6.17 \times 0.52 = 3.20$$

$$\Rightarrow T_b = 373 + 3.2 = 376.2 \text{ K}$$

$$40. \lim_{m \rightarrow 0} \left(\frac{\Delta T_f}{m} \right) = K_f \text{ (Cryoscopic constant)}$$

$$41. 1 + \Delta T_f = iK_f m$$

$$\Delta T_f = 0 - (-0.0558^\circ\text{C}) = 0.0558^\circ\text{C}$$

$$\Rightarrow i \text{ (van't Hoff's factor)} = \frac{0.0558}{186 \times 0.01} = 3$$

This indicates that complex upon ionisation produces three ions as:



Thus, only one Cl is inside the coordination sphere.

$$42. MX_2 \longrightarrow M^{2+} + 2X^-$$

van't Hoff factor for any salt can be calculated by using equation
 $i = 1 + \alpha (n - 1)$

where, n = number of constituent ions

$$\therefore i(MX_2) = 1 + \alpha (3 - 1) = 1 + 2\alpha$$

$$\frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{theoretical}}} = i = 1 + 2\alpha$$

$$\therefore i = 1 + 2 \times 0.5 \Rightarrow i = 2$$

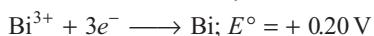
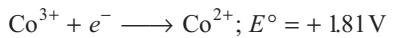
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Electrochemistry

Topic 1 Electrochemical Cells

Objective Questions I (Only one correct option)

1. Given,

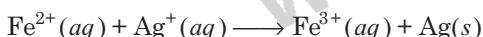


Oxidising power of the species will increase in the order
(2019 Main, 12 April I)

- (a) $\text{Ce}^{4+} < \text{Pb}^{4+} < \text{Bi}^{3+} < \text{Co}^{3+}$
- (b) $\text{Bi}^{3+} < \text{Ce}^{4+} < \text{Pb}^{4+} < \text{Co}^{3+}$
- (c) $\text{Co}^{3+} < \text{Ce}^{4+} < \text{Bi}^{3+} < \text{Pb}^{4+}$
- (d) $\text{Co}^{3+} < \text{Pb}^{4+} < \text{Ce}^{4+} < \text{Bi}^{3+}$

2. A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode? (2019 Main, 9 April II)
(a) 0.20 (b) 0.10 (c) 0.15 (d) 0.05

3. Calculate the standard cell potential (in V) of the cell in which following reaction takes place



Given that, $E^\circ_{\text{Ag}^+/\text{Ag}} = x \text{ V}$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = y \text{ V}$$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}} = z \text{ V}$$
 (2019 Main, 8 April II)

- (a) $x + 2y - 3z$
- (b) $x - y$
- (c) $x + y - z$
- (d) $x - z$

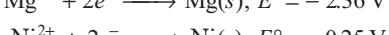
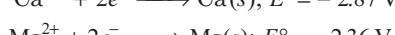
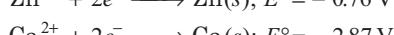
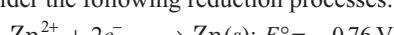
4. Given, that $E^\circ_{\text{O}_2/\text{H}_2\text{O}} = +1.23 \text{ V}$;

$$E^\circ_{\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}} = 2.05 \text{ V}; E^\circ_{\text{Br}_2/\text{Br}^-} = +1.09 \text{ V}, E^\circ_{\text{Au}^{3+}/\text{Au}} = +1.4 \text{ V}$$

The strongest oxidising agent is (2019 Main, 8 April I)

- (a) Au^{3+}
- (b) O_2
- (c) $\text{S}_2\text{O}_8^{2-}$
- (d) Br_2

5. Consider the following reduction processes:



The reducing power of the metals increases in the order

(2019 Main, 10 Jan I)

- (a) $\text{Zn} < \text{Mg} < \text{Ni} < \text{Ca}$
- (b) $\text{Ni} < \text{Zn} < \text{Mg} < \text{Ca}$
- (c) $\text{Ca} < \text{Zn} < \text{Mg} < \text{Ni}$
- (d) $\text{Ca} < \text{Mg} < \text{Zn} < \text{Ni}$

6. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of PbSO_4 electrolysed in g during the process is (Molar mass of $\text{PbSO}_4 = 303 \text{ g mol}^{-1}$) (2019 Main, 9 Jan I)
(a) 11.4 (b) 7.6 (c) 15.2 (d) 22.8

7. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane?
(Atomic weight of B = 10.8μ) (2018 Main)
(a) 6.4 hours (b) 0.8 hours (c) 3.2 hours (d) 1.6 hours

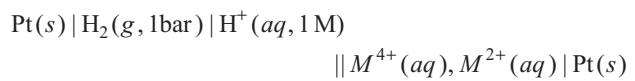
8. Given, $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}, E^\circ_{\text{Cr}^{3+}/\text{Cr}} = - 0.74 \text{ V}$

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}, E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$$

Among the following, the strongest reducing agent is (2017 Main)

- (a) Cr
- (b) Mn^{2+}
- (c) Cr^{3+}
- (d) Cl^-

9. For the following electrochemical cell at 298 K,



$$E_{\text{cell}} = 0.092 \text{ V} \text{ when } \frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x$$

$$\text{Given : } E^\circ_{M^{4+}/M^{2+}} = 0.151 \text{ V}; 2.303 \frac{RT}{F} = 0.059 \text{ V}$$

The value of x is (2016 Adv.)

- (a) -2
- (b) -1
- (c) 1
- (d) 2

10. Two Faraday of electricity is passed through a solution of CuSO_4 . The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 u) (2015 Main)
(a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

11. Given, $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = - 0.74 \text{ V}; E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}; E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$$

Based on the data given above strongest oxidising agent will be (2013 Main)

- (a) Cl
- (b) Cr^{3+}
- (c) Mn^{2+}
- (d) MnO_4^-

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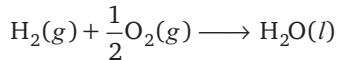
Objective Questions II

(One or more than one correct option)

25. In a galvanic cell, the salt-bridge (2014 Adv.)
(a) does not participate chemically in the cell reaction
(b) stops the diffusion of ions from one electrode to another
(c) is necessary for the occurrence of the cell reaction
(d) ensures mixing of the two electrolytic solutions
26. For the reduction of NO_3^- ion in an aqueous solution E° is + 0.96 V. Values of E° for some metal ions are given below
 $\text{V}^{2+}(\text{aq}) + 2e^- \rightarrow \text{V}; E^\circ = -1.19\text{ V}$
 $\text{Fe}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Fe}; E^\circ = -0.04\text{ V}$
 $\text{Au}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Au}; E^\circ = +1.40\text{ V}$
 $\text{Hg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Hg}; E^\circ = +0.86\text{ V}$
- The pair(s) of metals that is/are oxidised by NO_3^- in aqueous solution is (are) (2009)
(a) V and Hg (b) Hg and Fe (c) Fe and Au (d) Fe and V

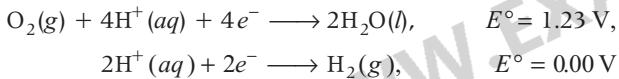
Numerical Answer Type Questions

27. Consider a 70% efficient hydrogen-oxygen fuel cell working under standard conditions at 1 bar and 298 K. Its cell reaction is



The work derived from the cell on the consumption of 1.0×10^{-3} mole of $\text{H}_2(g)$ is used to compress 1.00 mole of a monoatomic ideal gas in a thermally insulated container. What is the change in the temperature (in K) of the ideal gas?

The standard reduction potentials for the two half-cells are given below:



Use, $F = 96500\text{ C mol}^{-1}$, $R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$. (2020 Adv.)

28. For the electrochemical cell,



The standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is _____.
(Given, $\frac{F}{R} = 11500\text{ K V}^{-1}$, where F is the Faraday constant and R is the gas constant, $\ln(10) = 2.30$) (2018 Adv.)

29. Consider an electrochemical cell : $A(s)|A^{n+}(\text{aq}, 2\text{ M})||B^{2n+}(\text{aq}, 1\text{ M})|B(s)$. The value of ΔH^\ominus for the cell reaction is twice of ΔG^\ominus at 300 K. If the emf of the cell is zero, the ΔS^\ominus (in $\text{J K}^{-1}\text{ mol}^{-1}$) of the cell reaction per mole of B formed at 300 K is

(Given : $\ln(2) = 0.7$, R (universal gas constant) = $8.3\text{ J K}^{-1}\text{ mol}^{-1}$. H, S and G are enthalpy, entropy and Gibbs energy, respectively.) (2018 Adv.)

Passage Based Questions

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200, 1 F = 96500 C). (2007, 3 × 4M = 12M)

30. The total number of moles of chlorine gas evolved is
(a) 0.5 (b) 1.0
(c) 2.0 (d) 3.0
31. If the cathode is a Hg electrode, the maximum weight (in gram) of amalgam formed from this solution is
(a) 200 (b) 225
(c) 400 (d) 446
32. The total charge (coulombs) required for complete electrolysis is
(a) 24125 (b) 48250
(c) 96500 (d) 193000

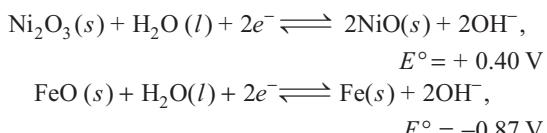
Subjective Questions

33. The following electrochemical cell has been set-up :
 $\text{Pt}(1)|\text{Fe}^{3+}, \text{Fe}^{2+} (\text{a} = 1)|\text{Ce}^{4+}, \text{Ce}^{3+} (\text{a} = 1)|\text{Pt}(2)$
 $E^\circ (\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77\text{ V}$
and $E^\circ (\text{Ce}^{4+}, \text{Ce}^{3+}) = 1.61\text{ V}$
If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current, will the current increases or decreases with time? (2000, 2M)
34. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 min. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. (2000, 3M)
35. A cell, $\text{Ag}|\text{Ag}^+||\text{Cu}^{2+}|\text{Cu}$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h. (1999, 6M)
36. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 h at a current of 8.46 A? What is the area of the tray, if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3 . (1997, 3M)

37. The Edison storage cell is represented as:

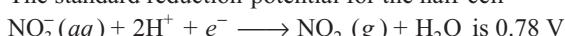


The half-cell reactions are :



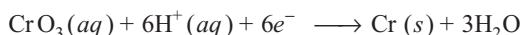
- (i) What is the cell reaction?
- (ii) What is the cell emf ? How does it depend on the concentration of KOH?
- (iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ? (1994, 4M)

38. The standard reduction-potential for the half-cell



- (i) Calculate the reduction-potential in 8M H^+ .
- (ii) What will be the reduction-potential of the half-cell in a neutral solution? Assume all the other species to be at unit concentration. (1993, 2M)

39. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation.



Calculate (i) How many grams of chromium will be plated out by 24,000 C and (ii) How long will it take to plate out 1.5 g of chromium by using 12.5 A current? (1993, 2M)

40. An aqueous solution of NaCl on electrolysis gives $\text{H}_2(g)$, $\text{Cl}_2(g)$ and NaOH according to the reaction.



A direct current of 25 A with a current efficiency of 62% is passed through 20 L of NaCl solution (20% by weight). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1kg of Cl_2 ? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation) (1992, 3M)

41. For the galvanic cell,



Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

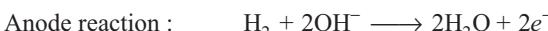
$$[K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}, K_{sp}(\text{AgBr}) = 3.3 \times 10^{-13}] \quad (1992, 4M)$$

42. A current of 1.70 A is passed through 300.0 mL of 0.160M solution of a ZnSO_4 for 230 s with a current efficiency of 90%. Find out the molarity of Zn^{2+} after the deposition Zn. Assume the volume of the solution to remain constant during the electrolysis. (1991, 4M)

43. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 V, how much energy will be consumed? (1990, 3M)

44. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 A. Calculate the volume of gases evolved at NTP during the entire electrolysis. (1989, 5M)

45. In a fuel cell hydrogen and oxygen react to produces electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 L of H_2 at STP react in 15 min, what is the average current produced? If the entire current is used for electro deposition of copper from copper (II) solution, how many grams of copper will be deposited?

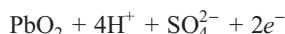


46. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode. (1988, 2M)

47. A 100 watt, 110 V incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 h? (1987, 5M)

48. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 g/mL is 39% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 L of the acid and the volume remained practically constant during the discharge.

Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are



49. How long a current of 3 A has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer?

Density of silver is 10.5 g/cm^3 . (1985, 3M)

50. In an electrolysis experiment current was passed for 5 h through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in ampere.

(Atomic weight of Au = 197 and atomic weight of Cu = 63.5) (1983, 3M)

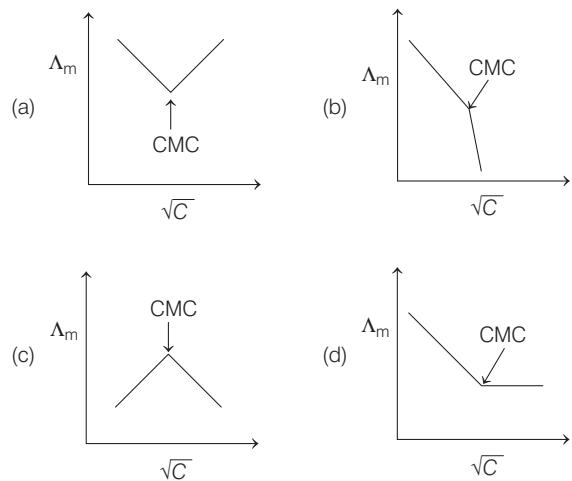
51. A current of 3.7 A is passed for 6 h between nickel electrodes in 0.5 L of a 2.0 M solution of $\text{Ni}(\text{NO}_3)_2$. What will be the molarity of solution at the end of electrolysis? (1978, 2M)

Topic 2 Conductivity of Electrolytic Solutions and their Measurement and Nernst Equation

Objective Questions I (Only one correct option)

1. Molar conductivity (Λ_m) of aqueous solution of sodium stearate, which behaves as a strong electrolyte, is recorded at varying concentrations (C) of sodium stearate. Which one of the following plots provides the correct representation of micelle formation in the solution?

(critical micelle concentration (CMC) is marked with an arrow in the figures) (2019 Adv.)



2. The decreasing order of electrical conductivity of the following aqueous solution is

0.1 M formic acid (*A*),

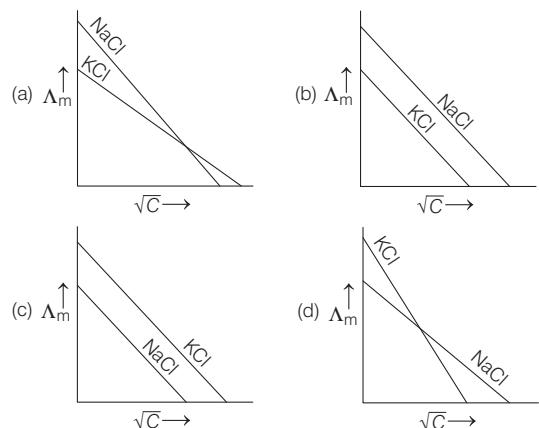
0.1 M acetic acid (*B*),

0.1 M benzoic acid (*C*). (2019 Main, 12 April II)

- (a) *A* > *C* > *B* (b) *C* > *B* > *A*
 (c) *A* > *B* > *C* (d) *C* > *A* > *B*

3. Which one of the following graphs between molar conductivity (Λ_m) versus \sqrt{C} is correct?

(2019 Main, 10 April II)



4. Consider the statements S_1 and S_2 :

S_1 : Conductivity always increases with decrease in the concentration of electrolyte.

S_2 : Molar conductivity always increases with decrease in the concentration of electrolyte.

The correct option among the following is

(2019 Main, 10 April I)

- (a) S_1 is correct and S_2 is wrong
 (b) S_1 is wrong and S_2 is correct
 (c) Both S_1 and S_2 are wrong
 (d) Both S_1 and S_2 are correct

5. The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is



$$E^\circ = 2\text{V at } 298\text{ K}$$

(Faraday's constant, $F = 96000 \text{ C mol}^{-1}$) (2019 Main, 9 April I)

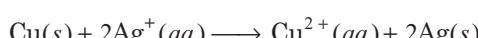
- (a) 384 (b) 192 (c) -384 (d) -192

6. Λ_m° for NaCl , HCl and NaA are 126.4 , 425.9 and $100.5 \text{ S cm}^2 \text{ mol}^{-1}$, respectively. If the conductivity of 0.001 M HA is $5 \times 10^{-5} \text{ S cm}^{-1}$, degree of dissociation of HA is

(2019 Main, 12 Jan II)

- (a) 0.25 (b) 0.50 (c) 0.75 (d) 0.125

7. Given the equilibrium constant (K_C) of the reaction :



is 10×10^{15} , calculate the E_{cell}° of this reaction at 298 K.

$$\left[2.303 \frac{RT}{F} \text{ at } 298\text{ K} = 0.059 \text{ V} \right]$$

(2019 Main, 11 Jan II)

- (a) 0.4736 V (b) 0.04736 mV
 (c) 0.4736 mV (d) 0.04736 V

8. For the cell, $\text{Zn}(s) | \text{Zn}^{2+}(aq) || M^{x+}(aq) | M(s)$, different half cells and their standard electrode potentials are given below.

$M^{x+}(aq)/M(s)$	$\text{Au}^{3+}(aq)/\text{Au}(s)$	$\text{Ag}^+(aq)/\text{Ag}(s)$	$\text{Fe}^{3+}(aq)/\text{Fe}^{2+}(aq)$	$\text{Fe}^{2+}(aq)/\text{Fe}(s)$
$E^\circ_{M^{x+}/M} / \text{V}$	1.40	0.80	0.77	-0.44

If $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, which cathode will give a maximum value of E_{cell}° per electron transferred? (2019 Main, 11 Jan I)

- (a) $\frac{\text{Ag}^+}{\text{Ag}}$ (b) $\frac{\text{Fe}^{2+}}{\text{Fe}}$ (c) $\frac{\text{Au}^{3+}}{\text{Au}}$ (d) $\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$

9. In the cell,

$\text{Pt}(s) | \text{H}_2(g, 1 \text{ bar}) | \text{HCl}(aq) | \text{AgCl}(s) | \text{Ag}(s) | \text{Pt}(s)$ the cell potential is 0.92 V when a 10^{-6} molal HCl solution is used.

- The standard electrode potential of (AgCl/ Ag, Cl⁻) electrode is $\left\{ \text{Given, } \frac{2.303RT}{F} = 0.06 \text{ V at } 298 \text{ K} \right\}$
- (a) 0.40 V (b) 0.20 V (c) 0.94 V (d) 0.76 V
- 10.** If the standard electrode potential for a cell is 2V at 300 K, the equilibrium constant (K) for the reaction,
 $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Cu}(s)$
 at 300 K is approximately
 $(R = 8 \text{ JK}^{-1} \text{ mol}^{-1}, F = 96000 \text{ C mol}^{-1})$
- (2019 Main, 9 Jan II)
- (a) e^{-160} (b) e^{160} (c) e^{-80} (d) e^{320}
- 11.** For the following cell,
 $\text{Zn}(s) \mid \text{ZnSO}_4(aq) \parallel \text{CuSO}_4(aq) \mid \text{Cu}(s)$
 when the concentration of Zn²⁺ is 10 times the concentration of Cu²⁺, the expression for ΔG (in J mol⁻¹) is
 [F is Faraday constant; R is gas constant;
 T is temperature; $E^\circ(\text{cell}) = 1.1 \text{ V}$]
- (2017 Adv.)
- (a) $2.303 RT + 1.1 F$ (b) $1.1 F$
 (c) $2.303 RT - 2.2 F$ (d) $-2.2 F$
- 12.** Galvanisation is applying a coating of
- (2016 Main)
- (a) Cr (b) Cu (c) Zn (d) Pb
- 13.** Given below are the half-cell reactions
- (2014 Main)
- $\text{Mn}^{2+} + 2e^- \longrightarrow \text{Mn}; E^\circ = -1.18 \text{ eV}$
 $2(\text{Mn}^{3+} + e^- \longrightarrow \text{Mn}^{2+}); E^\circ = +1.51 \text{ eV}$
- The E° for $3\text{Mn}^{2+} \rightarrow \text{Mn} + 2\text{Mn}^{3+}$ will be
 (a) -2.69 V ; the reaction will not occur
 (b) -2.69 V ; the reaction will occur
 (c) -0.33 V ; the reaction will not occur
 (d) -0.33 V ; the reaction will occur
- 14.** The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ , respectively. The correct relationship between λ_C and λ_∞ is given as (where, the constant B is positive)
- (2014 Main)
- (a) $\lambda_C = \lambda_\infty + (B)C$ (b) $\lambda_C = \lambda_\infty - (B)C$
 (c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$
- 15.** Resistance of 0.2 M solution of an electrolyte is 50Ω . The specific conductance of the solution of 0.5 M solution of same electrolyte is 1.4 S m^{-1} and resistance of same solution of the same electrolyte is 280Ω . The molar conductivity of 0.5 M solution of the electrolyte in $\text{Sm}^2 \text{mol}^{-1}$ is
- (2014 Main)
- (a) 5×10^{-4} (b) 5×10^{-3} (c) 5×10^3 (d) 5×10^2
- 16.** The standard reduction potential data at 25°C is given below.
 $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}; E^\circ(\text{Fe}^2/\text{Fe}) = -0.44 \text{ V};$
 $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}; E^\circ(\text{Cu}^+/\text{Cu}) = +0.52 \text{ V};$
 $E^\circ(\text{O}_2(g) + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}) = +1.23 \text{ V};$
 $E^\circ(\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}) = +0.40 \text{ V}$
 $E^\circ(\text{Cr}^{3+}/\text{Cr}) = -0.74 \text{ V}; E^\circ(\text{Cr}^{2+}/\text{Cr}) = +0.91 \text{ V}$

Match E° of the rebox pair in Column I with the values given in Column II and select the correct answer using the code given below the lists.

(2013 Adv.)

Column I				Column II			
P.	$E^\circ(\text{Fe}^{3+}/\text{Fe})$			1.	-0.18 V		
Q.	$E^\circ(4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$			2.	-0.4 V		
R.	$E^\circ(\text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+)$			3.	-0.04 V		
S.	$E^\circ(\text{Cr}^{3+}, \text{Cr}^{2+})$			4.	-0.83 V		

Codes

P	Q	R	S	P	Q	R	S
(a) 4	1	2	3	(b) 2	3	4	1
(c) 1	2	3	4	(d) 3	4	1	2

- 17.** An aqueous solution of X is added slowly to an aqueous solution of Y as shown in Column I. The variation in conductivity of these reactions is given in Column II. Match Column I with Column II and select the correct answer using the codes given below the Columns.

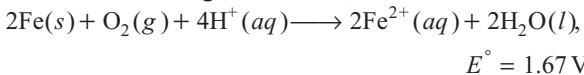
(2013 Adv.)

Column I				Column II			
P.	$(\text{C}_2\text{H}_5)_3\text{N} + \text{CH}_3\text{COOH}$	X	Y	1.	Conductivity decreases and then increases		
Q.	$\text{KI}(0.1 \text{ M}) + \text{AgNO}_3(0.01 \text{ M})$	X	Y	2.	Conductivity decreases and then does not change much		
R.	$\text{CH}_3\text{COOH} + \text{KOH}$	X	Y	3.	Conductivity increases and then does not change much		
S.	$\text{NaOH} + \text{HI}$	X	Y	4.	Conductivity does not change much and then increases		

Codes

P	Q	R	S	P	Q	R	S
(a) 3	4	2	1	(b) 4	3	2	1
(c) 2	3	4	1	(d) 1	4	3	2

- 18.** Consider the following cell reaction,

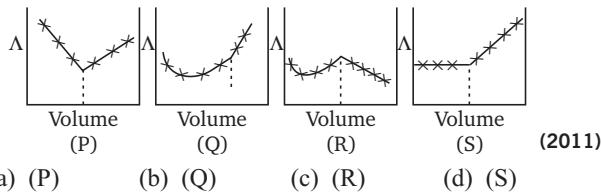


At $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$, $\text{P}(\text{O}_2) = 0.1 \text{ atm}$ and $\text{pH} = 3$, the cell potential at 25°C is

(2011)

- (a) 1.47 V (b) 1.77 V (c) 1.87 V (d) 1.57 V

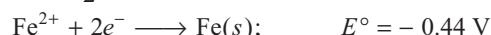
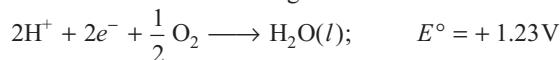
- 19.** AgNO₃ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of AgNO₃ is



- (a) (P) (b) (Q) (c) (R) (d) (S)

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20. The half cell reactions for rusting of iron are :



ΔG° (in kJ) for the reaction is (2005, 1M)
 (a) - 76 (b) - 322 (c) - 122 (d) - 176

21. $\text{Zn} | \text{Zn}^{2+} (a = 0.1\text{M}) || \text{Fe}^{2+} (a = 0.01\text{M}) | \text{Fe}$.

The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is (2004, 1M)

- (a) $10^{0.32/0.059}$ (b) $10^{0.32/0.0295}$
 (c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.295}$

22. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is (2001, 1M)

- (a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
 (c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

23. For the electrochemical cell, $(M|M^+)(|X^-|X)$, $E^\circ(M^+/M) = 0.44\text{ V}$ and $E^\circ(X^-/X) = 0.33\text{ V}$.

From this data one can deduce that (2000, 1M)

- (a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction
 (b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction
 (c) $E_{\text{cell}} = 0.77\text{ V}$
 (d) $E_{\text{cell}} = - 0.77\text{ V}$

24. The standard reduction potentials of Cu^{2+}/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half-cell is (1997, 1M)
 (a) 0.184 V (b) 0.827 V (c) 0.521 V (d) 0.490 V

Numerical Answer Type Questions

25. For the disproportionation reaction $2\text{Cu}^+(aq) \rightleftharpoons \text{Cu}(s) + \text{Cu}^{2+}(aq)$ at 298 K, $\ln K$ (where K is the equilibrium constant) is $\times 10^{-1}$.

Given : $(E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.16\text{ V}$,

$$E^\circ_{\text{Cu}^+/\text{Cu}} = 0.52\text{ V} \text{ and } \frac{RT}{F} = 0.025 \quad (\text{2020 Main, 2 Sep II})$$

26. An oxidation-reduction reaction in which 3 electrons are transferred has a ΔG° of 17.37 kJ mol^{-1} at 25°C . The value of E_{cell}° (in V) is $\times 10^{-2}$.
 $(1\text{ F} = 96,500\text{ C mol}^{-1}) \quad (\text{2020 Main, 5 Sep I})$

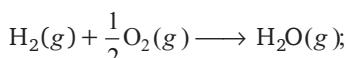
27. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below



p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{\text{H}_2})$ is
 (Given : total pressure = 1 bar, R (universal gas constant) = $8\text{ J K}^{-1}\text{ mol}^{-1}$, $\ln(10) = 2.30$ Cu(s) and Cu₂O(s) are mutually immiscible.)

At 1250 K : $2\text{Cu}(s) + 1/2\text{O}_2(g) \longrightarrow \text{Cu}_2\text{O}(s)$;

$$\Delta G^\circ = - 78,000\text{ J mol}^{-1}$$



$$\Delta G^\circ = - 1,78,000\text{ J mol}^{-1}; G \text{ is the Gibbs energy (2018 Adv.)}$$

Passage Based Questions

Passage I

The electrochemical cell shown below is a concentration cell. $M|M^{2+}$ (saturated solution of a sparingly soluble salt, $MX_2||M^{2+}$ (0.001 mol dm⁻³)| M). The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298K is 0.059 V.

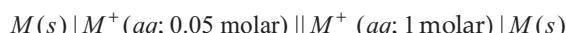
(2012)

28. The solubility product (K_{sp} : mol³dm⁻⁹) of MX_2 at 298 based on the information available the given concentration cell is (take $2.303 \times R \times 298/F = 0.059\text{ V}$)
 (a) 1×10^{-15} (b) 4×10^{-15} (c) 1×10^{-12} (d) 4×10^{-12}

29. The value of ΔG (kJ mol⁻¹) for the given cell is (take $1\text{ F} = 96500\text{ C mol}^{-1}$)
 (a) - 5.7 (b) 5.7 (c) 11.4 (d) - 11.4

Passage II

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :



For the above electrolytic cell the magnitude of the cell potential $|E_{\text{cell}}| = 70\text{ mV}$.

(2010)

30. For the above cell

- (a) $E_{\text{cell}} < 0; \Delta G > 0$ (b) $E_{\text{cell}} > 0; \Delta G < 0$
 (c) $E_{\text{cell}} < 0; \Delta G^\circ > 0$ (d) $E_{\text{cell}} > 0; \Delta G^\circ < 0$

31. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be

- (a) 35 mV (b) 70 mV
 (c) 140 mV (d) 700 mV

Passage III

Redox reaction play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their $E^\circ(V$ with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions 17–19.

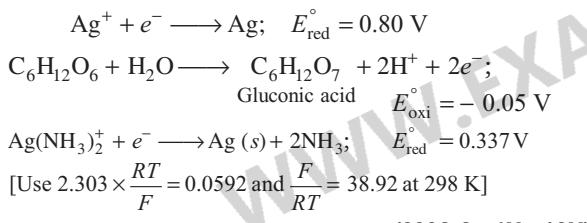
(2007, 4 × 3M = 12M)

$I_2 + 2e^- \rightarrow 2I^-$	$E^\circ = 0.54$
$Cl_2 + 2e^- \rightarrow 2Cl^-$	$E^\circ = 1.36$
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	$E^\circ = 1.50$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E^\circ = 0.77$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E^\circ = 1.23$

32. Among the following, identify the correct statement.
- Chloride ion is oxidised by O_2
 - Fe^{2+} is oxidised by iodine
 - Iodide ion is oxidised by chlorine
 - Mn^{2+} is oxidised by chlorine
33. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
- O_2 oxidises Mn^{2+} to Mn^{3+}
 - O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
 - Fe^{3+} oxidises H_2O to O_2
 - Mn^{3+} oxidises H_2O to O_2
34. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in the presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of
- $Fe_4[Fe(CN)_6]_3$
 - $Fe_3[Fe(CN)_6]_2$
 - $Fe_4[Fe(CN)_6]_2$
 - $Fe_3[Fe(CN)_6]_3$

Passage IV

Tollen's reagent is used for the detection of aldehydes. When a solution of $AgNO_3$ is added to glucose with NH_4OH , then gluconic acid is formed.

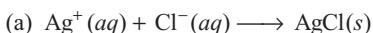


35. $2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7^- + 2H^+$
Find $\ln K$ of this reaction.
(a) 66.13 (b) 58.38 (c) 28.30 (d) 46.29
36. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?
(a) E_{oxi}° will increase by a factor of 0.65 from E_{oxi}°
(b) E_{oxi}° will decrease by a factor of 0.65 from E_{oxi}°
(c) E_{red}° will increase by a factor of 0.65 from E_{red}°
(d) E_{red}° will decrease by a factor of 0.65 from E_{red}°
37. Ammonia is always added in this reaction. Which of the following must be incorrect?
(a) NH_3 combines with Ag^+ to form a complex
(b) $Ag(NH_3)_2^+$ is a stronger oxidising reagent than Ag^+
(c) In the absence of NH_3 silver salt of gluconic acid is formed
(d) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode

Subjective Questions

38. We have taken a saturated solution of $AgBr$, K_{sp} is 12×10^{-14} . If 10^{-7} M of $AgNO_3$ are added to 1 L of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} Sm^{-1} units. **(2006, 6M)**
Given, $\lambda_{(Ag^+)}^\circ = 6 \times 10^{-3} Sm^2 mol^{-1}$,
 $\lambda_{(Br^-)}^\circ = 8 \times 10^{-3} Sm^2 mol^{-1}$,
 $\lambda_{(NO_3^-)}^\circ = 7 \times 10^{-3} Sm^2 mol^{-1}$.

39. Calculate ΔG_f° of the following reaction:

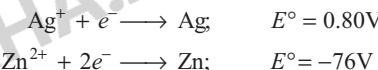


Given

$\Delta G_f^\circ(AgCl)$	-109 kJ/mol
$\Delta G_f^\circ(Cl^-)$	-129 kJ/mol
$\Delta G_f^\circ(Ag^+)$	77 kJ/mol

Represent the above reaction in form of a cell. Calculate E° of the cell. Find $\log_{10} K_{sp}$ of $AgCl$. **(2005, 6M)**

- (b) 6.539×10^{-2} g of metallic Zn ($u = 65.39$) was added to 100 mL of saturated solution of $AgCl$. Calculate $\log_{10} \frac{[Zn^{2+}]}{[Ag^+]}$. Given that



Also find how many moles of Ag will be formed?

40. Find the equilibrium constant for the reaction



Given that $E_{Cu^{2+}/Cu^+}^\circ = 0.15 V$,
 $E_{In^{2+}/In^+}^\circ = -0.4 V$,
 $E_{In^{3+}/In^+}^\circ = -0.42 V$ **(2004, 4M)**

41. (a) Will pH value of water be same at temperature $25^\circ C$ and $4^\circ C$? Justify in not more than 2 or 3 sentences.
(b) Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than the other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the concentration of $CuSO_4$ in the other cell. Given : $2.303 RT/F = 0.06 V$. **(2003, 2M)**

42. The standard potential of the following cell is 0.23 V at $15^\circ C$ and 0.21 V at $35^\circ C$.



- (i) Write the cell reaction.

- (ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range $15^\circ C$ to $35^\circ C$.

- (iii) Calculate the solubility of $AgCl$ in water at $25^\circ C$.

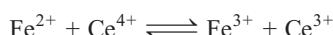
Given, the standard reduction potential of the $(Ag^+(aq)/Ag(s))$ is 0.80 V at $25^\circ C$. **(2001, 10M)**

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43. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the emf of the cell $\text{Ag} | \text{Ag}^+$ (Saturated Ag_2CrO_4 solution.) || Ag^+ (0.1 M) | Ag is 0.164 V at 298 K. (1998, 6M)

44. Calculate the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- couples. (1998, 3M)

45. Calculate the equilibrium constant for the reaction



Given, $E^\circ (\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.44$ V, $E^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.68$ V (1997, 2M)

46. The standard reduction potential for Cu^{2+}/Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $\text{Cu}(\text{OH})_2$ is 1.0×10^{-19} . (1996, 3M)

47. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+} . It is found that 5 % of Fe^{3+} remains at equilibrium at 25°C. Calculate $E^\circ (\text{Hg}^{2+}/\text{Hg})$ assuming that the only reaction that occurs is



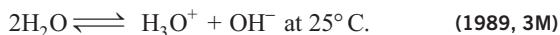
Given, $E^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77$ V (1995, 4M)

48. The standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI , $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI . Also calculate the standard reduction potential of the $\text{I}^-/\text{AgI}/\text{Ag}$ electrode. (1994, 3M)

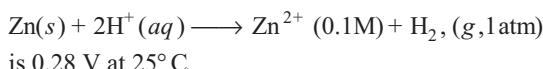
49. Zinc granules are added in excess to a 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni are –0.75 V and –0.24 V respectively. Find out the concentration of Ni^{2+} in solution at equilibrium. (1991, 2M)

50. The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 V respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell, at 25°C, be zero if the concentration of Cu^{2+} is 0.01 M? (1990, 3M)

51. The standard reduction potential at 25°C of the reaction, $2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$, is –0.8277 V. Calculate the equilibrium constant for the reaction,



52. The emf of a cell corresponding to the reaction.



Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.



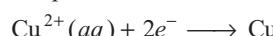
53. Give reasons in one or two sentences.

“Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor.” (1985, 1M)

54. Consider the cell,



The standard reduction potentials are 0.350 V for



and –0.763 V for $\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}$

(i) Write down the cell reaction.

(ii) Calculate the emf of the cell.

(iii) Is the cell reaction spontaneous or not? (1982, 2M)

Integer Answer Type Questions

55. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinised Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2 . The conductance of this solution was found to be 5×10^{-7} S. The pH of the solution is 4. The value of limiting molar conductivity (Λ_m°) of this weak monobasic acid in aqueous solution is $Z \times 10^2 \text{ S cm}^{-1} \text{ mol}^{-1}$. The value of Z is (2017 Adv.)

56. All the energy released from the reaction $X \rightarrow Y, \Delta_r G^\circ = -193 \text{ kJ mol}^{-1}$ is used for oxidising M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E^\circ = -0.25$ V.

Under standard conditions, the number of moles of M^+ oxidised when one mole of X is converted to Y is [F = 96500 C mol⁻¹] (2015 Adv.)

Answers

Topic 1

- | | | | |
|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (a) | 4. (c) |
| 5. (b) | 6. (b) | 7. (c) | 8. (a) |
| 9. (d) | 10. (b) | 11. (d) | 12. (b) |
| 13. (c) | 14. (a) | 15. (c) | 16. (a) |
| 17. (a) | 18. (b) | 19. (d) | 20. (c) |
| 21. (d) | 22. (c) | 23. (c) | 24. (a) |

- | | | | |
|--------------------------------------|--------------------------------------|-----------------------------|--------------------------|
| 25. (a, b) | 26. (a,b,d) | 27. (13.32) | 28. (10) |
| 29. ($-11.62 \text{ JK mol}^{-1}$) | 30. (b) | 31. (d) | |
| 32. (d) | 34. ($8 \times 10^{-5} \text{ M}$) | 35. (0.01 V) | 36. (300 cm^2) |
| 37. (-245.11 kJ) | 40. (1.4085 M) | 41. (-0.037 V) | 42. (0.154 M) |
| 43. (347.40 kJ) | 45. (190.50 g) | 46. (10^{-4} M) | 47. (19.1 g) |
| 48. (265 Ah) | 49. (125 s) | 50. (0.80 A) | 51. (1.172 M) |

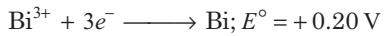
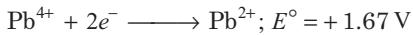
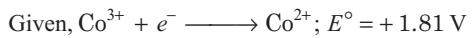
Topic 2

1. (b) 2. (a) 3. (c) 4. (b)
 5. (c) 6. (d) 7. (a) 8. (a)
 9. (b) 10. (b) 11. (c) 12. (c)
 13. (a) 14. (c) 15. (a) 16. (d)
 17. (a) 18. (d) 19. (d) 20. (b)
 21. (b) 22. (b) 23. (b) 24. (c)
 25. (144) 26. (-6) 27. (-14.16) 28. (b)

29. (d) 30. (b) 31. (c) 32. (c)
 33. (d) 34. (a) 35. (b) 36. (c)
 37. (d) 38. (55) 40. (10^{10}) 41. (0.05 M)
 43. (2.45×10^{-12}) 44. (5.89×10^7)
 45. (6.88×10^{12}) 46. (-0.222 V) 47. (0.7926 V) 49. (1.7×10^{17})
 50. (1.57×10^{-9}) 51. (1.04×10^{-14}) 52. (8.6)
 55. (6×10^2 S cm $^{-1}$ mol $^{-1}$) 56. (4 mol)

Hints & Solutions**Topic 1 Electrochemical Cells**

- 1.** **Key Idea** Negative E° means that redox couple is weaker oxidising agent than H $^+$ / H₂ couple. Positive E° means that redox couple is a stronger oxidising agent than H $^+$ / H₂ couple



Oxidising power of the species increases in the order of Bi $^{3+}$ < Ce $^{4+}$ < Pb $^{4+}$ < Co $^{3+}$.

Higher the emf value, stronger the oxidising power. The maximum value of emf is possessed by Co $^{3+}$. Hence, it has maximum oxidising power. Whereas Bi $^{3+}$ possess the lowest emf value. Hence, it has minimum oxidising power.

- 2.** A solution of Ni(NO₃)₂ is electrolysed between platinum electrodes using 0.1 Faraday electricity. It means that 0.1 equivalent of Ni $^{2+}$ will be discharged.

Electrolysis of Ni(NO₃)₂ gives



Number of equivalents = Number of moles \times number of electrons.

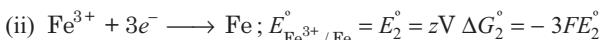
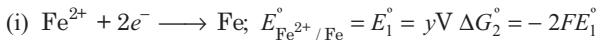
0.1 = Number of moles \times 2

$$\therefore \text{Number of moles of Ni} = \frac{0.1}{2} = 0.05$$

- 3.** Fe $^{2+}$ (aq) + Ag $^+$ (aq) \longrightarrow Fe $^{3+}$ (aq) + Ag(s)

$$\therefore E_{\text{cell}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = xV - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ \quad \dots (\text{i})$$

Now, for two half-cells



So, Fe $^{3+}$ + e $^-$ \longrightarrow Fe $^{2+}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = E_3^\circ = ?$

$$; \Delta G_3^\circ = -1 \times FE_3^\circ$$

Again, $\Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ$

$$\Rightarrow -FE_3^\circ = -3FE_2^\circ - (-2FE_1^\circ)$$

$$\Rightarrow -E_3^\circ = 2E_1^\circ - 3E_2^\circ \Rightarrow E_3^\circ = 3E_2^\circ - 2E_1^\circ$$

$$\Rightarrow E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = (3z - 2y)V$$

So, from equation (i)

$$E_{\text{cell}}^\circ = xV - (3z - 2y)V = (x - 3z + 2y)V$$

- 4.** Higher the standard reduction potential ($E_{M^{n+}/M}^\circ$), better is oxidising agent. Among the given, $E_{\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}}^\circ$ is highest, hence S₂O₈²⁻ is the strongest oxidising agent.

The decreasing order of oxidising agent among the given option is as follows:

$$\text{S}_2\text{O}_8^{2-} > \text{Au}^{3+} > \text{O}_2 > \text{Br}_2$$

- 5.** Reducing power of an element

$$\propto \frac{1}{\text{Standard reduction potential}}$$

Here, $E_{M^{2+}/M}^\circ$ values of the given metals are as,

Metals	Ni	Zn	Mg	Ca
$E^\circ(\text{V})$	-0.25	-0.76	-2.36	-2.87

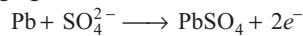
Reducing power

Thus, the correct order of increasing reducing power of the given metal is,

$$\text{Ni} < \text{Zn} < \text{Mg} < \text{Ca}.$$

- 6.** **Key Idea** This question is based upon Faraday's first law which states that "Mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

During charging:



$$\Rightarrow 1 \text{ F} \equiv 1 \text{ g-equiv. of PbSO}_4$$

$$= \frac{1}{2} \text{ mol of PbSO}_4 \Rightarrow \frac{303}{2} \text{ g PbSO}_4$$

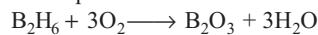
$$\therefore 0.05 \text{ F} \equiv \frac{303}{2} \times 0.05 \text{ g of PbSO}_4 = 7.575 \text{ g of PbSO}_4$$

- 7.** Given that, $i = 100$ amp. also, 27.66 g of diborane (B₂H₆)

$$\text{Molecular mass of B}_2\text{H}_6 = 10.8 \times 2 + 6 = 27.6$$

$$\text{Number of moles of B}_2\text{H}_6 \text{ in } 27.66 \text{ g} = \frac{\text{Given mass}}{\text{Molar mass}} = \frac{27.66}{27.6} \approx 1$$

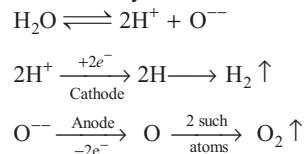
Now consider the equation



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From the equation we can interpret that 3 moles of oxygen is required to burn 1 mole (i.e. 27.6 g) B_2H_6 completely.

Also consider the electrolysis reaction of water i.e.



From the above equation it can be easily interpreted that in electrolysis of water for the production of 1 mole of oxygen from 1 mole of H_2O at anode 4 moles electrons are required.

Likewise for the production of 3 moles of O_2 $12(3 \times 4)$ moles of electrons will be needed.

So, the total amount of charge required to produce 3 moles of oxygen will be $12 \times F$ or 12×96500

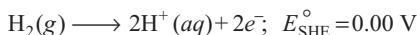
We know $Q = it$

$$\text{So, } 12 \times 96500 = 100 \times t \text{ in seconds}$$

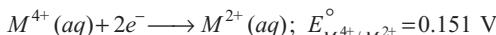
$$\text{or } \frac{12 \times 96500}{100 \times 3600} = t \text{ in hours} = 3.2 \text{ hours}$$

8. The substances which have lower reduction potentials are stronger reducing agents. Therefore, Cr ($E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.74 \text{ V}$) is the strongest reducing agent among all the other given options.

9. Oxidation at anode



Reduction at cathode



Net: $M^{4+}(\text{aq}) + \text{H}_2(\text{g}) \longrightarrow M^{2+}(\text{aq}) + 2\text{H}^+(\text{aq})$;

$$K = \frac{[M^{2+}] [H^+]^2}{[M^{4+}] P_{\text{H}_2}} (E_{\text{cell}}^\circ = 0.151 \text{ V}) = \frac{[M^{2+}]}{[M^{4+}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log K$$

$$0.092 = 0.151 - \frac{0.059}{2} \log \frac{[M^{2+}]}{[M^{4+}]}$$

$$0.059 = \frac{0.059}{2} \log 10^x$$

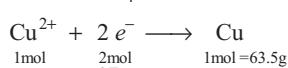
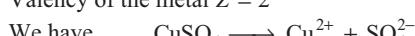
$$\therefore \log 10^x = 2$$

$$\therefore x = 2$$

10. Given, $Q = 2F$

Atomic mass of Cu = 63.5u

Valency of the metal $Z = 2$



Alternatively,

$$W = ZQ = \frac{E}{F} \cdot 2F = 2E = \frac{2 \times 63.5}{2} = 63.5$$

11. Higher the standard reduction potential, better is oxidising agent. Among the given $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ$ is highest, hence MnO_4^- is the strongest oxidising agent.

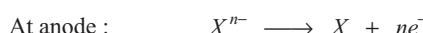
12. 0.01 mol of $\text{H}_2 = 0.02 \text{ g equivalent}$

$$\Rightarrow \text{Coulombs required} = 0.02 \times 96500 = 1930 \text{ C}$$

$$\Rightarrow Q = It = 1930 \text{ C}$$

$$\Rightarrow t = \frac{1930}{10 \times 10^{-3}} = 19.3 \times 10^4 \text{ s}$$

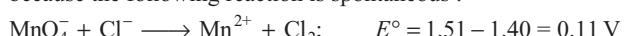
13. In electrolytic cell electrolysis occur at the cost of electricity : At cathode : $M^{n+} + ne \longrightarrow M$ (electron gone in solution)



(electron supplied to anode)

Therefore, electron is moving from cathode to anode via internal circuit.

14. MnO_4^- cannot be used for oxidation of Fe^{2+} in HCl medium because the following reaction is spontaneous :



In all other cases, the redox process between oxidising agent and medium (HCl or H_2SO_4) are non-spontaneous, would not interfere oxidation of Fe^{2+} .

15. One of the requirement for electrolyte used in salt-bridge is, both cation and anion must have comparable size so that they migrate towards electrodes of opposite polarity at comparable speeds.

16. Higher the value of reduction potential, stronger the oxidising agent.

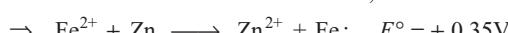
$$\therefore E^\circ : Z > Y > X$$

$\Rightarrow Y$ will oxidise X but not Z .

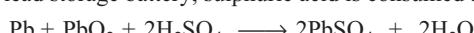
17. Lower the value of E° , stronger the reducing agent.

Reducing power:

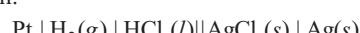
$$Y (E^\circ = -3.03 \text{ V}) > Z (E^\circ = -1.18 \text{ V}) > X (E^\circ = 0.52 \text{ V}).$$



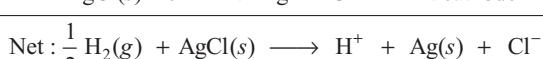
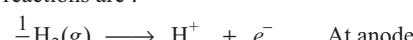
19. In a lead storage battery, sulphuric acid is consumed as :



20. In a galvanic cell, oxidation occur in the left hand electrode chamber and reduction in right hand electrode chamber. In the following cell.



The cell reactions are :



21. One gram equivalent of an electrolyte required 1.0 mole of electronic charge for discharging.

22. In aqueous solution, only those ions who are less electropositive than hydrogen ($E^\circ > 0$) would be deposited.

Therefore, in the present case, only Ag, Hg and Cu would be deposited on passing electricity through aqueous solution of these ions, Mg will not be deposited.

Also, higher the value of E° , easier will be their reduction, therefore, the sequence in which ions will be deposited on increasing voltage across the electrodes is :



- 23.** Faraday's law of electrolysis is related to equivalent weight of electrolytes as "the number of Faraday's passed is equal to the number of gram equivalent of electrolytes discharged."

- 24.** Lower the value of E° , stronger the reducing agent.

- 25. PLAN** This problem is based on characteristics of salt-bridge.

Functions of salt-bridge are

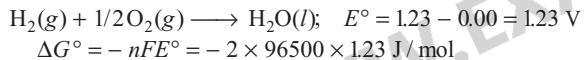
- (i) It connects the two half-cells and completes the cell circuit.
- (ii) It keeps the solutions of two half-cells and complete the cell circuit but does not participate chemically in the cell reaction.
- (iii) It maintains the diffusion of ions from one electrode to another electrode.
- (iv) A cell reaction may also occur in the absence of salt-bridge. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt-bridge." So, option (c) is incorrect.
- (v) This prevent mixing of two electrolytic solutions hence, option (d) is incorrect choice.

Hence, correct choices are (a), (b).

- 26.** Metals with E° value less than 0.96 V will be able to reduce NO_3^- in aqueous solution. Therefore, metals V ($E^\circ = -1.19$ V), Fe ($E^\circ = -0.04$ V), Hg ($E^\circ = 0.86$ V) will all reduce NO_3^- but Au ($E^\circ = 1.40$ V) cannot reduce NO_3^- in aqueous solution.

- 27.** Vessel is insulated, thus $q = 0$

For the given reaction :



Therefore, work derived from this fuel cell using 70% efficiency and on consumption of 1.0×10^{-3} mol of $\text{H}_2(g)$

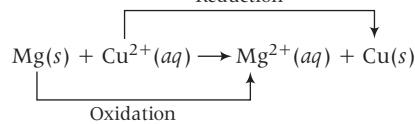
$$= 2 \times 96500 \times 1.23 \times 0.7 \times 1 \times 10^{-3}$$

$$= 166.17 \text{ J}$$

This work done = change in internal energy (for monoatomic gas, $C_{V,m} = 3R/2$),

$$166.17 = nC_{V,m}\Delta T \Rightarrow \Delta T = \frac{166.17 \times 2}{1 \times 3 \times 8.314} \Rightarrow 13.32 \text{ K}$$

- 28.** Equation of cell reaction according to the cell notation given, is



Given, $E_{\text{cell}}^\circ = 2.70 \text{ V}$, $T = 300 \text{ K}$

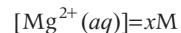
with $[\text{Mg}^{2+}(aq)] = 1 \text{ M}$ and $[\text{Cu}^{2+}(aq)] = 1 \text{ M}$

and $n=2$

Further, $E_{\text{cell}} = 2.67 \text{ V}$

with $[\text{Cu}^{2+}(aq)] = 1 \text{ M}$

and



and

$$\frac{F}{R} = 11500 \text{ KV}^{-1}$$

where F = Faraday constant, R = gas constant

From the formula,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \frac{[\text{Mg}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]}$$

After putting the given values

$$2.67 = 2.70 - \frac{RT}{2F} \ln \frac{x}{1}$$

$$\text{or} \quad 2.67 = 2.70 - \frac{R \times 300}{2F} \times \ln x$$

$$-0.03 = \frac{-R \times 300}{2F} \times \ln x$$

$$\text{or} \quad \ln x = \frac{0.03 \times 2}{300} \times \frac{F}{R} = \frac{0.03 \times 2 \times 11500}{300} = 2.30$$

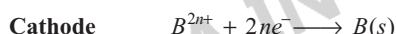
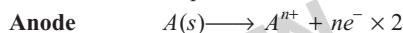
So, $\ln x = 2.30$

or $x = 10$ (as given $\ln(10) = 2.30$)

- 29.** Given,



So, reactions at respective electrode will be



Overall reaction



Further,

$\Delta H^\circ = 2\Delta G^\circ$ and $E_{\text{cell}} = 0$ is also given

Now by using the Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

After putting the values

$$0 = E_{\text{cell}}^\circ - \frac{RT}{2nF} \ln \frac{[A^{n+}]^2}{[B^{2n+}]}$$

$$\text{or} \quad E^\circ = \frac{RT}{2nF} \ln \frac{[2]^2}{[1]} = \frac{RT}{2nF} \ln 4 \quad \dots(i)$$

Further from the formula,

$$\Delta G^\circ = -nFE^\circ \Rightarrow \Delta G^\circ = -2nFE^\circ$$

Now putting the value of E° from eq. (i)

$$\Delta G^\circ = -2nF \times \frac{RT}{2nF} \ln 4 \quad \dots(ii)$$

$$\Delta G^\circ = -RT \ln 4$$

Finally, using the formula

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 2\Delta G^\circ - T\Delta S^\circ \quad (\text{as } \Delta H^\circ = 2\Delta G^\circ, \text{ given})$$

$$\Delta G^\circ = T\Delta S^\circ$$

$$\text{or} \quad \Delta S^\circ = \frac{\Delta G^\circ}{T} = \frac{-RT \ln 4}{T}$$

(from eq. (ii), $\Delta G^\circ = -RT \ln 4$)

$$= -R \ln 4 = -8.3 \times 2 \times 0.7$$

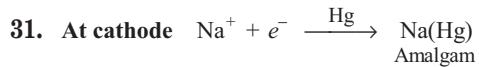
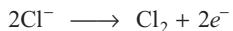
(as all values given)

$$= -11.62 \text{ J/K-mol}$$

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30. Moles of NaCl electrolysed = $4 \times \frac{500}{1000} = 2.0$

\Rightarrow moles of Cl_2 produced = 1.0



Two moles of Na formed during electrolysis would produce two moles of Na(Hg) amalgam.

$$\Rightarrow \text{mass of amalgam} = 2 \times (23 + 200) = 446 \text{ g}$$

32. Two Faraday of electric charge would be required for electrolysis of 2.0 moles of NaCl.

$$\Rightarrow \text{total coulombs} = 2 \times 96500 = 193000 \text{ C}$$

33. Since, activities of all the ions are unity, $E_{\text{cell}} = E_{\text{cell}}^\circ$. Also, left hand electrode is at lower reduction potential, it act as anode and $E^\circ = E^\circ(\text{Ce}^{4+}, \text{Ce}^{3+}) - E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.84$

i.e. electrons will flow from left to right hand electrode and current from right hand electrode [Pt (2)] to left hand electrode [Pt(1)].

Also, $E = E^\circ - 0.0592 \log \frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]}$

As electrolysis proceeds, E will decrease and therefore, current.

34. The number of Faraday's passed = $\frac{2 \times 10^{-3} \times 16 \times 60}{96500} = 1.99 \times 10^{-5}$

$$\Rightarrow \text{number of gram equivalent of } \text{Cu}^{2+} \text{ deposited} = 1.99 \times 10^{-5}$$

$$\Rightarrow \text{number of moles of } \text{Cu}^{2+} \text{ deposited} = \frac{1.99}{2} \times 10^{-5} \approx 10^{-5}$$

Absorbance is directly proportional to $[\text{Cu}^{2+}]$. Therefore, if 'C' be the initial molarity, 0.5 C will be the final molarity.

$$\Rightarrow 0.5 \text{ C} \times 0.25 = 10^{-5} \Rightarrow C = 8 \times 10^{-5} \text{ M}$$

35. The number of Faraday's passed = $\frac{9.65 \times 60 \times 60}{96500} = 0.36 \text{ F}$

After electrolysis : $[\text{Ag}^+] = 1.36 \text{ M}$

$$[\text{Cu}^{2+}] = 1 - \frac{0.36}{2} = 0.82 \text{ M}$$

E_1 (before electrolysis) = E°

$$E_2 \text{ (after electrolysis)} = E^\circ - \frac{0.0592}{2} \log \frac{[\text{Ag}^+]}{[\text{Cu}^{2+}]}$$

$$\Rightarrow E_1 - E_2 = \frac{0.0592}{2} \log \frac{(1.36)^2}{0.82} = 0.01 \text{ V (decreased)}$$

36. Coulombs passed = $8.46 \times 8 \times 60 \times 60 = 243648 \text{ C}$

$$\text{Number of Faraday's passed} = \frac{243648}{96500} = 2.52$$

$$\text{Weight of Cu plated} = 2.52 \times \frac{63.5}{2} \text{ g} = 80.01 \text{ g}$$

$$\text{Volume of Cu plated} = \frac{80.01}{10.5} = 7.62 \text{ cm}^3$$

$$\Rightarrow \text{Area plated out} = \frac{7.62}{0.00254} = 3000 \text{ cm}^2$$

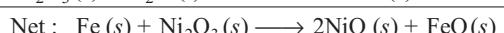
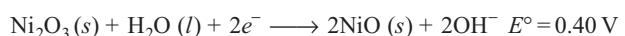
37. Given, $\text{FeO}(s)/\text{Fe}(s)$ $E^\circ = -0.87 \text{ V}$
and $\text{Ni}_2\text{O}_3/\text{NiO}(s)$ $E^\circ = +0.40 \text{ V}$

Electrode at lower reduction potential act as anode and that at higher reduction potential act as cathode.

(i) Electrodes reaction :



$$E^\circ = +0.87 \text{ V}$$



$$E^\circ = 1.27 \text{ V}$$

(ii) Emf is independent of concentration of KOH.

(iii) Maximum amount of energy that can be obtained = ΔG°
 $\Rightarrow \Delta G^\circ = -nEF = -2 \times 1.27 \times 96500 \text{ J} = -245.11 \text{ kJ}$
i.e. 245.11 kJ is the maximum amount of obtainable energy.

38. (i) $E = 0.78 - 0.0592 \log \frac{1}{8^2} = 0.887 \text{ V}$

(ii) $E = 0.78 - 0.0592 \log \frac{1}{(10^{-7})^2} = -0.0488 \text{ V}$

39. Molar mass of Cr = 52 g

$$\text{Equivalent mass of Cr} = \frac{52}{6} \text{ g}$$

(i) Mass of Cr deposited on passing 24000 Coulombs

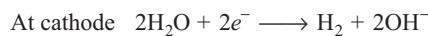
$$= \frac{24000}{96500} \times \frac{52}{6} \text{ g} = 2.15 \text{ g}$$

(ii) Number of gram equivalent of Cr = $\frac{1.5}{52} \times 6 = \frac{9}{52}$

$$\Rightarrow \text{Coulombs required for } 1.5 \text{ g Cr} = \frac{9}{52} \times 96500 = It$$

$$\Rightarrow t = \frac{9 \times 96500}{52 \times 12.5} \text{ s} = 22.27 \text{ min}$$

40. At anode $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e^-$



$$1 \text{ kg Cl}_2 = \frac{1000}{35.5} \text{ equivalent of Cl}_2 = 28.17 \text{ equivalent}$$

\Rightarrow Theoretical electricity requirement = 28.17 F

\therefore Efficiency is only 62%

\therefore Electricity requirement (experimental)

$$= \frac{28.17 \times 100}{62} \text{ F} = 45.44 \text{ F}$$

$$\Rightarrow 45.44 \times 96500 = 25 t \text{ (in second)}$$

$$\Rightarrow t = 48.72 \text{ h}$$

Also, gram equivalent of HO^- produced = 28.17

$$\Rightarrow \text{Molarity of } \text{HO}^- = \frac{28.17}{20} = 1.4085 \text{ M}$$

41. $[\text{Ag}^+]$ in left hand electrode chamber = $\frac{2.8 \times 10^{-10}}{0.2} = 1.4 \times 10^{-9} \text{ M}$

$$[\text{Ag}^+]$$
 in right hand electrode chamber = $\frac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10} \text{ M}$

$$\text{emf} = 0 - 0.0592 \log \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} \\ = -0.0592 \log \frac{1.4 \times 10^{-9}}{3.3 \times 10^{-10}} = -0.037 \text{ V}$$

Therefore, the cell as written is non-spontaneous and its reverse will be spontaneous with $\text{emf} = 0.037 \text{ V}$.

42. Faraday's passed $= \frac{1.7 \times 230}{96500} = 4.052 \times 10^{-3} \text{ F}$

Faradays used for reduction of $\text{Zn}^{2+} = 4.052 \times 10^{-3} \times 0.9$
 $= 3.65 \times 10^{-3}$

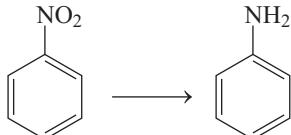
\Rightarrow Meq. of Zn^{2+} reduced = 3.65

Initial meq. of Zn^{2+} = $300 \times 0.16 \times 2 = 96$

\Rightarrow Meq. of Zn^{2+} remaining = $96 - 3.65 = 92.35$

\Rightarrow Molarity of $\text{Zn}^{2+} = \frac{92.35}{2} \times \frac{1}{300} = 0.154 \text{ M}$

43.



Change in oxidation number at nitrogen = $4 - (-2) = 6$

Equivalent weight of nitrobenzene = $\frac{123}{6} \text{ g}$

\Rightarrow gram equivalent of nitrobenzene = $\frac{12.3 \times 6}{123} = 0.60$

\Rightarrow Theoretical requirement = $0.60 \times 96500 \text{ C} = 57900 \text{ C}$

\Rightarrow Actual requirement of electricity = $2 \times 57900 = 115800 \text{ C}$

$\therefore V \times C = J$

\Rightarrow Energy consumed = $115800 \times 3 \text{ J} = 347.40 \text{ kJ}$

44. If the salt is CuSO_4

During deposition of Cu at cathode, $\text{O}_2(g)$ will evolve at anode
 gram-equivalent of Cu deposited = $\frac{0.4 \times 2}{63.5} = 0.0126$

Volume of O_2 liberated at NTP at anode

= $0.0126 \times 5600 \text{ mL} = 70.56 \text{ mL}$

In the next 7 min, H_2 at cathode and O_2 at anode would be produced.

Faraday's passed = $\frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$

\Rightarrow Volume of H_2 (at NTP) = $5.22 \times 10^{-3} \times 11200 \text{ mL}$
 $= 58.46 \text{ mL}$

Volume of O_2 (at NTP) = $5.22 \times 10^{-3} \times 5600 \text{ mL} = 29.23 \text{ mL}$

Therefore, $\text{O}_2(g)$ at NTP = $70.56 + 29.23 = 99.79 \text{ mL}$

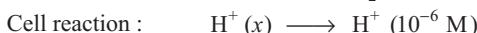
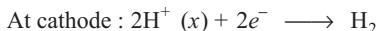
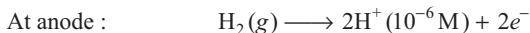
$\text{H}_2(g)$ at NTP = 58.46 mL

45. Total number of gram equivalent of H_2 used = $\frac{67.2}{11.2} = 6$

$\Rightarrow 6 \times 96500 = 15 \times 60 \times I \Rightarrow I = 643.33 \text{ A}$

Mass of Cu deposited = $6 \times \frac{63.5}{2} \text{ g} = 190.50 \text{ g}$

46. \because Emf = 0.118 V > 0, it is galvanic cell and anode is negative electrode :



Emf = 0.118 V = $0 - 0.0592 \log \frac{10^{-6}}{x} \Rightarrow x = 10^{-4} \text{ M}$

47. 100 W lamp will produce 100 Js^{-1} .

$\Rightarrow 100 \text{ J} = 110 \times C \Rightarrow C = \frac{10}{11} \text{ Coulombs}$

Therefore, total Coulomb passed in 10 h

$$= \frac{10}{11} \times 10 \times 60 \times 60 = 32727.27 \text{ C}$$

Number of gram equivalent of Cd^{2+} deposited

$$= \frac{32727.27}{96500} = 0.34$$

Weight of Cd deposited = $0.34 \times \frac{112.4}{2} \text{ g} = 19.1 \text{ g}$

48. For 1.0 L H_2SO_4 :

Initial mass of $\text{H}_2\text{SO}_4 = 1294 \times \frac{39}{100} = 504.66 \text{ g}$

Final mass of $\text{H}_2\text{SO}_4 = 1139 \times \frac{20}{100} = 227.80 \text{ g}$

$\Rightarrow \text{H}_2\text{SO}_4$ consumed/litre = $504.66 - 227.80 = 276.86 \text{ g}$

\Rightarrow Total H_2SO_4 used up = $276.86 \times 3.5 = 969.01 \text{ g}$
 $= \frac{969.01}{98} \text{ mol} = 9.888 \text{ mol}$

\because 1 mole of H_2SO_4 is associated with transfer of 1.0 mole of electrons, total of 9.888 moles of electron transfer has occurred.

Coulomb produced = 9.888×96500

Ampere-hour = $\frac{9.888 \times 96500}{3600} = 265 \text{ Ah}$

49. Volume of Ag coating = $80 \text{ cm}^2 \times \frac{0.005}{10} \text{ cm} = 0.04 \text{ cm}^3$

\Rightarrow mass of Ag coating = $0.04 \times 10.5 \text{ g} = 0.42 \text{ g}$

\Rightarrow gram equivalent of Ag = $\frac{0.42}{108} = \text{number of Faraday's}$

$\Rightarrow \frac{0.42}{108} \times 96500 \text{ C} = 3 \times t \Rightarrow t = 125 \text{ s}$

50. Moles of Au deposited = $\frac{9.85}{197} = 0.05$

\Rightarrow gram equivalent of Au deposited = $0.05 \times 3 = 0.15$

Now, according to Faraday's law of electrolysis, if same quantity of electricity is passed through different cells connected in series, same number of gram equivalents of electrolytes are discharged at respective electrodes.

\Rightarrow gram equivalent of Cu deposited = 0.15

\Rightarrow amount of Cu deposited = $0.15 \times \frac{63.5}{2} = 4.7625 \text{ g}$

Also, Coulombs passed = $0.15 \times 96500 = I \times 5 \times 60 \times 60$

$\Rightarrow I = \frac{0.15 \times 96500}{5 \times 3600} = 0.80 \text{ A}$

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51. During electrolysis, Ni^{2+} will be reduced at cathode and H_2O will be oxidised at anode.

$$\text{Number of Faraday's passed} = \frac{3.7 \times 6 \times 60 \times 60}{96500} = 0.828$$

\Rightarrow 0.828 g equivalent of Ni^{2+} will be deposited at cathode.

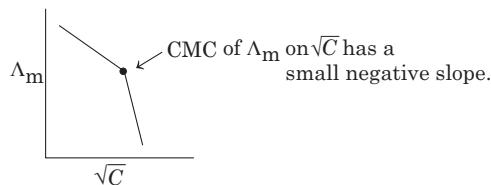
Initial moles of Ni^{2+} ion = $2 \times 0.5 = 1.0$

$$\text{Moles of } \text{Ni}^{2+} \text{ ion remaining after electrolysis} = 1.0 - \frac{0.828}{2} = 0.586$$

$$\Rightarrow \text{Molarity of } \text{Ni}^{2+} \text{ in final solution} = \frac{0.586}{0.50} = 1.172 \text{ M}$$

Topic 2 Conductivity of Electrolytic Solutions and their Measurement and Nernst Equation

1. **Key Idea** The aqueous solution of ionic surfactant, i.e. sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$) acts as a strong univalent type of electrolyte in the concentration range below the CMC and the linear function of dependence of Λ_m on \sqrt{C} has a small negative slope.

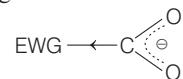


At normal or low concentration, sodium stearate [$\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$] behaves as strong electrolyte and for strong electrolyte, molar conductance (Λ_m) decreases with increase in concentration.

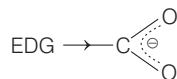
Above particular concentration, sodium stearate forms aggregates known as micelles. The concentration is called as CMC. Since, number of ions decreases and hence Λ_m also decreases.

Hence, option (b) is correct.

2. Electrical conductivity of the given aqueous solutions depends on the degree of ionisation. Degree of ionisation is directly proportional to the acidic strength. Electron withdrawing groups (EWGs) increases the stability of the carboxylate ion by dispersing the negative charge through resonance effect on the conjugate while electron donating groups (EDGs) decreases the stability of the carboxylate ion by intensifying the negative charge.



Acidity of carboxylic acids increases due to the presence of electron withdrawing groups (EWGs)



Acidity of carboxylic acids decreases due to the presence of electron donating groups

The correct order of acidic strength and electrical conductivity is as follows:



3. NaCl and KCl are strong electrolytes. So, the study of their molar conductances (Λ_m) can be experimentally verified by Debye-Hückel Onsager equation,

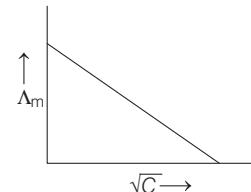
$$\Lambda_m^c = \Lambda_m^0 - B\sqrt{C}$$

Λ_m^c = molar conductance at concentration.

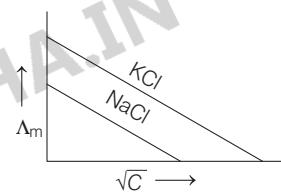
Λ_m^0 = molar conductance at infinite dilution. i.e. $C \rightarrow 0$

B = Debye-Hückel Onsager constant.

For (both NaCl and KCl) a strong binary electrolyte like AB , the nature of the plot of Λ_m vs \sqrt{C} will be



Size of Na^+ is being smaller than K^+ and Na^+ will remain in more hydrated state, i.e. larger sized in aqueous solution. As a result, ionic mobility as well as ionic conductance of Na^+ (or NaCl as Cl^- is common to NaCl and KCl) will be lower than K^+ (or KCl). Thus, the plot of Λ_m vs \sqrt{C} for NaCl and KCl is as follows :



4. The explanation of statements (S_1 and S_2) are as follows :

In conductivity cell, conductivity (κ) is equal to the sum of ionic conductances (c), of an electrolytic solution present in unit volume of the solution enclosed by two electrodes of unit area ($a \neq 1$) separated by a unit length ($l = 1$).

$$\kappa = c \times \frac{l}{a}$$

$$\Rightarrow \kappa = cw \text{ when } l = 1, a = 1$$

So, with decrease in the concentration of electrolyte, number of ions in the given unit volume also decreases, i.e. κ [conductivity] also decreases.

Thus, statement S_1 is wrong. S_2 : Molar conductivity (Λ_m) is defined as the conducting power of all the ions present in a solution containing 1 mole of an electrolyte.

$$\Lambda_m = \kappa \times V_{\text{mL}} = \kappa \times \frac{1000}{M}$$

where, V_{mL} = volume in mL containing 1 mole of electrolyte

m = molar concentration (mol/L)

So, in a conductivity cell

$$\Lambda_m \propto \frac{1}{M}$$

i.e. molar conductivity increases with decrease in the concentration (M) of electrolyte.

Thus, statement S_2 is correct.

5. **Key Idea** Gibbs energy of the reaction is related to E°_{cell} by the following formula

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ \Delta G^\circ &= \text{Gibbs energy of cell} \\ nF &= \text{amount of charge passed} \\ E &= \text{EMF of a cell}\end{aligned}$$

Given reaction is,



$$E^\circ_{\text{cell}} = 2.0 \text{ V}$$

$$F = 96000 \text{ C}$$

$$n = 2$$

To find the value of ΔG° (kJ mol⁻¹), we use the formula

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ \Delta G^\circ &= -2 \times 96000 \times 2 = -384000 \text{ J/mol}\end{aligned}$$

$$\text{In terms of kJ/mol, } \Delta G^\circ = \frac{-384000}{1000} = -384 \text{ kJ/mol}$$

6. According to Kohlrausch's law, the molar conductivity of HA at infinite dilution is given as,

$$\begin{aligned}\Lambda_m^\circ(\text{HA}) &= [\Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{Cl}^-)] + [\Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{A}^-)] \\ &\quad - [\Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{Cl}^-)] \\ &= 425.9 + 100.5 - 126.4 = 400 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Also, molar conductivity at given concentration is given as,

$$\Lambda_m = \frac{1000 \times \kappa}{M}$$

Given, $\kappa = \text{conductivity} \Rightarrow 5 \times 10^{-5} \text{ S cm}^{-1}$

$$M = \text{Molarity} \Rightarrow 0.001 \text{ M}$$

$$\therefore \Lambda_m = \frac{1000 \times 5 \times 10^{-5} \text{ S cm}^{-1}}{10^{-3} \text{ M}} = 50 \text{ S cm}^2 \text{ mol}^{-1}$$

Therefore, degree of dissociation (α) of HA is,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{50 \text{ S cm}^2 \text{ mol}^{-1}}{400 \text{ S cm}^2 \text{ mol}^{-1}} = 0.125$$

7. According to Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log Q$$

$$\text{Given, } \frac{2.303 RT}{F} = 0.059 \text{ V}$$

$$\therefore E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q$$

At equilibrium, $E_{\text{cell}} = 0$

$$E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_C$$

For the given reaction, $n = 2$

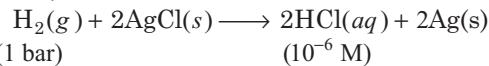
$$\text{Also, } K_C = 10 \times 10^{15}$$

$$\therefore E^\circ_{\text{cell}} = \frac{0.059}{2} \log (10 \times 10^{15}) = 0.472 \text{ V} \approx 0.473 \text{ V}$$

8.

Cell	E°_{cell} (SRP) = $E^\circ_C - E^\circ_A$	E°_{cell} free e^- transfer
Anode (A) Cathode (C)		
Zn Ag 1. $[\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}]$	$0.80 - (-0.76) = + 1.56 \text{ V}$ for $2e^-$	$+ \frac{1.56}{2} = + 0.78 \text{ V}$
Zn Fe 2. $[\text{Zn} + \text{Fe}^{2+} \rightarrow \text{Zn}^{2+} + \text{Fe}]$	$-0.44 - (-0.76) = + 0.32 \text{ V}$ for $2e^-$	$+ \frac{0.32}{2} = + 0.16 \text{ V}$
Zn Au 3. $[3\text{Zn} + 2\text{Au}^{3+} \rightarrow 3\text{Zn}^{2+} + 2\text{Au}]$	$1.40 - (-0.76) = + 2.4 \text{ V}$ for $6e^-$	$+ \frac{2.16}{6} = + 0.36 \text{ V}$
Zn Fe 4. $[3\text{Zn} + 2\text{Fe}^{3+} \rightarrow \text{Zn}^{2+} + 2\text{Fe}^{2+}]$	$0.77 - (-0.76) = + 1.53 \text{ V}$ for $2e^-$	$+ \frac{1.53}{2} = + 0.765 \text{ V}$

9. It is an electrochemical cell. The overall cell reaction can be written, as



(i) According to Nernst equation,

$$E_{\text{cell}} = (E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}) - \frac{2.303 \times RT}{n \times F} \log \frac{[\text{HCl}]^2 [\text{Ag}]^2}{p_{\text{H}_2} [\text{AgCl}]^2}$$

Here, (i) $E_c^\circ = E_{\text{AgCl}/\text{Ag}, \text{Cl}^-}^\circ = E_{\text{cathode}}^\circ$

(ii) $E_a^\circ = E_{2\text{H}^+/\text{H}_2}^\circ = 0.00 \text{ V}$

(Standard hydrogen electrode)

$$\begin{aligned}\Rightarrow 0.92 &= (E_c^\circ - 0) - 0.06 \times \log \frac{(10^{-6})^2 \times 1^2}{1 \times 1^2} \\ &= E_c^\circ + 0.06 \times 6 \times 2 \\ \Rightarrow E_c^\circ &= 0.92 - 0.72 = 0.20 \text{ V}\end{aligned}$$

Note 10^{-6} molal HCl is a very dilute solution.
So, $10^{-6} \text{ M} \approx 10^{-6} \text{ M}$

10. The relationship between standard electrode potential (E°) and equilibrium constant (K) of the cell reaction,



can be expressed as,

$$E^\circ = \frac{RT}{nF} \ln K \Rightarrow K = e^{nFE^\circ / RT}$$

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Given, $n = 2$, $F = 96000 \text{ C mol}^{-1}$

$$E^\circ = 2 \text{ V}, R = 8 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

$$\therefore K = e^{\frac{2 \times 96000 \times 2}{8 \times 300}} = e^{160}$$

11. The redox reaction is : $\text{Zn}(s) + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$\begin{aligned} \text{The Nernst equation is } E &= E^\circ - \frac{2.303RT}{2F} \log 10 \\ &= 1.1 - \frac{2.303RT}{2F} \end{aligned}$$

$$\begin{aligned} \text{Also, } \Delta G &= -nEF = -2F \left(1.1 - \frac{2.303RT}{2F} \right) \\ &= -2.2F + 2.303RT \\ &= 2.303RT - 2.2F \end{aligned}$$

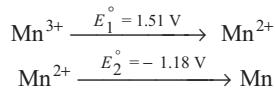
12. Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

13. Standard electrode potential of reaction [E°] can be calculated as

$$E_{\text{cell}}^\circ = E_R - E_P$$

where, E_R = SRP of reactant, E_P = SRP of product

If E_{cell}° = +ve, then reaction is spontaneous otherwise non-spontaneous.



\therefore For Mn^{2+} disproportionation,

$$E^\circ = -1.51 \text{ V} - 1.18 \text{ V} = -2.69 \text{ V} < 0$$

Thus, all reaction will not occur.

14. According to Debye Huckel Onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

where, λ_C = limiting equivalent conductivity at concentration C
 λ_∞ = limiting equivalent conductivity at infinite dilution

C = concentration

15. In order to solve the problem, calculate the value of cell constant of the first solution and then use this value of cell constant to calculate the value of k of second solution. Afterwards, finally calculate molar conductivity using value of k and m .

For first solution,

$$k = 1.4 \text{ Sm}^{-1}, R = 50 \Omega, M = 0.2$$

$$\text{Specific conductance } (\kappa) = \frac{1}{R} \times \frac{l}{A}$$

$$1.4 \text{ Sm}^{-1} = \frac{1}{50} \times \frac{l}{A}$$

$$\Rightarrow \frac{l}{A} = 50 \times 1.4 \text{ m}^{-1}$$

$$\text{For second solution, } R = 280, \frac{l}{A} = 50 \times 1.4 \text{ m}^{-1}$$

$$\kappa = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}$$

Now, molar conductivity

$$\begin{aligned} \lambda_m &= \frac{\kappa}{1000 \times m} \\ &= \frac{1/4}{1000 \times 0.5} = \frac{1}{2000} \\ &= 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

16. **PLAN** When different number of electrons are involved in a redox reaction

$$\begin{aligned} \Delta G_{\text{net}}^\circ &= \Delta G_1^\circ + \Delta G_2^\circ \\ -n_3FE_3^\circ &= -n_1FE_1^\circ - n_2FE_2^\circ \\ \therefore E_3^\circ &= \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3} \end{aligned}$$

(P) $E_3^\circ \text{ Fe}^{3+}/\text{Fe}$

Net reaction $\text{Fe}^{3+} \longrightarrow \text{Fe}$

$$\begin{array}{c} \text{is obtained from} \\ \text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+} & \frac{n}{n_1 = 1} & \frac{E^\circ}{E_1^\circ d = 0.77 \text{ V}} \\ \text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe} & n_2 = 2 & E_2^\circ = -0.44 \text{ V} \\ \therefore \frac{\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe}}{n_3 = 3} & n_3 = 3 & E_3^\circ = ? \\ E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3} = \frac{0.77 + 2(-0.44)}{3} = \frac{-0.11}{3} = -0.04 \text{ V} \end{array}$$

Thus, P — (3)

Net reaction

$$\begin{array}{c} 4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^- \\ \text{is obtained from} \\ 2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4e^- & \frac{n}{n_1 = 4} & \frac{E^\circ}{E_1^\circ = -1.23 \text{ V}} \\ 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \longrightarrow 4\text{OH}^- & n_2 = 4 & + 0.40 \text{ V} \\ \hline 4\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + 4e^- & n_3 = 4 & ? \\ E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3} = E_1^\circ + E_2^\circ \\ & & = -1.23 + 0.40 = -0.83 \text{ V} \end{array}$$

Thus, Q — (4)

(R) $\text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+$

For thus E° of $\text{Cu}^{2+} \longrightarrow \text{Cu}^+$

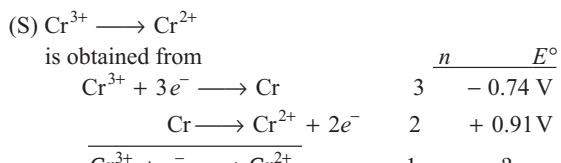
is also required.

$$\begin{array}{c} \text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu} & \frac{n}{n_1 = 2} & \frac{E^\circ}{E_1^\circ = 0.34 \text{ V}} \\ \text{Cu} \longrightarrow \text{Cu}^+ + e^- & n_2 = 1 & -0.52 \text{ V} \\ \hline \text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+ & n_3 = 1 & ? \\ E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3} = \frac{2 \times 0.34 + 1 \times (-0.52)}{1} = 0.16 \text{ V} \end{array}$$

Also,

$$\begin{array}{c} \text{Cu} \longrightarrow \text{Cu}^+ + e^- & \frac{n}{n_1 = 1} & \frac{E^\circ}{E_1^\circ = -0.52 \text{ V}} \\ \text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+ & n_2 = 1 & 0.10 \text{ V} \\ \hline \text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+ & n_3 = 2 & ? \\ E^\circ = -0.52 + 0.10 = -0.36 \text{ V} \end{array}$$

Thus, (R) — (1)



$$E_3^{\circ} = \frac{-0.74 \times 3 + 2 \times 0.91}{1} = -0.4 \text{ V}$$

Thus, S = (2)

P — (3), Q — (4), R — (1), S — (2)

17. The variation in conductivities in general can be seen as :

	In burette acid	In flask base	Curve
I.	Strong (HI)	Strong (NaOH)	Conductance first decreases due to formation of H_2O and then increases due to addition of strong electrolyte.
II.	Strong (CH_3COOH)	Weak (KOH)	Conductance increases slightly as NH_4^+ (salt) is hydrolysed forming HCl. After neutral point, it increases rapidly due to addition of strong
III.	Weak (CH_3COOH)	Strong (KOH)	Conductivity decreases due to neutralisation of conducting strong base and then remains constant due to addition of weak acid.

Conductance

 Volume of acid added

Conductance

 Volume of acid added

Conductance

 Weak acid added to strong base

In burette acid	In flask base	Curve	
IV.	Weak $[(\text{C}_2\text{H}_5)_3\text{N}]$	Weak (CH_3COOH)	Conductivity increases due to formation of ions and then remains constant due to addition of weak base.
V.	KX	AgNO_3	Insoluble salt AgX is formed, hence conductance remains constant. It increases due to addition of KX .

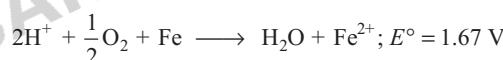
18. The half reactions are $\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2e^- \times 2$
 $\text{O}_2(g) + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}$
 $2\text{Fe}(s) + \text{O}_2(g) + 4\text{H}^+ \longrightarrow 2\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O}(l);$
 $E = E^{\circ} - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4(0.1)} = 1.57\text{V}$

19. As AgNO_3 is added to solution, KCl will be displaced according to following reaction.



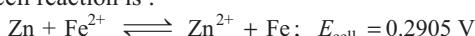
For every mole of KCl displaced from solution, one mole of KNO_3 comes in solution resulting in almost constant conductivity. As the end point is reached, added AgNO_3 remain in solution increasing ionic concentration, hence conductivity increases.

20. The net reaction is



$$\Delta G^{\circ} = -nE^{\circ}F = -\frac{2 \times 1.67 \times 96500}{1000} \text{ kJ} = -322.31 \text{ kJ}$$

21. The cell reaction is :



$$\Rightarrow E = E^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}$$

$$\Rightarrow E^{\circ} = 0.2905 + \frac{0.059}{2} \log \frac{0.1}{0.01} = 0.32 \text{ V}$$

$$\text{Also } E^{\circ} = \frac{0.059}{n} \log K$$

$$\Rightarrow \log K = \frac{2E^{\circ}}{0.059} = \frac{0.32}{0.0295}$$

$$\Rightarrow K = (10)^{0.32/0.0295}$$

22. In LiCl , NaCl and KCl , anions are same.

Cations have same charge but different size. Smaller cations are more heavily hydrated in aqueous solution giving larger hydrated radius and thus smaller ionic speeds and equivalent conductance.

⇒ Equivalent conductance : $\text{KCl} > \text{NaCl} > \text{LiCl}$

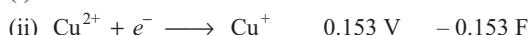
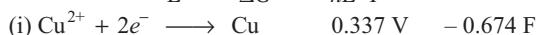
23. The spontaneous cell reaction is



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24. E° is an intensive property :

$$E^\circ \quad \Delta G^\circ = -nE^\circ F$$



Subtracting (ii) from (i) gives :



$$\Rightarrow E^\circ = 0.521 \text{ V}$$

$$\therefore n = 1$$



For the cell reaction,

$$E_{\text{Cell}}^\circ = E_{\text{Cu}^+/ \text{Cu}}^\circ - E_{\text{Cu}^{2+}/ \text{Cu}^+}^\circ = (0.52 - 0.16) \text{ V} = 0.36 \text{ V}$$

$$\Rightarrow \Delta G^\circ = -nF E_{\text{Cell}}^\circ$$

$$\Rightarrow -RT \ln K = -nF E_{\text{Cell}}^\circ$$

$$\Rightarrow \ln K = n \times \frac{E}{RT} \times E_{\text{Cell}}^\circ = 1 \times \frac{1}{0.025} \times 0.36 \\ = 14.4 = 144 \times 10^{-1}$$

$$26. \therefore \Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$\text{Here, } \Delta G^\circ = 17.37 \text{ kJ mol}^{-1}$$

n = number of electrons

$$F = \text{Faraday constant} = 96500 \text{ C/mol}$$

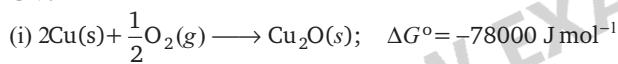
$$= 17.37 \times 1000 \text{ J mol}^{-1}$$

$$17.37 \times 1000 = -3 \times 96500 \times E_{\text{cell}}^\circ$$

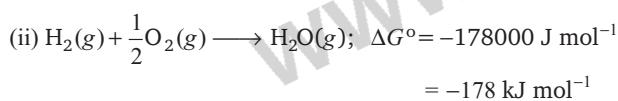
$$E_{\text{cell}}^\circ = \frac{17.37 \times 1000}{3 \times 96500}$$

$$E_{\text{cell}}^\circ = -0.06 = -6 \times 10^{-2}$$

27. Given

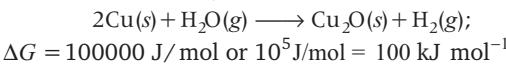


$$= -78 \text{ kJ mol}^{-1}$$



$$= -178 \text{ kJ mol}^{-1}$$

So, net reaction is (By (i)-(ii))



Now, for the above reaction

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \right]$$

and to prevent above reaction,

$$\Delta G \geq 0$$

So,

$$\Delta G^\circ + RT \ln \left[\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \right] \geq 0$$

After putting the values,

$$10^5 + 8 \times 1250 \ln \left[\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \right] \geq 0$$

$$\text{or} \quad 10^5 + 10^4 \ln \left[\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \right] \geq 0$$

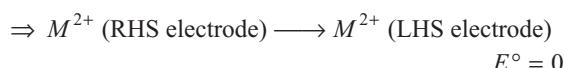
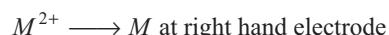
$$\text{or} \quad 10^4 (\ln P_{\text{H}_2} - \ln P_{\text{H}_2\text{O}}) \geq -10^5$$

$$\text{or} \quad \ln P_{\text{H}_2} \geq -10 + \ln P_{\text{H}_2\text{O}}$$

$$\text{or} \quad \ln P_{\text{H}_2} \geq -10 + 2.3 \log(0.01) \text{ (as } P_{\text{H}_2\text{O}} = 1\%) \\ \geq -10 - 4.6$$

$$\text{so} \quad \ln P_{\text{H}_2} \geq -14.6$$

28. For the given concentration cell, the cell reaction are $M \longrightarrow M^{2+}$ at left hand electrode.



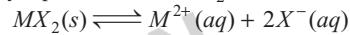
Applying Nernst equation

$$E_{\text{cell}} = 0.059 = 0 - \frac{0.059}{2} \log \frac{[M^{2+}] \text{ at LHS electrode}}{0.001}$$

$$\Rightarrow \log \frac{[M^{2+}] \text{ at LHS electrode}}{0.001} = -2$$

$$\Rightarrow [M^{2+}] \text{ at LHS electrode} = 10^{-2} \times 0.001 = 10^{-5} \text{ M}$$

The solubility equilibrium for MX_2 is



$$\text{Solubility product, } K_{\text{sp}} = [[M^{2+}][X^-]^2 \\ = 10^{-5} \times (2 \times 10^{-5})^2 = 4 \times 10^{-15}$$

$$[\because \text{In saturated solution of } MX_2, [X^-] = 2[M^{2+}]]$$

$$29. \Delta G = -nEF = -\frac{2 \times 0.059 \times 96500}{1000} \text{ kJ} = -11.4 \text{ kJ}$$

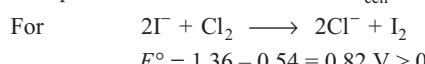


$$E_{\text{cell}} = 0 - \frac{2.303 RT}{F} \log \frac{0.05}{1} > 0$$

Hence, $|E_{\text{cell}}| = E_{\text{cell}} = 0.70 \text{ V}$ and $\Delta G < 0$ for spontaneity of reaction.

$$31. E_{\text{cell}} = E^\circ - \frac{0.0538}{1} \log 0.0025 = 0.139 \text{ V} \approx 140 \text{ mV}$$

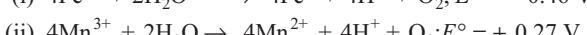
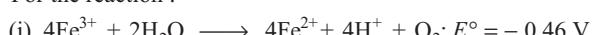
32. For spontaneous redox reaction : $E_{\text{cell}}^\circ > 0$



i.e. Cl_2 will spontaneously oxidise I^- .

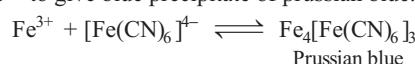
In other cases $E_{\text{cell}}^\circ < 0$, they are non-spontaneous.

33. For the reaction :



As evidenced above, reaction (i) is non-spontaneous, therefore, Fe^{3+} is stable in acid solution. However, reaction (ii) is spontaneous. Mn^{3+} oxidises H_2O to O_2 and itself reduced to Mn^{2+} in acidic medium.

34. Sodium fusion extract from aniline produces NaCN which reacts with Fe^{2+} to form $[\text{Fe}(\text{CN})_6]^{4-}$. The complex ion then reacts with Fe^{3+} to give blue precipitate of prussian blue.





$+ \text{C}_6\text{H}_{12}\text{O}_7^- + 2\text{H}^+$ is 0.75 V

$$\text{Also } E^\circ = \frac{0.0592}{2} \log K \Rightarrow \log K = \frac{2E^\circ}{0.0592} = 25.33$$

$$\Rightarrow \ln K = 2.303 \log K = 58.35$$

36. On increasing concentration of NH_3 , the concentration of H^+ ion decreases, therefore,

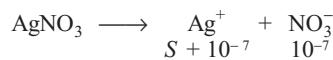
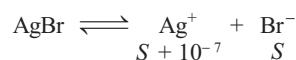
$$E_{\text{red}} = E_{\text{red}}^\circ - \frac{0.0592}{2} \log [\text{H}^+]^2 = 0 - \frac{0.0592}{2} \times 2 \log 10^{-11}$$

$$= 0.65 \text{ V}$$

i.e. E_{red} increases by 0.65 V.

37. NH_3 has no effect on the E° of glucose/gluconic acid electrode.

38. The solubility of AgBr in 10^{-7} M AgNO_3 solution is determined as



$$K_{\text{sp}} = 14 \times 10^{-14} = S(S + 10^{-7})$$

Solving for S gives : $S = 3 \times 10^{-7}$ M

$$\Rightarrow [\text{Br}^-] = 3 \times 10^{-7} \text{ M},$$

$$[\text{Ag}^+] = 4 \times 10^{-7} \text{ M},$$

$$[\text{NO}_3^-] = 10^{-7} \text{ M}$$

$$\begin{aligned} \Rightarrow \kappa (\text{sp. conductance}) &= \kappa_{\text{Br}^-} + \kappa_{\text{Ag}^+} + \kappa_{\text{NO}_3^-} \\ &= [8 \times 10^{-3} \times 3 \times 10^{-7} + 6 \times 10^{-3} \times 4 \times 10^{-7}] 1000 \\ &\quad + 7 \times 10^{-3} \times 10^{-7}] 1000 \\ &= 24 \times 10^{-7} + 24 \times 10^{-7} + 7 \times 10^{-7} \\ &= 55 \times 10^{-7} \text{ S m}^{-1} = 55 \text{ (in terms of } 10^{-7} \text{ S m}^{-1}) \end{aligned}$$

39. (a) $\Delta G^\circ = \Sigma \Delta G_f^\circ (\text{products}) - \Sigma \Delta G_f^\circ (\text{reactants})$

$$= -109 - (-129 + 77) \text{ kJ} = -57 \text{ kJ}$$

Cell : $\text{Ag} | \text{AgCl}, \text{Cl}^- || \text{Ag}^+ | \text{Ag}$

For K_{sp} ; reaction is $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

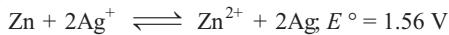
$$\Delta G^\circ = +57 \text{ kJ} \Rightarrow \Delta G^\circ = -RT \ln K_{\text{sp}}$$

$$\Rightarrow \log K_{\text{sp}} = -\frac{\Delta G^\circ}{2.3 RT} = -\frac{57 \times 1000}{2.3 \times 8.314 \times 298} = -10$$

Now, E° of $\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}$

$$E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{57000}{96500} = 0.59 \text{ V}$$

(b) The cell reaction is :



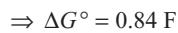
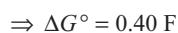
$$\Rightarrow 0 = E^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\Rightarrow \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{2E^\circ}{0.059} = \frac{2 \times 1.56}{0.059} = 52.88$$

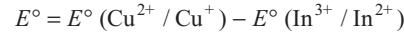
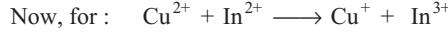
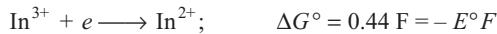
$$\text{Moles of Zn added} = \frac{6.539 \times 10^{-2}}{65.39} = 10^{-3}$$

$$\Rightarrow \text{Moles of Ag formed} = 2 \times 10^{-3}.$$

40. Given,



Subtracting (i) from (ii)



$$= 0.15 - (-0.44) = 0.59 \text{ V}$$

$$\text{Also } E^\circ = 0.0590 \log K$$

$$\Rightarrow \log K = \frac{E^\circ}{0.059} = 10 \Rightarrow K = 10^{10}$$

41. (a) $\text{pH} = -\log [\text{H}^+]$

In pure water, $[\text{H}^+]$ depends on value of K_w which is

$$K_w = [\text{H}^+] [\text{OH}^-]$$

$\because K_w$ is a function of temperature, $[\text{H}^+]$ will change with temperature.

- (b) Let the emf of first cell be X volt.

\Rightarrow emf of 2nd cell $= (X + 0.03)$ volt

$[\text{Cu}^{2+}]$ in 2nd cell $= 0.50 \text{ M}$

$[\text{Cu}^{2+}]$ in 1st cell $= ?$

$$E_1 = E_1^\circ - \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E_2 = E_1^\circ - \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]_l}$$

$$\Rightarrow E_2 - E_1 = \frac{2.303 RT}{2F} \left[\log \frac{[\text{Cu}^{2+}]_l}{[\text{Cu}^{2+}]_i} \right]$$

$$\Rightarrow 0.03 = 0.03 \log \frac{0.50}{[\text{Cu}^{2+}]_i}$$

$$\Rightarrow \frac{0.50}{[\text{Cu}^{2+}]_i} = 10 \Rightarrow [\text{Cu}^{2+}]_i = 0.05 \text{ M}$$

42. At anode $\frac{1}{2} \text{H}_2 \longrightarrow \text{H}^+ + e^-; E^\circ = 0$

- At cathode $\text{AgCl}(s) + e^- \longrightarrow \text{Ag} + \text{Cl}^-; E^\circ = ?$

- (i) Cell reaction : $\frac{1}{2} \text{H}_2 + \text{AgCl}(s) \longrightarrow \text{Ag} + \text{H}^+ + \text{Cl}^-$

- (ii) $\Delta G^\circ = -nE^\circ F = \Delta H^\circ - T \Delta S^\circ$

$$\text{At } 15^\circ\text{C} : -0.23 \times 96500 = \Delta H^\circ - 288 \Delta S^\circ \quad \dots(i)$$

$$\text{At } 35^\circ\text{C} : -0.21 \times 96500 = \Delta H^\circ - 308 \Delta S^\circ \quad \dots(ii)$$

$$\Rightarrow 96500 (0.23 - 0.21) = -20 \Delta S^\circ$$

$$\Rightarrow \Delta S^\circ = -\frac{96500 \times 0.02}{20} = -96.5 \text{ J}$$

Substituting value of ΔS° in (i)

$$\Delta H^\circ = 288 \times (-96.5) - 0.23 \times 96500 = -49.987 \text{ kJ}$$

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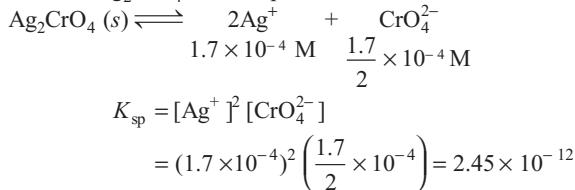
(iii) At 25°C

$$\begin{aligned}
 & -E^\circ \times 96500 = -49987 - 298 (-96.5) \\
 \Rightarrow & E^\circ = 0.22 \text{ V} \\
 \Rightarrow & \text{AgCl}(s) + e^- \longrightarrow \text{Ag} + \text{Cl}^-; E^\circ = 0.22 \text{ V} \\
 & \text{Ag} \longrightarrow \text{Ag}^+ + e^-; E^\circ = -0.80 \text{ V} \\
 \text{Adding : } & \text{AgCl}(s) \longrightarrow \text{Ag}^+ + \text{Cl}^-; E^\circ = -0.58 \text{ V} \\
 \Rightarrow & E^\circ = 0.0592 \log K_{\text{sp}} \\
 \Rightarrow & \log K_{\text{sp}} = \frac{-0.58}{0.0592} = -9.79 \\
 \Rightarrow & K_{\text{sp}} = 1.6 \times 10^{-10}
 \end{aligned}$$

$$\begin{aligned}
 43. \quad E &= 0 - \frac{0.0592}{1} \log \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} \\
 \Rightarrow & 0.164 = -0.0592 \log \frac{[\text{Ag}^+]_{\text{anode}}}{0.10}
 \end{aligned}$$

$$\Rightarrow [\text{Ag}^+]_{\text{anode}} = 1.7 \times 10^{-4} \text{ M}$$

In saturated Ag_2CrO_4 solution present in anode chamber :



$$44. \text{ For } 2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$$

$$\begin{aligned}
 E^\circ &= E^\circ (\text{Fe}^{3+} / \text{Fe}^{2+}) - E^\circ (\text{I}_3^- / \text{I}^-) \\
 &= 0.77 - 0.54 = 0.23 \text{ V}
 \end{aligned}$$

$$\therefore E^\circ = \frac{0.0592}{2} \log K \quad (n=2)$$

$$\log K = \frac{2E^\circ}{0.0592} = \frac{2 \times 0.23}{0.0592} = 7.77$$

$$\Rightarrow K = 5.89 \times 10^7$$

$$45. \quad \text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$$

$$\begin{aligned}
 E^\circ &= E^\circ (\text{Ce}^{4+} / \text{Ce}^{3+}) - E^\circ (\text{Fe}^{3+} / \text{Fe}^{2+}) \\
 &= 1.44 - 0.68 = 0.76 \text{ V}
 \end{aligned}$$

$$\therefore E^\circ = 0.0592 \log K$$

$$\Rightarrow \log K = \frac{E^\circ}{0.0592} = \frac{0.76}{0.0592} = 12.83$$

$$\Rightarrow K = 6.88 \times 10^{12}$$

46. pH = 14

$$\Rightarrow \text{pOH} = 0 \Rightarrow [\text{OH}^-] = 1.0 \text{ M}$$

$$K_{\text{sp}} = 10^{-19} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

$$\Rightarrow [\text{Cu}^{2+}] = \frac{10^{-19}}{[\text{OH}^-]^2} = 10^{-19}$$

For reaction : $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}; E^\circ = 0.34 \text{ V}$

$$\begin{aligned}
 E &= E^\circ - \frac{0.0592}{2} \log \frac{1}{[\text{Cu}^{2+}]} \\
 &= 0.34 - \frac{0.0592}{2} \log 10^{19} = -0.222 \text{ V}
 \end{aligned}$$

47. For reaction,



Initial :	10^{-3} M	0	0
Equilibrium :	5×10^{-5}	4.75×10^{-4}	9.5×10^{-4}

$$K = \frac{[\text{Fe}^{2+}]^2 [\text{Hg}_2^{2+}]}{[\text{Fe}^{3+}]^2}$$

$$= \frac{(9.5 \times 10^{-4})^2 (4.75 \times 10^{-4})}{(5 \times 10^{-5})^2} = 0.17$$

$$\therefore E^\circ = \frac{0.0592}{2} \log K$$

$$= -0.0226 \text{ V}$$

$$= E^\circ (\text{Fe}^{3+} / \text{Fe}^{2+}) - E^\circ (\text{Hg}_2^{2+} / \text{Hg})$$

$$\begin{aligned}
 \Rightarrow E^\circ (\text{Hg}_2^{2+} / \text{Hg}) &= 0.77 + 0.0226 \\
 &= 0.7926 \text{ V}
 \end{aligned}$$

48. In a saturated AgI solution;

$$\begin{aligned}
 [\text{Ag}^+] &= \sqrt{8.7 \times 10^{-17}} \text{ M} \\
 &= 9.32 \times 10^{-9} \text{ M}
 \end{aligned}$$

$$\begin{aligned}
 \Rightarrow E_{\text{Ag}^+/\text{Ag}} &= E^\circ - 0.0592 \log \frac{1}{[\text{Ag}^+]} \\
 &= 0.799 - 0.0592 \log \frac{1}{9.32 \times 10^{-9}} \\
 &= 0.324 \text{ V}
 \end{aligned}$$

$$\text{Also, for } \text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^-; E^\circ = 0.0592 \log K_{\text{sp}}$$

$$= -0.95 \text{ V}$$

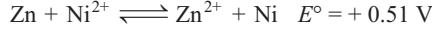
$$\text{Ag} \longrightarrow \text{Ag}^+ + e^-; E^\circ = -0.799 \text{ V}$$

$$\text{AgI} + e^- \longrightarrow \text{Ag} + \text{I}^- \quad E^\circ = x$$

$$\begin{aligned}
 \text{Adding : } \quad \text{AgI} \longrightarrow \text{Ag}^+ + \text{I}^-; E^\circ &= -0.95 \text{ V} \\
 &= x - 0.799
 \end{aligned}$$

$$\Rightarrow x = -0.151 \text{ V}$$

49. The redox reaction is



$$\Rightarrow E^\circ = \frac{0.0592}{2} \log K$$

$$\Rightarrow \log K = \frac{0.51 \times 2}{0.0592} = 17.23$$

$$\Rightarrow K = 1.7 \times 10^{17}$$

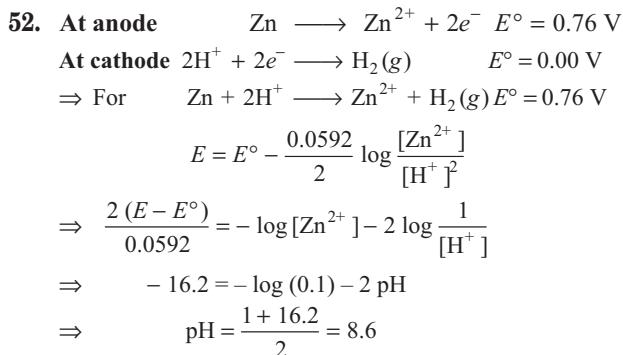
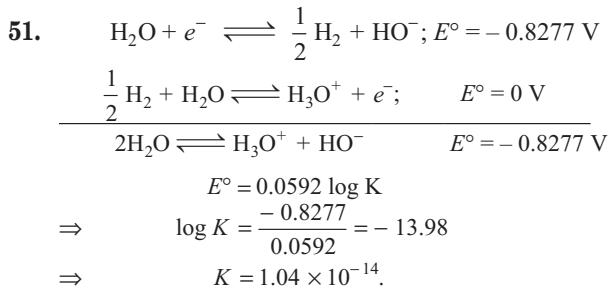
Such a high value of equilibrium constant indicates that the reaction is almost complete. Therefore, concentration of Zn^{2+} in solution will be equal to initial concentration of Ni^{2+} ion, i.e. 1.0 M.

50. The galvanic cell is : $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^+ | \text{Ag}$

Cell reaction : $\text{Cu} + 2\text{Ag}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{Ag}; E^\circ = 0.462 \text{ V}$

$$E = 0.462 - \frac{0.0592}{2} \log \frac{(0.01)}{[\text{Ag}^+]^2}$$

$$\Rightarrow [\text{Ag}^+] = 1.57 \times 10^{-9} \text{ M}$$



53. For conductivity, the charge carriers are required. In anhydrous state, HCl is not ionised and no charge carrier ions are available, hence bad conductor. However, in aqueous solution, HCl is fully ionised producing H^+ and Cl^- and conducts electricity.

54. (i) The cell reaction is



$$\text{(ii)} \quad E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.350 - (-0.763) = 1.113 \text{ V}$$

$$\because \text{Both } \text{Zn}^{2+} \text{ and } \text{Cu}^{2+} \text{ are at unit concentrations,}$$

$$E = E^\circ = 1.113 \text{ V}$$

$$\text{(iii)} \because E_{\text{cell}} = 1.113 \text{ V} > 0$$

$$\Delta G = -nEF < 0$$

Therefore, the cell reaction is spontaneous.

55. $\text{pH} = C\alpha = 10^{-4}$

$$\Rightarrow \alpha = \frac{10^{-4}}{0.0015}$$

Also, conductance (G) = $\kappa \left(\frac{A}{l} \right)$

$$\Rightarrow \kappa = G \left(\frac{l}{A} \right) = 5 \times 10^{-7} \times \frac{120}{1}$$

$$= 6 \times 10^{-5}$$

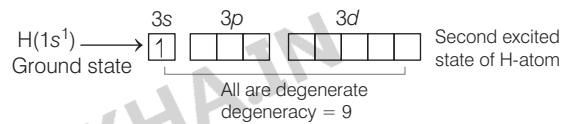
$$\Rightarrow \Lambda^c = \frac{\kappa \times 1000}{C}$$

$$= \frac{6 \times 10^{-5} \times 1000}{0.0015}$$

$$\Rightarrow \Lambda^\infty = \frac{\Lambda^c}{\alpha} = \frac{6 \times 10^{-5} \times 1000}{0.0015} \times \frac{0.0015}{10^{-4}}$$

$$= 600 = 6 \times 10^2 \text{ S cm}^{-1} \text{ mol}^{-1}$$

56. Energy obtained as one mole X is converted into Y is 193 kJ.



Energy consumed in converting one mole of M^+ to M^{3+}
 $= -nE^\circ F = 2 \times 96500 \times 0.25 \text{ J} = \frac{96500}{2} \text{ J}$

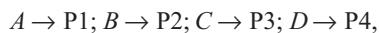
$$\Rightarrow 193 \times 10^3 = n \left(\frac{96500}{2} \right) \Rightarrow n = 4 \text{ mol}$$

11

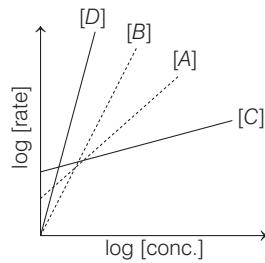
Chemical Kinetics

Objective Questions I (Only one correct option)

1. Consider the following reactions



The order of the above reactions are a, b, c and d , respectively. The following graph is obtained when $\log[\text{rate}]$ vs $\log[\text{conc.}]$ are plotted:



Among the following, the correct sequence for the order of the reactions is

(2020 Main, 6 Sep I)

- (a) $D > A > B > C$
 (b) $A > B > C > D$
 (c) $C > A > B > D$
 (d) $D > B > A > C$

2. NO_2 required for a reaction is produced by the decomposition of N_2O_5 in CCl_4 as per the equation,



The initial concentration of N_2O_5 is 3.00 mol L^{-1} and it is 2.75 mol L^{-1} after 30 minutes. The rate of formation of NO_2 is

(2019 Main, 12 April II)

- (a) $4.167 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$
 (b) $1.667 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$
 (c) $8.333 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$
 (d) $2.083 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

3. In the following reaction; $xA \rightarrow yB$

$$\log_{10} \left[-\frac{d[A]}{dt} \right] = \log_{10} \left[\frac{d[B]}{dt} \right] + 0.3010$$

A and B respectively can be

(2019 Main, 12 April I)

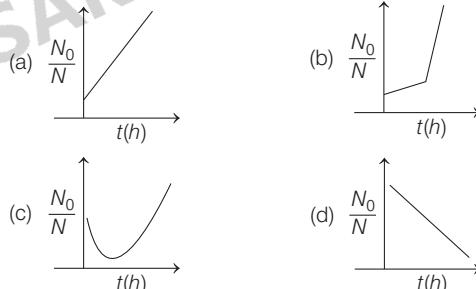
- (a) n -butane and iso -butane
 (b) C_2H_2 and C_6H_6
 (c) C_2H_4 and C_4H_8
 (d) N_2O_4 and NO_2

4. For the reaction of H_2 with I_2 , the rate constant is $2.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 327°C and $1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 527°C . The activation energy for the reaction, in kJ mol^{-1} is ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) (2019 Main, 10 April II)

- (a) 59
 (b) 72
 (c) 150
 (d) 166

5. A bacterial infection in an internal wound grows as $N'(t) = N_0 \exp(t)$, where the time t is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} = -5N^2$. What will be the plot of $\frac{N_0}{N}$ vs t after 1 hour?

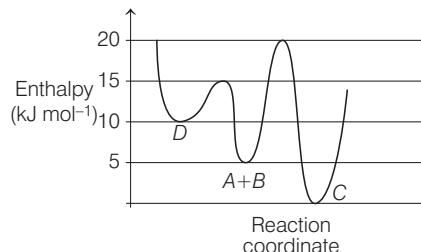
(2019 Main, 10 April I)



6. Consider the given plot of enthalpy of the following reaction between A and B . $A + B \longrightarrow C + D$

Identify the incorrect statement.

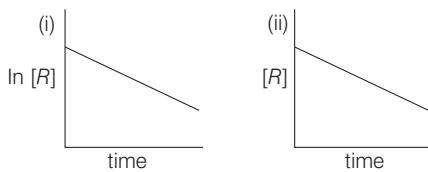
(2019 Main, 9 April II)



- (a) D is kinetically stable product.
 (b) Formation of A and B from C has highest enthalpy of activation.
 (c) C is the thermodynamically stable product.
 (d) Activation enthalpy to form C is 5 kJ mol^{-1} less than that to form D .

7. The given plots represent the variation of the concentration of a reaction R with time for two different reactions (i) and (ii). The respective orders of the reactions are

(2019 Main, 9 April I)



- (a) 1, 1 (b) 0, 2
(c) 0, 1 (d) 1, 0

8. For a reaction scheme, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, if the rate of formation of B is set to be zero then the concentration of B is given by

(2019 Main, 8 April II)

- (a) $k_1 k_2 [A]$ (b) $\left(\frac{k_1}{k_2}\right)[A]$
(c) $(k_1 - k_2)[A]$ (d) $(k_1 + k_2)[A]$

9. For the reaction, $2A + B \rightarrow C$, the values of initial rate at different reactant concentrations are given in the table below. The rate law for the reaction is

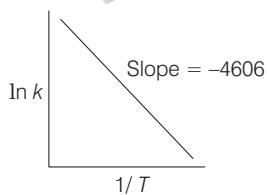
(2019 Main, 8 April I)

[A](mol L ⁻¹)	[B](mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72

- (a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$
(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$

10. For a reaction, consider the plot of $\ln k$ versus $1/T$ given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s⁻¹, then the rate constant at 500 K is

(2019 Main, 12 Jan II)



- (a) 4×10^{-4} s⁻¹ (b) 10^{-6} s⁻¹
(c) 10^{-4} s⁻¹ (d) 2×10^{-4} s⁻¹

11. Decomposition of X exhibits a rate constant of $0.05 \mu\text{g}/\text{year}$. How many years are required for the decomposition of $5 \mu\text{g}$ of X into $2.5 \mu\text{g}$?

(2019 Main, 12 Jan I)

- (a) 20 (b) 25 (c) 40 (d) 50

12. The reaction, $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be

(2019 Main, 11 Jan II)

- (a) 7.2 h (b) 18.0 h (c) 12.0 h (d) 9.0 h

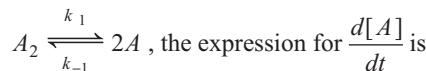
13. If a reaction follows the Arrhenius equation, the plot $\ln k$ vs $1/(RT)$ gives straight line with a gradient ($-y$) unit.

The energy required to activate the reactant is

(2019 Main, 11 Jan I)

- (a) $\frac{y}{R}$ unit (b) $-y$ unit (c) yR unit (d) y unit

14. For an elementary chemical reaction,

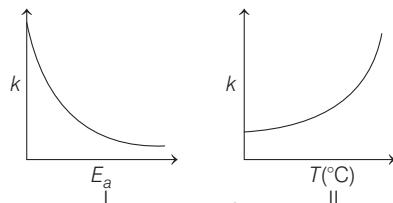


(2019 Main, 10 Shift II)

- (a) $2k_1[A_2] - k_{-1}[A]^2$ (b) $k_1[A_2] - k_{-1}[A]^2$
(c) $2k_1[A_2] - 2k_{-1}[A]^2$ (d) $k_1[A_2] + k_{-1}[A]^2$

15. Consider the given plots for a reaction obeying Arrhenius equation ($0^\circ\text{C} < T < 300^\circ\text{C}$): (k and E_a are rate constant and activation energy, respectively)

(2019 Main, 10 Jan I)



Choose the correct option.

- (a) Both I and II are wrong
(b) Both I and II are correct
(c) I is wrong but II is right
(d) I is right but II is wrong

16. For the reaction, $2A + B \rightarrow \text{products}$

When concentration of both (A and B) becomes double, then rate of reaction increases from $0.3 \text{ mol L}^{-1} \text{ s}^{-1}$ to $2.4 \text{ mol L}^{-1} \text{ s}^{-1}$.

When concentration of only A is doubled, the rate of reaction increases from $0.3 \text{ mol L}^{-1} \text{ s}^{-1}$ to $0.6 \text{ mol L}^{-1} \text{ s}^{-1}$.

Which of the following is true?

- (a) The whole reaction is of 4th order
(b) The order of reaction w.r.t. B is one
(c) The order of reaction w.r.t. B is 2
(d) The order of reaction w.r.t. A is 2

17. The following results were obtained during kinetic studies of the reaction;

(2019 Main, 9 Jan I)



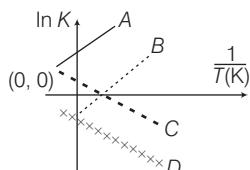
Experiment	[A] (in mol L ⁻¹)	[B] (in mol L ⁻¹)	Initial rate of reaction (in mol L ⁻¹ min ⁻¹)
I.	0.10	0.20	6.93×10^{-3}
II.	0.10	0.25	6.93×10^{-3}
III.	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of A is

- (a) 5 (b) 10
(c) 100 (d) 1

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18. Which of the following lines correctly show the temperature dependence of equilibrium constant, K , for an exothermic reaction? (2018 Main)



- (a) A and B
(b) B and C
(c) C and D
(d) A and D

19. At 518°C , the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is : (2018 Main)

- (a) 2
(b) 3
(c) 1
(d) 0

20. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1} . If k_1 and k_2 are rate constants for reactions R_1 and R_2 , respectively at 300 K, then $\ln\left(\frac{k_2}{k_1}\right)$ is equal to ($R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$) (2017 Main)

- (a) 8
(b) 12
(c) 6
(d) 4

21. Decomposition of H_2O_2 follows a first order reaction. In 50 min, the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be (2016 Main)

- (a) $6.93 \times 10^{-4} \text{ mol min}^{-1}$
(b) 2.66 L min^{-1} at STP
(c) $1.34 \times 10^{-2} \text{ mol min}^{-1}$
(d) $6.93 \times 10^{-2} \text{ mol min}^{-1}$

22. Higher order (>3) reactions are rare due to (2015 Main)
- low probability of simultaneous collision of all the reacting species
 - increase in entropy and activation energy as more molecules are involved
 - shifting of equilibrium towards reactants due to elastic collisions
 - loss of active species on collision

23. For the elementary reaction, $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M . The order of the reaction with respect to M is (2014 Adv.)

- (a) 4
(b) 3
(c) 2
(d) 1

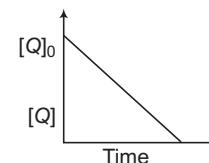
24. For the non-stoichiometric reaction, $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. (2014 Main)

	Initial concentration [A]	Initial concentration [B]	Initial rate of formation of C ($\text{mol L}^{-1}\text{s}^{-1}$)
(i)	0.1 M	0.1 M	1.2×10^{-3}
(ii)	0.1 M	0.2 M	1.2×10^{-3}
(iii)	0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

- (a) $\frac{dC}{dt} = k[A][B]$
(b) $\frac{dC}{dt} = k[A]^2[B]$
(c) $\frac{dC}{dt} = k[A][B]^2$
(d) $\frac{dC}{dt} = k[A]$

25. In the reaction, $P + Q \rightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P . The concentration of Q varies with reaction time as shown in the figure. The overall order of the re(2013 Adv.)

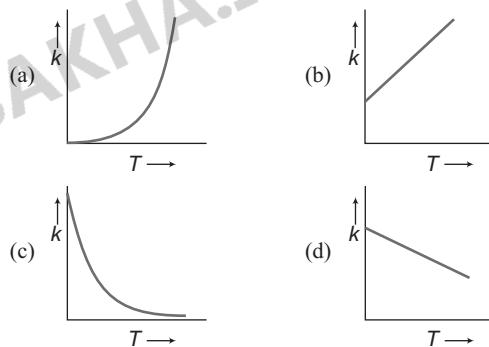


- (a) 2
(b) 3
(c) 0
(d) 1

26. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$)

- (a) 53.6 kJ mol^{-1}
(b) 48.6 kJ mol^{-1} (2013 Main)
(c) 58.5 kJ mol^{-1}
(d) 60.5 kJ mol^{-1}

27. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is (2010)



28. For a first order reaction, $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation :

$$\log k = \frac{2000}{T} + 6.0$$

the pre-exponential factor A and the activation energy E_a , respectively, are (2009)

- (a) $1.0 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) $1.0 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}
(d) $1.0 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol^{-1}

29. Under the same reaction conditions, initial concentration of $1.386 \text{ mol dm}^{-3}$ of a substance becomes half in 40 s and 20 s through first order and zero order kinetics

respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is

(2008, 3M)

- (a) $0.5 \text{ mol}^{-1} \text{ dm}^3$ (b) 1.0 mol dm^{-3}
 (c) 1.5 mol dm^{-3} (d) $2.0 \text{ mol}^{-1} \text{ dm}^3$

30. Consider a reaction, $aG + bH \rightarrow$ products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is (2007, 3M)
- (a) 0 (b) 1
 (c) 2 (d) 3

31. Which one of the following statement(s) is incorrect about order of reaction? (2005, 1M)

- (a) Order of reaction is determined experimentally
 (b) Order of reaction is equal to sum of the power of concentration terms in differential rate law
 (c) It is not affected with stoichiometric coefficient of the reactants
 (d) Order cannot be fractional

32. (A) follows first order reaction, $(A) \rightarrow$ product. Concentration of A , changes from 0.1 M to 0.025 M in 40 min . Find the rate of reaction of A when concentration of A is 0.01 M .

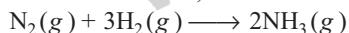
(2004, 1M)

- (a) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (b) $3.47 \times 10^{-5} \text{ M min}^{-1}$
 (c) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (d) $1.73 \times 10^{-5} \text{ M min}^{-1}$

33. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ s}$. The rate constant of reaction in s^{-1} is (2003, 1M)

- (a) 2×10^4 (b) 3.45×10^{-5}
 (c) 1.386×10^{-4} (d) 2×10^{-4}

34. Consider the chemical reaction,



The rate of this reaction can be expressed in terms of time derivatives of concentration of $\text{N}_2(g)$, $\text{H}_2(g)$ or $\text{NH}_3(g)$. Identify the correct relationship amongst the rate expressions

- (a) Rate = $-\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$ (2002, 3M)
 (b) Rate = $-\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$
 (c) Rate = $\frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$
 (d) Rate = $-\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

35. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process.

$AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to

- (a) C (b) I
 (c) I^2 (d) $C \cdot I$

36. The rate constant for the reaction, $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ is $3.0 \times 10^{-5} \text{ s}^{-1}$. If the rate is $2.40 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$, then the concentration of N_2O_5 (in mol L^{-1}) is (2000, 1M)

- (a) 1.4 (b) 1.2
 (c) 0.04 (d) 0.8

37. The half-life period of a radioactive element is 140 days. After 650 days, one gram of the element will reduce to (1986)

- (a) $\frac{1}{2} \text{ g}$ (b) $\frac{1}{4} \text{ g}$ (c) $\frac{1}{8} \text{ g}$ (d) $\frac{1}{16} \text{ g}$

38. A catalyst is a substance which (1983, 1M)
- (a) increases the equilibrium concentration of the product
 (b) changes the equilibrium constant of the reaction
 (c) shortens the time to reach equilibrium
 (d) supplies energy to the reaction

39. The specific rate constant of a first order reaction depends on the (1983, 1M)

- (a) concentration of the reactant
 (b) concentration of the product
 (c) time
 (d) temperature

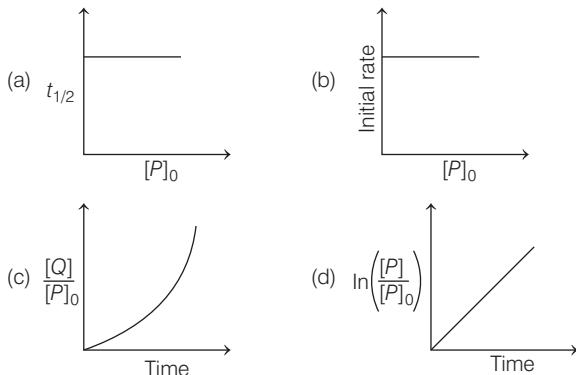
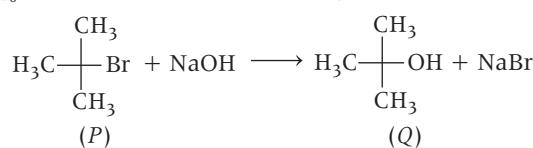
40. The rate constant of a reaction depends on (1981, 1M)
- (a) temperature
 (b) initial concentration of the reactants
 (c) time of reaction
 (d) extent of reaction

Objective Questions II

(One or more than one correct option)

41. Which of the following plots is(are) correct for the given reaction?

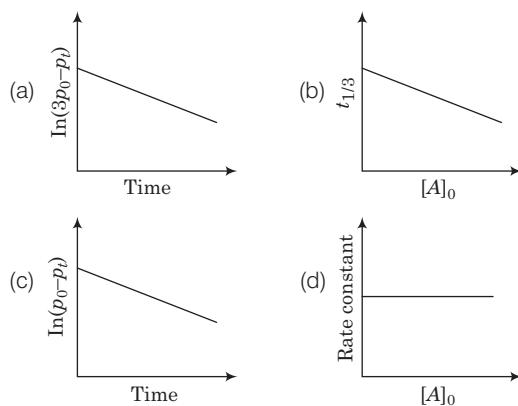
$([P]_0)$ is the initial concentration of P (2020 Adv.)



42. For a first order reaction, $A(g) \longrightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning ($t = 0$) and at time t are p_0 and p_t , respectively.

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Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{\text{rd}}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases) (2018 Adv.)



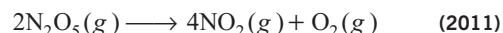
43. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. the correct option(s) among the following is(are) (2017 Adv.)

- (a) The activation energy of the reaction is unaffected by the value of the steric factor
- (b) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
- (c) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
- (d) Since $P = 4.5$, the reaction will not proceed unless an effective catalyst is used

44. According to the Arrhenius equation, (2016 Adv.)

- (a) a high activation energy usually implies a fast reaction
- (b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
- (c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
- (d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy

45. For the first order reaction,



- (a) the concentration of the reactant decreases exponentially with time
- (b) the half-life of the reaction decreases with increasing temperature
- (c) the half-life of the reaction depends on the initial concentration of the reactant
- (d) the reaction proceeds of 99.6% completion in eight half-life duration

46. The following statement (s) is are correct (1999, 3M)

- (a) A plot of $\log K_p$ vs $\frac{1}{T}$ is linear
- (b) A plot of $\log [X]$ vs time is linear for a first order reaction, $x \rightarrow p$
- (c) A plot of $\log p$ vs $\frac{1}{T}$ is linear at constant volume
- (d) A plot of p vs $\frac{1}{V}$ is linear at constant temperature

47. For the first order reaction, (1998, 2M)

- (a) the degree of dissociation is equal to $(1 - e^{-kt})$
- (b) a plot of reciprocal concentration of the reactant vs time gives a straight line
- (c) the time taken for the completion of 75% reaction is thrice the $\frac{1}{2}$ of the reaction
- (d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

48. A catalyst (1984, 1M)

- (a) increases the average kinetic energy of reacting molecules
- (b) decreases the activation energy
- (c) alters the reaction mechanism
- (d) increases the frequency of collisions of reacting species

Numerical Answer Type Questions

49. If 75% of a first order reaction was completed in 90 minutes, 60% of the same reaction would be completed in approximately (in minutes)

(Take : $\log 2 = 0.30$; $\log 2.5 = 0.40$) (2020 Main, 4 Sep I)

50. Consider the kinetic data given in the following table for the reaction $A + B + C \longrightarrow \text{Product}$

Experiment No.	[A] (mol dm ⁻³)	[B] (mol dm ⁻³)	[C] (mol dm ⁻³)	Rate of reaction (mol dm ⁻³ s ⁻¹)
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

The rate of the reaction for $[A] = 0.15 \text{ mol dm}^{-3}$, $[B] = 0.25 \text{ mol dm}^{-3}$ and $[C] = 0.15 \text{ mol dm}^{-3}$ is found to be $Y \times 10^{-5} \text{ mol dm}^{-3}\text{s}^{-1}$. The value of Y is

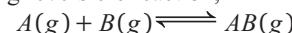
(2019 Adv.)

51. The decomposition reaction

$2\text{N}_2\text{O}_5(g) \xrightarrow{\Delta} 2\text{N}_2\text{O}_4(g) + \text{O}_2(g)$ is started in a closed cylinder under isothermal isochoric condition at an initial pressure of 1 atm. After $Y \times 10^3$ s, the pressure inside the cylinder is found to be 1.45 atm. If the rate constant of the reaction is $5 \times 10^{-4} \text{ s}^{-1}$, assuming ideal gas behaviour, the value of Y is

(2019 Adv.)

52. Consider the following reversible reaction,

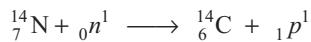


The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol⁻¹). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^\ominus (in J mol⁻¹) for the reaction at 300 K is

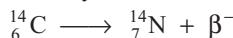
(Given ; $\ln(2) = 0.7$ $RT = 2500 \text{ J mol}^{-1}$ at 300 K and G is the Gibbs energy) (2018 Adv.)

Passage Based Questions

Carbon-14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.



^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C-14 undergoes



The half-life period of ^{14}C is 5770 yr.

The decay constant (λ) can be calculated by using the following formula $\lambda = \frac{0.693}{t_{1/2}}$.

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 yr. The proportion of ^{14}C to ^{12}C in living matter is $1 : 10^{12}$.

(2006, 3 × 4M = 12M)

53. Which of the following option is correct?

- (a) In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism
- (b) Carbon dating can be used to find out the age of earth crust and rocks
- (c) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbons content remains constant in living organisms
- (d) Carbon dating cannot be used to determine concentration of ^{14}C in dead beings

54. What should be the age of fossil for meaningful determination of its age?

- (a) 6 yr
- (b) 6000 yr
- (c) 60,000 yr
- (d) It can be used to calculate any age

55. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

$$\text{(a) the age of fossil will increase at the place where explosion has taken place and } T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

$$\text{(b) the age of fossil will decrease at the place where explosion has taken place and } T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(c) the age of fossil will be determined to be the same

$$\text{(d) } \frac{T_1}{T_2} = \frac{C_1}{C_2}$$

Fill in the Blanks

56. In Arrhenius equation, $k = A \exp(-E_a/RT)$. A may be termed as the rate constant at (1997, 1M)

57. For the reaction : $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$

Under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg/h^{-1} . The rate of conversion of H_2 under the same condition is kg/h^{-1} . (1994, 1M)

58. The hydrolysis of ethyl acetate in medium is a order reaction. (1986, 1M)

59. The rate of chemical change is directly proportional to (1985, 1M)

True/False

60. For a first order reaction, the rate of the reaction doubles as the concentration of the reaction (s) doubles. (1986, 1M)

Integer Answer Type Questions

61. An organic compound undergoes first order decomposition. The time taken for its decomposition to $1/8$ and $1/10$ of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? ($\log_{10} 2 = 0.3$) (2012)

62. The concentration of R in the reaction $R \longrightarrow P$ was measured as a function of time and the following data is obtained :

[R] (molar)	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

The order of the reaction is (2010)

Subjective Questions

63. $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

- (a) order of reaction
- (b) rate constant
- (c) time taken for 75% completion of reaction
- (d) total pressure when $p_x = 700 \text{ mm}$

(2005, 4M)

64. For the given reaction, $A + B \longrightarrow \text{Products}$

Following data are given

Initial conc. (m/L)	Initial conc. (m/L)	Initial rate [mL ⁻¹ s ⁻¹]
$[A]_0$	$[B]_0$	
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

(a) Write the rate equation.

(b) Calculate the rate constant.

(2004, 2M)

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65. ^{64}Cu (half-life = 12.8 h) decays by β emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. (2002)

66. The rate of first order reaction is $0.04 \text{ mol L}^{-1}\text{s}^{-1}$ at 10 min and $0.03 \text{ mol L}^{-1}\text{s}^{-1}$ at 20 min after initiation. Find the half-life of the reaction. (2001, 5M)

67. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol $^{-1}$. (2000, 3M)

68. The rate constant for an isomerisation reaction, $A \rightarrow B$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. (1999, 4M)

69. (i) The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a . (1998, 5M)

- (ii) For the reaction, $\text{N}_2\text{O}_5(g) \longrightarrow 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g)$,

calculate the mole fraction $\text{N}_2\text{O}_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

70. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log k(\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

- (i) What is the energy of activation for the reaction?
(ii) At what temperature will its half-life period be 256 min? (1997, 5M)

71. One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nucleide has a half-life of 28.1 yr. Suppose one microgram was absorbed by a new-born child, how much Sr^{90} will remain in his bones after 20 yr. (1995, 2M)

72. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol $^{-1}$. Calculate the time required for 75% decomposition at 450°C. (1995, 4M)

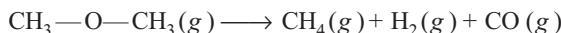
73. From the following data for the reaction between A and B

[A], (mol/L)	[B], (mol/L)	Initial rate (mol L $^{-1}$ s $^{-1}$) at	
		300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

Calculate

- (i) the order of the reaction with respect to A and with respect to B .
(ii) the rate constant at 300 K.
(iii) the pre-exponential factor. (1994, 5M)

74. The gas phase decomposition of dimethyl ether follows first order kinetics



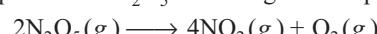
The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal gas behaviour. (1993, 4M)

75. A first order reaction, $A \rightarrow B$, requires activation energy of 70 kJ mol $^{-1}$. When a 20% solution of A was kept at 25°C for 20 min, 25% decomposition took place. What will be the percentage decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. (1993, 4M)

76. Two reactions (i) $A \rightarrow$ products (ii) $B \rightarrow$ products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A . If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K. (1992, 3M)

77. The nucleic ratio, ${}^3\text{H}$ to ${}^1\text{H}$ in a sample of water is $8.0 \times 10^{-18} : 1$. Tritium undergoes decay with a half-life period of 12.3 yr. How many tritium atoms would 10.0 g of such a sample contain 40 yr after the original sample is collected. (1992, 4M)

78. The decomposition of N_2O_5 according to the equation,



is a first order reaction. After 30 min from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg. On complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. (1991, 6M)

79. In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol $^{-1}$ respectively. If the reaction is of first order, at what temperature will its half-life period be 10 min? (1990, 3M)

80. An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of ${}_{42}\text{Mo}^{99}$, which is a beta emitter, is 66.6 h. Find the minimum amount of ${}_{42}\text{Mo}^{99}$ required to carry out the experiment in 6.909 h. (1989, 5M)

81. A first order gas reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change in the product? What is the half-life of this reaction? (1987, 5M)

82. While studying the decomposition of gaseous N_2O_5 , it is observed that a plot of logarithm of its partial pressure *versus* time is linear. What kinetic parameters can be obtained from this observation? (1985, 2M)

83. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr^{-1}) for the decay? What fraction would remain after 11540 yr? (1984, 3M)

84. A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant of the reaction, and
(ii) the time taken for the reaction to go to 75% completion. (1983, 2M)

85. Rate of reaction, $A + B \rightarrow \text{products}$ is given below as a function of different initial concentrations of A and B

$[A]$ mol/L	$[B]$ (mol/L)	Initial rate (mol $\text{L}^{-1} \text{min}^{-1}$)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and B . What is the half-life of A in the reaction? (1982, 4M)

Answers

- | | | | | | | | |
|-------------|-------------|-----------|-------------|---|--|---|-------------------|
| 1. (d) | 2. (b) | 3. (c) | 4. (d) | 49. (60) | 50. (6.75) | 51. (2.3) | 52. (+8500J/ mol) |
| 5. (a) | 6. (d) | 7. (d) | 8. (b) | 53. (c) | 54. (b) | 55. (a) | 56. $T = \infty$ |
| 9. (a) | 10. (c) | 11. (d) | 12. (b) | 57. 0.0015 | 60. T | 61. (9) | 62. (0) |
| 13. (d) | 14. (c) | 15. (b) | 16. (c) | 63. (950 mm Hg) | 66. (25 min) | 67. (100 kJ mol $^{-1}$) | |
| 17. (b) | 18. (a) | 19. (a) | 20. (d) | 68. (3.26×10^{-3} mol L $^{-1}$ min $^{-1}$) | 71. (6.1×10^{-7} g) | 72. (20.74 min) | |
| 21. (a) | 22. (a) | 23. (b) | 24. (d) | 74. (0.75 atm) | 75. (67 %) | 76. (3.26×10^{-2} min $^{-1}$) | |
| 25. (d) | 26. (a) | 27. (a) | 28. (d) | 77. (5.6×10^5) | 78. (5.2×10^{-3} min $^{-1}$) | | |
| 29. (a) | 30. (d) | 31. (d) | 32. (a) | 79. (311.34 K) | 80. (3.56×10^{-16} g) | | 81. |
| 33. (c) | 34. (a) | 35. (d) | 36. (d) | 82. (128.33 h) | 83. (0.25) | 85. (1.386 min) | |
| 37. (d) | 38. (c) | 39. (d) | 40. (a) | | | | |
| 41. (a) | 42. (a,d) | 43. (a,c) | 44. (b,c,d) | | | | |
| 45. (a,b,d) | 46. (a,b,d) | 47. (a,d) | 48. (b,c) | | | | |

Hints & Solutions

1. We know that,

$$\text{Rate} = k (\text{concentration})^n$$

[n = order of reaction and k = rate constant]

Taking log both side,

$$\log(\text{Rate}) = \log k + n \log [\text{concentration}]$$

Slope of graph is the order of reaction greater the slope, greater is the order of reaction.

∴ Correct sequence for the order of reaction is $D > B > A > C$.

Hence, the correct option is (d).

2. **Key Idea** The rate of a chemical reaction means the speed with which the reaction takes place.

For $R \longrightarrow P$

Rate of disappearance of R

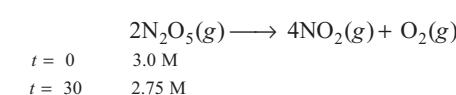
$$= \frac{\text{Decrease in conc. of } R}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t}$$

Rate of appearance of P

$$= \frac{\text{Increase in conc. of } P}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t}$$

Given, $[\text{N}_2\text{O}_5]_{\text{initial}} = 3.00 \text{ mol L}^{-1}$

After 30 min, $[\text{N}_2\text{O}_5] = 2.75 \text{ mol L}^{-1}$



From the equation, it can be concluded that

$$\begin{aligned} \frac{1}{2} \times \frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} &= \frac{1}{4} \times \frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= \frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{-(2.75 - 3.00) \text{ mol L}^{-1}}{30} \Rightarrow \frac{0.25}{30} \\ \text{and } \frac{\Delta[\text{NO}_2]}{\Delta t} &= -2 \frac{\Delta(\text{N}_2\text{O}_5)}{\Delta t} \Rightarrow \frac{\Delta[\text{NO}_2]}{\Delta t} = -2 \times \frac{0.25}{30} \\ &= -1.667 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

3. In the given reaction; $x A \longrightarrow y B$

$$\log_{10} \left[\frac{-d[A]}{dt} \right] = \log_{10} \left[\frac{d[B]}{dt} \right] + 0.3010$$

Value of $\log 2 = 0.3010$

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Substituting 0.3010 by log 2

$$\log_{10} \left[-\frac{d[A]}{dt} \right] = \log_{10} \left[\frac{d[B]}{dt} \right] + \log 2$$

Using logarithm rules,

$$\left[-\frac{d[A]}{dt} \right] = 2 \times \left[\frac{d[B]}{dt} \right] \Rightarrow -\frac{1}{2} \left[\frac{d[A]}{dt} \right] = \left[\frac{d[B]}{dt} \right] \quad \dots(i)$$

Using the rate equation (i) to determine the reaction involved is



Option that fits correct in the above reaction is (c).



4.

Key Idea The Arrhenius equation for rate constants at two different temperatures is

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad [\text{where, } T_2 > T_1]$$

where, k_1 and k_2 are rate constants at temperatures T_1 and T_2 , respectively.

R = Gas constant, E_a = Activation energy

For the reaction, $H_2 + I_2 \longrightarrow 2HI$

Given $k_1 = 2.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

$T_1 = (273 + 327) \text{ K} = 600 \text{ K}$

$k_2 = 1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $T_2 = (273 + 527) \text{ K} = 800 \text{ K}$

$$\text{Now, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \log \frac{1}{2.5 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left(\frac{800 - 600}{600 \times 800} \right)$$

$$\Rightarrow \log \frac{(10 \times 10^3)}{2.5} = \frac{E_a}{0.019} \times \frac{200}{48 \times 10^4}$$

$$\Rightarrow \log 4 + 3 \log 10 \approx E_a \times 0.022$$

$$\Rightarrow E_a = \frac{2 \times \log 2 + 3}{0.022} = \frac{3.6}{0.022} \approx 163.6 \text{ kJ mol}^{-1}$$

5. The expression for bacterial growth is

$$N = N_0 e^t$$

$$\frac{N_0}{N} = e^{-t}$$

From 0 to 1 hour $N'(t) = N_0 e^t$

From 1 hour onwards, $\frac{dN}{dt} = -5N^2$

On differentiating the above equation from N' to N we get.

$$\int_{eN_0}^N N^{-2} dN = -5 \int_1^t dt \quad [\because \text{At 1 hour, } N' = eN_0]$$

$$\left[\frac{1}{N} - \frac{1}{eN_0} \right] = 5(t-1)$$

Multiply both sides by N_0 , we get

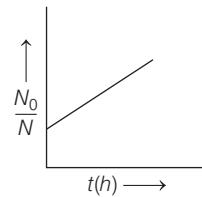
$$\frac{N_0}{N} - \frac{1}{e} = 5N_0(t-1) \text{ or, } \frac{N_0}{N} = 5N_0(t-1) + \frac{1}{e}$$

$$\frac{N_0}{N} = 5N_0 t + \left[\frac{1}{e} - 5N_0 \right]$$

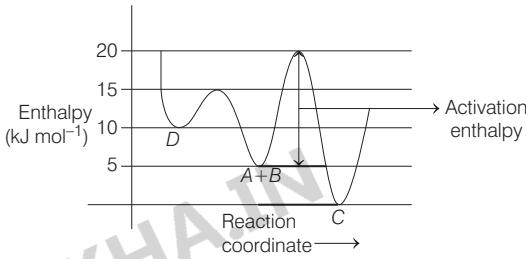
On comparing the above equation with equation of straight line,
 $y = mx + c$

We get $m = 5N_0$, $c = \frac{1}{e} - 5N_0$

\therefore Plot of $\frac{N_0}{N}$ vs t is shown aside.

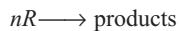


6. Only statement (d) is incorrect. Corrected statement is "Activation enthalpy to form C is 15 kg mol⁻¹ more than 5 kg mol⁻¹ that is required to form D." It can be easily explained by following graph.



Activation enthalpy (or energy) is the extra energy required by the reactant molecules that result into effective collision between them to form the products.

7. In first order reaction, the rate expression depends on the concentration of one species only having power equal to unity.



$$\frac{-d[R]}{dt} = k[R]$$

On integration, $-\ln[R] = kt - \ln[R_0]$

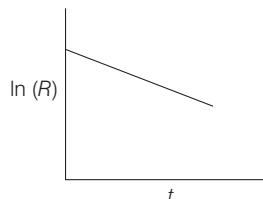
or $\ln(R) = \ln(R_0) - kt$

$$y = c + mx$$

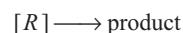
m = slope = $-k$ (negative)

c = intercept = $\ln(R_0)$

The graph for first order reactions is



In zero order reaction,



$$\therefore \frac{-d[R]}{dt} = k \text{ or } -d[R]_t = kdt$$

On integrating, $-[R]_t = kt + c$

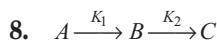
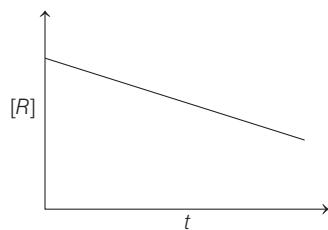
If

$$t = 0, [R]_t = [R]_0$$

$$\therefore \begin{aligned} -[R]_t &= kt - [R]_0 \\ [R]_t &= [R]_0 - kt \end{aligned}$$

Thus, the graph plotted between $[R]_t$ and t gives a straight line with negative slope ($-k$) and intercept equal to $[R]_0$.

The graph for zero order reaction is



Rate of formation of B is

$$\begin{aligned} \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \Rightarrow 0 &= k_1[A] - k_2[B] \quad \left[\because \text{Given, } \frac{d[B]}{dt} = 0 \right] \\ \Rightarrow k_2[B] &= k_1[A] \\ \Rightarrow \text{Concentration of } B, [B] &= \frac{k_1}{k_2}[A] \end{aligned}$$

9. Let the rate equation be $k[A]^x[B]^y$

From 1st values,

$$0.045 = k[0.05]^x[0.05]^y \quad \dots(i)$$

From 2nd values,

$$0.090 = k[0.10]^x[0.05]^y \quad \dots(ii)$$

From 3rd values,

$$0.72 = k[0.20]^x[0.10]^y \quad \dots(iii)$$

On dividing equations (i) by (ii), we get

$$\frac{0.045}{0.09} = \left[\frac{0.05}{0.10} \right]^x$$

$$\left[\frac{0.05}{0.10} \right]^1 = \left[\frac{0.05}{0.10} \right]^x$$

$$\therefore x = 1$$

Similarly on dividing Eq. (ii) by (iii) we get

$$\frac{0.09}{0.72} = \left[\frac{0.1}{0.2} \right]^x \left[\frac{0.05}{0.10} \right]^y$$

$$\frac{0.01}{0.08} = \frac{0.1}{0.2} \left[\frac{0.05}{0.10} \right]^y$$

$$0.25 = \left[\frac{0.05}{0.10} \right]^y$$

$$0.25 = [0.5]^y$$

$$[0.5]^2 = [0.5]^y$$

$$\therefore y = 2$$

Hence, the rate law for the reaction

$$\text{Rate} = k[A][B]^2$$

10. The temperature dependence of a chemical reaction is expressed by Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad \dots(i)$$

Taking natural logarithm on both sides, the Arrhenius equation becomes,

$$\ln k = \ln A - \frac{E_a}{RT}$$

where, $-\frac{E_a}{R}$ is the slope of the plot and $\ln A$ gives the intercept.

Eq. (i) at two different temperatures for a reaction becomes,

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots(ii)$$

\Rightarrow In the given problem,

$$T_1 = 400\text{K}, T_2 = 500\text{K}$$

$$k_1 = 10^{-5}\text{s}^{-1}, k_2 = ?$$

$$-\frac{E_a}{R} (\text{Slope}) = -4606$$

On substituting all the given values in Eq. (ii), we get

$$\ln \frac{k_2}{10^{-5}} = 4606 \left(\frac{1}{400} - \frac{1}{500} \right)$$

$$\ln \frac{k_2}{10^{-5}} = 2.303$$

$$\frac{k_2}{10^{-5}} = 10 \Rightarrow k_2 = 10^{-4}\text{s}^{-1}$$

Therefore, rate constant for the reaction at 500 K is 10^{-4}s^{-1} .

11. Given, rate constant (k) = 0.05\mu g/year

Thus, from the unit of k , it is clear that the reaction is zero order. Now, we know that

$$\text{half-life } (t_{1/2}) \text{ for zero order reaction} = \frac{a_0}{2k}$$

where, a_0 = initial concentration,

k = rate constant

$$t_{1/2} = \frac{5\text{\mu g}}{2 \times 0.05\text{\mu g/year}} = 50\text{ years}$$

Thus, 50 years are required for the decomposition of 5\mu g of X into 2.5\mu g .

12. For zero order reaction,

$$[A_0] - [A_t] = kt \quad \dots(i)$$

where, $[A_0]$ = initial concentration

$[A_t]$ = final concentration at time ' t '

k = rate constant

$$\text{Also, for zero order reaction, } t_{1/2} = \frac{[A_0]}{2k}$$

Given, $t_{1/2} = 6\text{ h}$ and $[A_0] = 0.2\text{ M}$

$$\therefore 6 = \frac{0.2}{2k}$$

$$\text{or, } k = \frac{0.2}{2 \times 6} = \frac{1}{60}$$

Now, from Eq. (i)

$$[A_0] - [A_t] = kt$$

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Given, $[A_0] = 0.5 \text{ M}$, $[A_t] = 0.2 \text{ M}$

$$\therefore \frac{0.5 - 0.2}{0.5} = \frac{1}{60} \times t \quad \left[\because k = \frac{1}{60} \right]$$

$$0.3 = \frac{1}{60} \times t \Rightarrow t = 0.3 \times 60 = 18 \text{ h}$$

- 13.** The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation as, $k = A e^{-E_a/RT}$... (i)
where, A = Arrhenius factor or frequency factor or pre-exponential factor

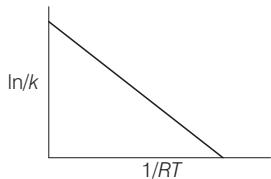
R = Gas constant, E_a = Activation energy

Taking log on both sides of the Eq. (i), the equation becomes

$$\ln k = \ln A - \frac{E_a}{RT}$$

On comparing with equation of straight line ($y = mx + c$), the nature of the

plot of $\ln k$ vs $\frac{1}{RT}$ will be:



(i) Intercept = $C = \ln A$

(ii) Slope/gradient = $m = -E_a = -y \Rightarrow E_a = y$

So, the energy required to activate the reactant, (activation energy of the reaction, E_a) is $= y$)

- 14.** The elementary reaction, $A_2 \xrightleftharpoons[k_{-1}]{k_1} 2A$

follows opposing or reversible kinetics,

(i) Rate of the reaction,

$$r = r_{\text{forward}} - r_{\text{backward}} = k_1[A_2] - k_{-1}[A]^2 \quad \dots (\text{i})$$

(ii) Again, rate of the reaction can be expressed as,

$$r = -\frac{d[A_2]}{dt} = +\frac{1}{2} \frac{d[A]}{dt}$$

So, the rate of appearance of A , i.e.

$$\frac{d[A]}{dt} = 2r = 2k_1[A_2] - 2k_{-1}[A]^2 \quad [\text{from Eq. (i)}]$$

- 15.** The Arrhenius equation is,

$$k = A \cdot e^{-E_a/RT}$$

where, k = rate constant,

A = Arrhenius constant, E_a = activation energy,

and T = temperature in K

From the equation, it is clear that k decreases exponentially with E_a . So, the plot-I is correct.

In the plot-II, k is plotted with temperature (in $^{\circ}\text{C}$ but not in K). So, at 0°C , $k \neq 0$ and k will increase exponentially with temperature upto 300°C . Therefore, the plot-II is also correct.

- 16.** For the reaction, $2A + B \rightarrow \text{products}$.

Let, the rate expression is

$$r \propto [A]^a[B]^b$$

Expt 1 $\frac{r_2}{r_1} = \left(\frac{2A}{A}\right)^a \left(\frac{2B}{B}\right)^b$

$$\Rightarrow \frac{2.4}{0.3} = 2^a \times 2^b \Rightarrow 2^3 = 2^{a+b} \Rightarrow 3 = a + b \quad \dots (\text{i})$$

Expt 2 $\frac{r_2}{r_1} = \left(\frac{2A}{A}\right)^a \left(\frac{B}{B}\right)^b$

$$\Rightarrow \frac{0.6}{0.3} = 2^a \times 1 \Rightarrow 2^1 = 2^a \Rightarrow a = 1 \quad \dots (\text{ii})$$

\therefore From Eq. (i), $1 + b = 3 \Rightarrow b = 2$

\Rightarrow Order of the reaction (n) = $a + b = 1 + 2 = 3$

\Rightarrow Order of the reaction wrt. $A = 1$

\Rightarrow Order of the reaction wrt. $B = 2$

- 17.** Let, the rate expression is $r \propto [A]^a [B]^b$.

From experiment I,

$$\frac{r_2}{r_1} = \left(\frac{0.1}{0.1}\right)^a \times \left(\frac{0.25}{0.20}\right)^b \Rightarrow \frac{6.93 \times 10^{-3}}{6.93 \times 10^{-3}} = 1 \times \left(\frac{5}{4}\right)^b$$

$$\Rightarrow 1 = \left(\frac{5}{4}\right)^b \Rightarrow \left(\frac{5}{4}\right)^0 = \left(\frac{5}{4}\right)^b \Rightarrow b = 0$$

$$\text{From experiment II, } \frac{r_3}{r_1} = \left(\frac{0.2}{0.1}\right)^a \times \left(\frac{0.30}{0.20}\right)^b$$

$$\Rightarrow \frac{1.386 \times 10^{-2}}{0.693 \times 10^{-2}} = (2)^a \times (1.5)^0$$

$$\Rightarrow 2 = 2^a \times 1 \Rightarrow 2^1 = 2^a \Rightarrow a = 1$$

$$\Rightarrow \text{So, } r \propto [A]^1 [B]^0 \Rightarrow r \propto [A]$$

Order of the reaction (n) = 1

\Rightarrow Now, let for the 1st experiment,

$$r_1 = k \cdot [A] \Rightarrow k = \frac{r_1}{[A]} = \frac{6.93 \times 10^{-3}}{0.1} = 6.93 \times 10^{-2} \text{ s}^{-1}$$

$$\Rightarrow t_{50} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-2}} = 10 \text{ s}$$

- 18.** From thermodynamics,

$$\ln k = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \dots (\text{i})$$

Mathematically, the equation of straight line is

$$y = c + mx \quad \dots (\text{ii})$$

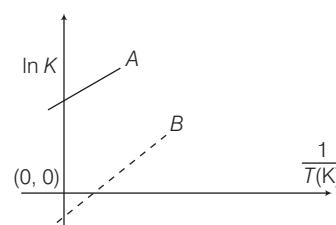
After comparing Eq. (ii) with (i) we get,

$$\text{slope} = \frac{-\Delta H^\circ}{R} \text{ and intercept} = \frac{\Delta S^\circ}{R}$$

Now, we know for exothermic reaction ΔH is negative (-ve). But here,

$$\text{Slope} = \frac{-\Delta H^\circ}{R} \text{ is positive}$$

So, lines A and B in the graph represent temperature dependence of equilibrium constant K for an exothermic reaction as shown below



19. For the reaction,



Let order of reaction with respect to CH_3CHO is m .

Its given, $r_1 = 1 \text{ torr/sec.}$ when CH_3CHO is 5% reacted i.e. 95% unreacted. Similarly, $r_2 = 0.5 \text{ torr/sec}$ when CH_3CHO is 33% reacted i.e., 67% unreacted.

Use the formula, $r \propto (a - x)^m$

where $(a - x)$ = amount unreacted

$$\text{so, } \frac{r_1}{r_2} = \frac{(a - x_1)^m}{(a - x_2)^m} \text{ or } \frac{r_1}{r_2} = \left[\frac{a - x_1}{a - x_2} \right]^m$$

Now putting the given values

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67} \right)^m \Rightarrow 2 = (1.41)^m \text{ or } m = 2$$

20. According to Arrhenius equation

$$k = A e^{-E_a/RT}$$

where, A = collision number or pre-exponential factor.

R = gas constant, T = absolute temperature

E_a = energy of activation

$$\text{For reaction } R_1, k_1 = A e^{-E_{a1}/RT} \quad \dots(i)$$

$$\text{For reaction } R_2, k_2 = A e^{-E_{a2}/RT} \quad \dots(ii)$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{k_2}{k_1} = e^{-\frac{(E_{a2} - E_{a1})}{RT}} \quad \dots(iii)$$

[∴ Pre-exponential factor ' A ' is same for both reactions]

Taking \ln on both the sides of Eq. (iii), we get

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a1} - E_{a2}}{RT}$$

$$\text{Given, } E_{a1} = E_{a2} + 10 \text{ kJ mol}^{-1} = E_{a2} + 10,000 \text{ J mol}^{-1}$$

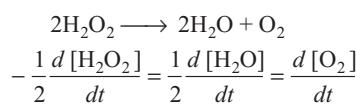
$$\therefore \ln\left(\frac{k_2}{k_1}\right) = \frac{10,000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}} = 4$$

21. For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$

Given, $t = 50 \text{ min}, a = 0.5 \text{ M}, a-x = 0.125 \text{ M}$

$$\therefore k = \frac{2.303}{50} \log \frac{0.5}{0.125} = 0.0277 \text{ min}^{-1}$$

Now, as per reaction



$$\text{Rate of reaction, } -\frac{d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2]$$

$$\therefore \frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{1}{2} k[\text{H}_2\text{O}_2] \quad \dots(i)$$

When the concentration of H_2O_2 reaches 0.05 M,

$$\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \times 0.0277 \times 0.05 \quad [\text{from Eq. (i)}]$$

$$\text{or } \frac{d[\text{O}_2]}{dt} = 6.93 \times 10^{-4} \text{ mol min}^{-1}$$

Alternative Method

In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M or in one half-life, concentration of H_2O_2 decreases from 0.5 to 0.25 M. In two half-lives, concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2t_{1/2} = 50 \text{ min}$

$$t_{1/2} = 25 \text{ min}$$

$$\therefore k = \left(\frac{0.693}{25} \right) \text{ min}^{-1}$$

$$\text{or } \frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{k[\text{H}_2\text{O}_2]}{2} = 6.93 \times 10^{-4} \text{ mol min}^{-1}$$

22. The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants.

Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.

23. For the elementary reaction, $M \longrightarrow N$

Rate law can be written as

$$\text{Rate} \propto [M]^n$$

$$\text{Rate} = k[M]^n \quad \dots(ii)$$

When we double the concentration of $[M]$,

rate becomes 8 times, hence new rate law can be written as

$$8 \times \text{Rate} = k[2M]^n \quad \dots(ii)$$

$$\frac{\text{Rate}}{8 \times \text{Rate}} = \frac{k[M]^n}{k[2M]^n} \Rightarrow \frac{1}{8} = \frac{1}{[2]^n}$$

$$\Rightarrow [2]^n = 8 = [2]^3 \Rightarrow n = 3$$

24. This problem can be solved by determining the order of reaction w.r.t. each reactant and then writing rate law equation of the given equation accordingly as

$$R = \frac{dC}{dt} = k[A]^x[B]^y$$

where, x = order of reaction w.r.t A

y = order of reaction w.r.t B

$$1.2 \times 10^{-3} = k(0.1)^x(0.1)^y$$

$$1.2 \times 10^{-3} = k(0.1)^x(0.2)^y$$

$$2.4 \times 10^{-3} = k(0.2)^x(0.1)^y$$

$$R = k[A]^1[B]^0$$

As shown above, rate of reaction remains constant as the concentration of reactant (B) changes from 0.1 M to 0.2 M and becomes double when concentration of A change from 0.1 to 0.2, (i.e. doubled).

25. PLAN Time of 75% reaction is twice the time taken for 50% reaction if it is first order reaction w.r.t. P . From graph, $[Q]$ decreases linearly with time, thus it is zeroth order reaction w.r.t. Q

$$\frac{dx}{dt} = bk[P]^a[Q]^b$$

Order w.r.t $P = a = 1$

Order w.r.t $Q = b = 0$

Thus, overall order of the reaction = $1 + 0 = 1$

26. From Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{-E_a}{2.303 R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\text{Given, } \frac{k_2}{k_1} = 2 \quad T_2 = 310 \text{ K}$$

$$T_1 = 300 \text{ K}$$

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On putting values,

$$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.314} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$\Rightarrow E_a = 53.603 \text{ kJ/mol}$$

27. According to Arrhenius equation, rate constant increases exponentially with temperature :

$$k = Ae^{-E_a/RT}$$

28. The logarithmic form of Arrhenius equation is

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$\text{Given : } \log k = 6 - \frac{2000}{T}$$

Comparing the above two equations :

$$\log A = 6 \Rightarrow A = 10^6$$

$$\text{and } \frac{E_a}{2.303 R} = 2000$$

$$\Rightarrow E_a = 2000 \times 2.303 \times 8.314 \text{ J} = 38.3 \text{ kJ mol}^{-1}$$

29. For first order reaction $t_{1/2} = \frac{\ln 2}{k_1} = 40 \text{ s}$... (i)

$$\text{For zero order reaction } t_{1/2} = \frac{[A]_0}{2k_0} = 20 \text{ s} \quad \dots (\text{ii})$$

$$\Rightarrow \text{Eq. (ii)/(i)} \quad = \frac{1}{2} = \frac{[A]_0}{2k_0} \times \frac{k_1}{\ln 2}$$

$$\Rightarrow \frac{k_1}{k_0} = \frac{\ln 2}{[A]_0} = \frac{0.693}{1.386} = 0.5$$

30. Rate $\propto [G]^m [H]^n$

\because Rate is double on doubling the concentration of G and maintaining H constant, $m = 1$, i.e. $R \propto [G]$.

Also, when both concentration of G and H are doubled, rate increases by a factor of 8. Here rate is increasing by a factor of 2 due to G (first order in G), therefore, factor due to H is 4.

$$\Rightarrow R \propto [H]^2 \Rightarrow \text{Overall order} = m + n = 1 + 2 = 3$$

31. Order of a reaction can take any real value, i.e. negative, integer, fraction etc.

32. For first order reaction,

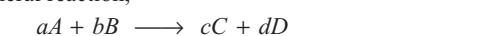
$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{0.1}{0.025} = 3.46 \times 10^{-2}$$

$$\text{Rate} = [k] A = 3.46 \times 10^{-2} \times 0.01 = 3.46 \times 10^{-4}$$

33. For a first order reaction, $kt = \ln \frac{[A]_0}{[A]}$

$$\Rightarrow k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{2 \times 10^4} \ln \frac{800}{50} = \frac{4 \ln 2}{2 \times 10^4} \text{ s}^{-1} \\ = 1.386 \times 10^{-4} \text{ s}^{-1}$$

34. For any general reaction,



$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

\Rightarrow For $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

$$\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

35. Rate will be directly proportional to both concentration and intensity, i.e. rate of formation of AB^* $\propto C \cdot I$.

36. The unit of rate constant (t^{-1}) indicating that the decomposition reaction following first order kinetics.

\Rightarrow Rate $= k[\text{N}_2\text{O}_5]$

$$[\text{N}_2\text{O}_5] = \frac{\text{Rate}}{k} = \frac{2.40 \times 10^{-5}}{3 \times 10^{-5}} = 0.8 \text{ M}$$

37. 560 days $= \frac{560}{140} = 4$ half-lives.

Amount of reactant remaining after n -half-lives

$$= \left(\frac{1}{2}\right)^n \times \text{initial amount} = \left(\frac{1}{2}\right)^4 \times 1.0 \text{ g} = \frac{1}{16} \text{ g}$$

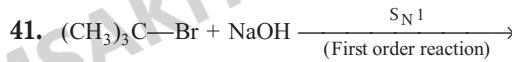
38. A catalyst increases the rate of reaction but by the same factor to both forward and backward directions. Hence, a catalyst shortens the time required to reach the equilibrium.

39. Specific rate constant of reaction depends on temperature.

40. The rate constant (k) of all chemical reactions depends on temperature.

$$k = Ae^{-E_a/RT}$$

where, A = pre-exponential factor, E_a = activation energy.



This is first order reaction and for first order reaction $t_{1/2} = \frac{0.693}{k}$

So, half-life is independent of initial concentration.

Therefore, the plot (a) correct.

For first order reaction, $(r) = k[(\text{CH}_3)_3\text{C}-\text{Br}]$

$$\ln\left(\frac{P_0}{P}\right) = k \cdot t \quad \text{or} \quad \ln\left(\frac{P}{P_0}\right) = -k \cdot t$$

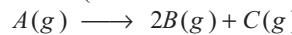
Hence, plot (b) and (d) are incorrect.

For first order reaction,

$$Q = [P_0](1 - e^{-kt}) \quad \text{or} \quad \frac{[Q]}{[P_0]} = (1 - e^{-kt})$$

Hence, plot (c) is incorrect.

42. Given for the reaction (at $T = 300 \text{ K}$ and constant volume = V)



at $t = 0$	P_0	—	—
at $t = t$	$P_0 - x$	$2x$	x
at $t = t_{1/3}$	$\left[P_0 - \frac{2P_0}{3}\right] = \frac{P_0}{3}$	$\frac{4P_0}{3}$	$\frac{2P_0}{3}$

We can calculate,

$$P_t = P_0 - x + 2x + x = P_0 + 2x$$

$$\text{or} \quad 2x = P_t - P_0 \quad \text{or} \quad x = \frac{P_t - P_0}{2}$$

Now for first order reaction,

$$t = \frac{1}{k} \ln \frac{P_0}{(P_0 - x)}$$

Putting the value of x in the equation,

$$t = \frac{1}{k} \ln \frac{p_0}{p_0 - \left(\frac{p_t - p_0}{2} \right)} = \frac{1}{k} \ln \frac{2p_0}{2p_0 - p_t + p_0}$$

$$\text{or } kt = \ln \frac{2p_0}{(3p_0 - p_t)} \quad \text{or } kt = \ln 2p_0 - \ln (3p_0 - p_t)$$

$$\text{or } \ln (3p_0 - p_t) = -kt + \ln 2p_0$$

It indicates graph between $\ln (3p_0 - p_t)$ vs 't' will be a straight line with negative slope, so option (a) is correct

$$t_{1/3} = \frac{1}{k} \ln \frac{p_0}{p_0/3} = \frac{1}{k} \ln 3$$

It indicates $t_{1/3}$ is independent of initial concentration so, option (b) is incorrect.

Likewise, rate constant also does not show its dependence over initial concentration. Thus, graph between rate constant and $[A]_0$ will be a straight line parallel to X -axis.

43. If steric factor is considered, the corrected Arrhenius equation will be

$$k = pAe^{\frac{-E_a}{RT}} \text{ where } A = \text{frequency factor by Arrhenius.}$$

$\therefore p > 1, pA > A$ hence, (a) is correct.

Activation energy is not related to steric factor.

44. Rate constant, $k = Ae^{-E_a/RT}$

where, E_a = activation energy and A = pre-exponential factor

(a) If E_a is high, it means lower value of k hence, slow reaction. Thus, incorrect.

(b) On increasing temperature, molecules are raised to higher energy (greater than E_a), hence number of collisions increases. Thus, correct.

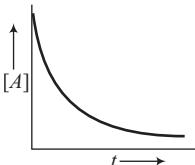
$$(c) \log k = \log A - \frac{E_a}{RT} \Rightarrow \frac{d(\log k)}{dT} = \frac{E_a}{RT^2}$$

Thus, when E_a is high, stronger is the temperature dependence of the rate constant. Thus, correct.

(d) Pre-exponential factor (A) is a measure of rate at which collisions occur. Thus, correct.

45. (a) For a first order reaction, the concentration of reactant remaining after time t is given by $[A] = [A]_0 e^{-kt}$

Therefore, concentration of reactant decreases exponentially with time.



(b) Rise in temperature increases rate constant (k) and therefore decreases half-life ($t_{1/2}$) as

$$t_{1/2} = \frac{\ln 2}{k}$$

(c) Half-life of first order reaction is independent of initial concentration.

(d) For a first order reaction, if 100 moles of reactant is taken initially, after n half-lives, reactant remaining is given by

$$\% A = 100 \left(\frac{1}{2} \right)^n = 100 \left(\frac{1}{2} \right)^8 = 0.3906$$

$$\Rightarrow A \text{ reacted} = 100 - 0.3906 = 99.6\%$$

46. Equilibrium constant is related to temperature

$$\log K_p = \text{constant} - \frac{\Delta H}{2.3 RT}$$

\Rightarrow Plot of $\log K_p$ vs $1/T$ will be a straight line.

For the first order reaction $X \rightarrow P$

$$\log \frac{[X]_0}{[X]} = \frac{kt}{2.3} \Rightarrow \log [X] = \log [X_0] - \frac{kt}{2.3},$$

i.e. $\log [X]$ vs 't' will give a straight line.

Also at constant temperature, $pV = \text{constant}$

$$\Rightarrow \text{Plot of } p \text{ vs } \frac{1}{V} \text{ will give a straight line.}$$

47. For a first order reaction :

$$kt = \ln \frac{1}{1-\alpha} \quad \text{where, } \alpha = \text{degree of dissociation.}$$

$$\Rightarrow 1-\alpha = e^{-kt} \Rightarrow \alpha = 1 - e^{-kt}$$

$$\text{Also } \frac{1}{[A]} = \frac{e^{kt}}{[A]_0}, \text{ i.e. plot of reciprocal of concentration of}$$

reactant vs time will be exponential.

$$\text{Time for } 75\% = \frac{1}{k} \ln \frac{100}{100-75} = \frac{2 \ln 2}{k} = 2(t_{1/2})$$

The Arrhenius equation is :

$$\ln k = \ln A - \frac{E_a}{RT}$$

The dimensions of k and A must be same. For first order reaction, dimensions of k is t^{-1} .

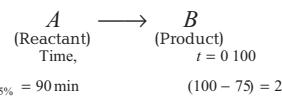
48. A catalyst lowers the activation energy by enabling the reaction to continue through an alternative path, i.e. catalyst changes the reaction mechanism. However, catalyst does not affect either average kinetic energies of reactants or the collision frequency.

49. Given, first order reaction,

$$t_{75} = 90 \text{ minute}$$

$$t_{60} = ?$$

Consider the following reaction,



For first order reaction,

$$t = \frac{2.303}{k} \log \left(\frac{a_0}{a} \right) \quad \left[a_0 = \text{Initial concentration} \right] \quad \left[a = \text{Concentration} \right]$$

For 75%,

t_{75\%} = \frac{2.303}{k} \log \left(\frac{100}{25} \right) \dots (i) \quad \left[\begin{array}{l} \text{Initial conc.} = 100 \\ \text{Conc.} = 100 - 75 = 25 \end{array} \right]

For 60%,

t_{60\%} = \frac{2.303}{k} \log \left(\frac{100}{40} \right) \dots (ii) \quad \left[\begin{array}{l} \text{Initial conc.} = 100 \\ \text{Conc.} = 100 - 60 = 40 \end{array} \right]

On equating Eqs. (i) and (ii),

$$\frac{t_{60\%}}{t_{75\%}} = \frac{\frac{2.303}{k} \log \left(\frac{100}{40} \right)}{\frac{2.303}{k} \log \left(\frac{100}{25} \right)}$$

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$$t_{60\%} = t_{75\%} \times \left(\frac{0.3979}{0.602} \right)$$

$$t_{60\%} = 90 \times \frac{0.3979}{0.602}$$

$$t_{60\%} = 59.48 \text{ minute} \approx 60 \text{ min}$$

50. Rate = $k[A]^x[B]^y[C]^z$

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{[0.2]^x [0.1]^y [0.1]^z}{[0.2]^x [0.2]^y [0.1]^z} = \frac{6 \times 10^{-5}}{6 \times 10^{-5}}$$

$$\Rightarrow y = 0$$

$$\frac{(\text{Rate})_1}{(\text{Rate})_3} = \frac{[0.2]^x [0.1]^y [0.1]^z}{[0.2]^x [0.1]^y [0.2]^z} = \frac{6 \times 10^{-5}}{1.2 \times 10^{-4}}$$

$$\Rightarrow z = 1$$

$$\frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{[0.2]^x [0.1]^y [0.1]^z}{[0.3]^x [0.1]^y [0.1]^2} = \frac{6 \times 10^{-5}}{9 \times 10^{-5}}$$

$$\Rightarrow x = 1$$

$$\text{So, rate} = k[A]^1[C]^1$$

From exp-Ist,

$$\text{Rate} = 6.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$6.0 \times 10^{-5} = k[0.2]^1[0.1]^1$$

$$k = 3 \times 10^{-3}$$

$$\text{Given, } [A] = 0.15 \text{ mol dm}^{-3}$$

$$[B] = 0.25 \text{ mol dm}^{-3}$$

$$[C] = 0.15 \text{ mol dm}^{-3}$$

$$\therefore \text{Rate} = (3 \times 10^{-3}) \times [0.15]^1 [0.25]^0 [0.15]^1 \\ = 3 \times 10^{-3} \times 0.15 \times 0.15$$

$$\text{Rate} = 6.75 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\text{Thus, } Y = 6.75$$

51. At constant V, T



At initial $t = 0$	1	0	0
$t = Y \times 10^3 \text{ sec}$	$1 - 2p$	$2p$	p

$$P_{\text{Total}} = 1 - 2p + 2p + p$$

$$1.4 = 1 + p$$

$$p = 0.45 \text{ atm}$$

According to first order reaction,

$$k = \frac{2.303}{t} \log \frac{p_i}{p_i - 2p}$$

$$p_i = \text{latm (given)}$$

$$2p = 2 \times 0.45 = 0.9 \text{ atm}$$

On substituting the values in above equation,

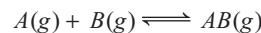
$$2k \cdot t = 2.303 \log \frac{1}{1 - 0.9}$$

$$2 \times 5 \times 10^{-4} \times Y \times 10^3 = 2.303 \log \frac{1}{0.1}$$

$$Y = 2.303 = 2.3$$

Note Unit of rate constant (k), i.e. s^{-1} represents that it is a first order reaction.

52. For the reaction,



$$\text{Given } E_{ab} = E_{af} + 2RT \quad \text{or} \quad E_{ab} - E_{af} = 2RT$$

Further

$$A_f = 4A_b \quad \text{or} \quad \frac{A_f}{A_b} = 4$$

Now, rate constant for forward reaction,

$$k_f = A_f e^{-E_{af}/RT}$$

Likewise, rate constant for backward reaction,

$$k_b = A_b e^{-E_{ab}/RT}$$

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$\text{i.e., } k_f = k_b \quad \text{or} \quad \frac{k_f}{k_b} = k_{eq}$$

$$\text{so } k_{eq} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}} = \frac{A_f}{A_b} e^{-(E_{af} - E_{ab})/RT}$$

After putting the given values

$$k_{eq} = 4e^2 \quad (\text{as } E_{ab} - E_{af} = 2RT \text{ and } \frac{A_f}{A_b} = 4)$$

$$\text{Now, } \Delta G^\circ = -RT \ln K_{eq} = -2500 \ln(4e^2)$$

$$= -2500 (\ln 4 + \ln e^2) = -2500 (1.4 + 2)$$

$$= -2500 \times 3.4 = -8500 \text{ J/mol}$$

$$\text{Absolute value} = 8500 \text{ J/mol}$$

53. Living plants maintain an equilibrium between the absorption of C^{14} (produced due to cosmic radiation) and the rate of decay of C^{14} present inside the plant. This gives a constant amount of C^{14} per gram of carbon in a living plant.

54. Fossil whose age is closest to half-life of C-14 (5770 yr) will yield the most accurate age by C-14 dating.

$$55. \lambda T = \ln \frac{N_0}{N}$$

where N_0 = Number of C^{14} in the living matter and N = Number of C^{14} in fossil. Due to nuclear explosion, amount of C^{14} in the near by area increases. This will increase N_0 because living plants are still taking C-14 from atmosphere, during photosynthesis, but N will not change because fossil will not be doing photosynthesis.

$\Rightarrow \lambda T$ (age) determined in the area where nuclear explosion has occurred will be greater than the same determined in normal area.

$$\text{Also, } \lambda T_1 = \ln \frac{C_1}{C} \Rightarrow \lambda T_2 = \ln \frac{C_2}{C} \Rightarrow T_1 - T_2 = \frac{1}{\lambda} = \ln \frac{C_1}{C_2}$$

C = Concentration of C-14 in fossil.

$$56. k = A e^{-E_a/RT} : \text{ At } T = \infty, k = A$$

$$57. -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

$$\Rightarrow -\frac{d[H_2]}{dt} = \frac{3}{2} \frac{d[NH_3]}{dt} = \frac{3}{2} \times 0.001 = 0.0015 \text{ kg h}^{-1}$$

58. acidic, first or basic, second.

59. Rate is directly proportional to concentration of reactants.

60. $R \propto [\text{Reactant}]$

On doubling the concentration of reactant, rate would be double.

61. For a first order process $kt = \ln \frac{[A]_0}{[A]}$

where, $[A]_0$ = initial concentration.

$[A]$ = concentration of reactant remaining at time "t".

$$\Rightarrow kt_{1/8} = \ln \frac{[A]_0}{[A]_0/8} = \ln 8 \quad \dots(\text{i})$$

$$\text{and } kt_{1/10} = \ln \frac{[A]_0}{[A]_0/10} = \ln 10 \quad \dots(\text{ii})$$

$$\text{Therefore, } \frac{t_{1/8}}{t_{1/10}} = \frac{\ln 8}{\ln 10} = \log 8 = 3 \log 2 = 3 \times 0.3 = 0.9$$

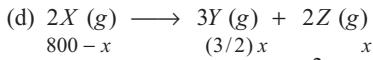
$$\Rightarrow \frac{t_{1/8}}{t_{1/10}} \times 10 = 0.9 \times 10 = 9$$

62. Rate of reaction is constant with time.

63. (a) Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

$$(b) k \times 100 = \ln \frac{800}{400} = \ln 2 \Rightarrow k = 6.93 \times 10^{-3} \text{ min}^{-1}$$

(c) For 75% reaction; time required = 2 × half-life = 200 min



$$\text{Total pressure} = 800 + \frac{3}{2}x$$

$$\text{Also } 800 - x = 700 \Rightarrow x = 100$$

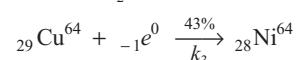
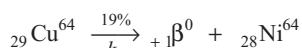
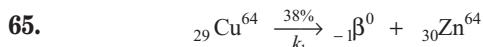
$$\Rightarrow \text{Total pressure} = 800 + \frac{3}{2} \times 100 = 950 \text{ mm Hg}$$

64. $\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{0.05}{0.10} = \frac{1}{2} = \left(\frac{1}{2}\right)^a \Rightarrow a = 1; \text{ order w.r.t } A.$

Order w.r.t $B = 0$

(a) Rate = $k[A]$

$$(b) k = \frac{\text{Rate}}{[A]} = \frac{0.05}{0.10} = 0.5 \text{ s}^{-1}$$



Above are the parallel reactions occurring from Cu^{64} .

$$\frac{k_1}{k_2} = \frac{38}{19} = 2 = \frac{T_2}{T_1} \quad \text{and} \quad \frac{k_1}{k_3} = \frac{38}{43} = \frac{T_3}{T_1}$$

T_1, T_2 and T_3 are the corresponding partial half-lives.

Also $k = k_1 + k_2 + k_3$

$$\Rightarrow \frac{\ln 2}{T} = \frac{\ln 2}{T_1} + \frac{\ln 2}{T_2} + \frac{\ln 3}{T_3}$$

$$\Rightarrow \frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_3} = \frac{1}{T_1} + \frac{1}{2T_1} + \frac{43}{38T_1}$$

$$= \frac{1}{T_1} \left(1 + \frac{1}{2} + \frac{43}{38}\right) = \frac{1}{T_1} \left(\frac{38 + 19 + 43}{38}\right) = \frac{100}{38T_1}$$

$$\Rightarrow T_1 = \frac{100T}{38} = \frac{100}{38} \times 12.8 = 33.68 \text{ h}$$

$$T_2 = 2T_1 = 67.36 \text{ h}$$

$$T_3 = \frac{38T_1}{43} = \frac{38 \times 33.68}{43} = 29.76 \text{ h}$$

66. $R = k[A] \Rightarrow R_1 = k[A]_1 \text{ and } R_2 = k[A]_2$

$$\Rightarrow \frac{R_1}{R_2} = \frac{4}{3} = \frac{[A]_1}{[A]_2}$$

$$\text{Also } k(t_2 - t_1) = \ln \frac{[A]_1}{[A]_2} = \ln \frac{4}{3} \Rightarrow \frac{\ln 2}{t_{1/2}} \times 10 = \ln \frac{4}{3}$$

$$\Rightarrow t_{1/2} = \frac{10 \log 3}{\log 4 - \log 3} = \frac{3}{0.6 - 0.48} = 25 \text{ min}$$

67. $k_{500} = A e^{-E_1/RT_1}$

$$k_{400} = A e^{-E_2/RT_2}$$

$$\therefore k_{500} = k_{400}$$

$$\frac{E_1}{RT_1} = \frac{E_2}{RT_2} \Rightarrow \frac{E_2}{E_1} = \frac{T_2}{T_1} = \frac{400}{500} = \frac{4}{5}$$

$$\text{Also } E_1 = E_2 + 20000 \text{ J}$$

$$\Rightarrow \frac{E_1 - 20,000}{E_1} = \frac{4}{5} \Rightarrow E_1 = 100,000 \text{ J} = 100 \text{ kJ mol}^{-1}$$

68. $kt = \ln \frac{[A]_0}{[A]}$

$$\Rightarrow 4.5 \times 10^{-3} \times 60 = \ln \frac{1}{[A]} \Rightarrow [A] = 0.76 \text{ M}$$

$$\Rightarrow \text{Rate} = k[A] = 4.5 \times 10^{-3} \times 0.76 = 3.42 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

69. (i) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

$$\Rightarrow \ln \left(\frac{4.5 \times 10^7}{1.5 \times 10^7} \right) = \frac{E_a}{8.314} \left(\frac{50}{323 \times 373} \right) \Rightarrow E_a = 22 \text{ kJ}$$

$$\text{Also } \ln k = \ln A - \frac{E_a}{RT}$$

$$\text{At } 50^\circ\text{C} : \ln A = \ln (1.5 \times 10^7) - \frac{22 \times 1000}{8.314 \times 323} = 8.33$$

$$\Rightarrow A = 4.15 \times 10^3 \text{ s}^{-1}$$

(ii) $\text{N}_2\text{O}_5(g) \longrightarrow 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g)$

$$600 - p \qquad \qquad 2p \qquad \qquad p/2$$

$$\text{Total pressure} = 960 = 600 + \frac{3}{2}p \Rightarrow p = 240 \text{ mm}$$

$$\Rightarrow \text{Partial pressure of } \text{N}_2\text{O}_5(g) \text{ remaining} = 600 - 240 = 360 \text{ mm}$$

$$\Rightarrow \text{Mole fraction} = \frac{360}{960} = 0.375$$

70. (i) The Arrhenius equation is

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

Comparing with the given equation :

$$1.25 \times 10^4 = \frac{E_a}{2.303 R} \Rightarrow E_a = 239.33 \text{ kJ mol}^{-1}$$

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(ii) When half-life = 256 min,

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{256 \times 60} \text{ s}^{-1} = 4.5 \times 10^{-5} \text{ s}^{-1}$$

$$\Rightarrow \frac{1.25 \times 10^4}{T} = 14.34 - \log 4.5 \times 10^{-5} = 16.68$$

$$\Rightarrow T = \frac{1.25 \times 10^4}{16.68} = 669 \text{ K}$$

$$71. k_t = \ln \frac{w_0}{w} \Rightarrow \frac{\ln 2}{28.1} \times 20 = \ln \frac{10^{-6} \text{ g}}{w} \Rightarrow w = 6.1 \times 10^{-7} \text{ g}$$

72. For 1st order reaction :

$$k \propto \frac{1}{t_{1/2}}$$

$$\Rightarrow \ln \left\{ \frac{k(450^\circ\text{C})}{k(380^\circ\text{C})} \right\} = \ln \left\{ \frac{t_{1/2}(380^\circ\text{C})}{t_{1/2}(450^\circ\text{C})} \right\} = \frac{E_a}{R} \left(\frac{450 - 380}{727 \times 653} \right)$$

$$\Rightarrow \ln \left\{ \frac{360}{t_{1/2}(450^\circ\text{C})} \right\} = \frac{200 \times 10^3}{8.314} \times \frac{70}{727 \times 653} = 3.54$$

$$\Rightarrow t_{1/2}(450^\circ\text{C}) = 10.37 \text{ min}$$

$$\Rightarrow \text{Time for 75% reaction at } 450^\circ\text{C}$$

$$= 2 \times t_{1/2} = 2 \times 10.37 = 20.74 \text{ min}$$

73. Comparing the data of experiment number 2 and 3 :

$$\frac{R_3}{R_2} = \frac{1.6 \times 10^{-2}}{4 \times 10^{-3}} = \left(\frac{1.0 \times 10^{-3}}{5 \times 10^{-4}} \right)^m$$

$$\Rightarrow m = 2, \text{ order w.r.t. } A$$

Now comparing the data of experiment number 1 and 2 :

$$\frac{R_2}{R_1} = \frac{4 \times 10^{-3}}{5 \times 10^{-4}} = \left(\frac{5 \times 10^{-4}}{2.5 \times 10^{-4}} \right)^2 \left(\frac{6.0 \times 10^{-5}}{3.0 \times 10^{-5}} \right)^n$$

$$\Rightarrow 8 = (2)^2 (2)^n \Rightarrow n = 1, \text{ order w.r.t. } B.$$

(i) Order with respect to $A = 2$, order with respect to $B = 1$.

(ii) At 300 K, $R = k [A]^2 [B]$

$$\Rightarrow k = \frac{R}{[A]^2 [B]} = \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})} = 2.66 \times 10^8 \text{ s}^{-1} \text{ L}^2 \text{ mol}^{-2}$$

(iii) From first experiment :

$$\text{Rate (320 K)} = k(320 \text{ K}) (2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})$$

$$\Rightarrow k(320 \text{ K}) = \frac{2 \times 10^{-3}}{(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})} = 1.066 \times 10^9 \text{ s}^{-1} \text{ L}^2 \text{ mol}^{-2}.$$

$$\Rightarrow \ln \left\{ \frac{k(320 \text{ K})}{k(300 \text{ K})} \right\} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

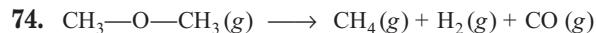
$$\Rightarrow \ln \left(\frac{1.066 \times 10^9}{2.66 \times 10^8} \right) = \frac{E_a}{8.314} \left(\frac{20}{300 \times 320} \right)$$

$$\Rightarrow E_a = 55.42 \text{ kJ mol}^{-1}$$

$$\text{Now } \ln k = \ln A - \frac{E_a}{RT}$$

$$\text{At 300 K : } \ln (2.66 \times 10^8) = \ln A - \frac{55.42 \times 10^3}{8.314 \times 300}$$

$$\text{Solving : } \ln A = 41.62 \Rightarrow A = 1.2 \times 10^{18}$$



$$\text{At 12 min : } \begin{matrix} 0.40-p & p & p & p \end{matrix}$$

$$\text{Total pressure} = 0.4 + 2p$$

$$\text{Also } k \times 12 = \ln \frac{0.40}{0.40-p} = \frac{\ln 2}{14.5} \times 12 = 1.77 \Rightarrow p = 0.175$$

$$\Rightarrow \text{Total pressure} = 0.4 + 2p = 0.4 + 2 \times 0.175 = 0.75 \text{ atm}$$

$$75. \ln \left\{ \frac{k(40^\circ\text{C})}{k(25^\circ\text{C})} \right\} = \frac{E_a}{R} \left(\frac{15}{298 \times 313} \right) = \frac{70 \times 1000}{8.314} \times \frac{15}{298 \times 313} = 1.35$$

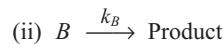
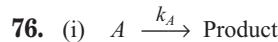
$$\Rightarrow \frac{k(40^\circ\text{C})}{k(25^\circ\text{C})} = 3.87$$

$$\text{Also } k(25^\circ\text{C}) = \frac{1}{20} \ln \frac{100}{75} = \frac{1}{20} \ln \frac{4}{3}$$

$$\Rightarrow k(40^\circ\text{C}) = 3.87 \times k(25^\circ\text{C}) = 3.87 \times \frac{1}{20} \ln \frac{4}{3} = 55.66 \times 10^{-3} \text{ min}^{-1}$$

$$\text{Now } k(40^\circ\text{C}) \times 20 = \ln \frac{100}{100-x}$$

$$\Rightarrow 55.66 \times 10^{-3} \times 20 = \ln \frac{100}{100-x} \Rightarrow x = 67\%$$



$$\text{For (i) } \frac{E_a}{R} \left(\frac{10}{300 \times 310} \right) = \ln 2$$

$$\Rightarrow E_a \text{ (i)} = 9300 R \ln 2 = 53.6 \text{ kJ}$$

$$\Rightarrow E_a \text{ (ii)} = \frac{E_a \text{ (i)}}{2} = 26.8 \text{ kJ}$$

$$\text{At 310 K } t_{1/2} \text{ (i)} = 30 \text{ min}$$

$$\because \text{Rate of (ii)} = 2 \text{ rate of (i)}$$

$$\Rightarrow t_{1/2} \text{ (ii)} = 15 \text{ min}$$

Now for reaction (ii) :

$$\ln \left\{ \frac{k_B(310)}{k_B(300)} \right\} = \ln \left\{ \frac{t_{1/2}(300)}{t_{1/2}(310)} \right\} = \frac{E_a \text{ (ii)}}{R} \left(\frac{10}{300 \times 310} \right)$$

$$\Rightarrow \ln \left\{ \frac{t_{1/2}(300)}{15} \right\} = \frac{\ln 2}{2} \Rightarrow t_{1/2}(300) = 21.2 \text{ min}$$

$$\Rightarrow k_B(300) = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{21.2} = 3.26 \times 10^{-2} \text{ min}^{-1}$$

77. Initially :

$$N(^1\text{H}^3 + ^1\text{H}^1) = \frac{10}{8} \times 2 \times 6 \times 10^{23} = \frac{20}{3} \times 10^{23}$$

$$\Rightarrow 1 + \frac{N(^1\text{H}^1)}{N(^1\text{H}^3)} = \frac{20 \times 10^{23}}{3N(^1\text{H}^3)}$$

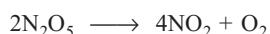
$$\Rightarrow 1 + \frac{1}{8 \times 10^{-18}} = \frac{20 \times 10^{23}}{3N(^1\text{H}^3)} \approx 1.25 \times 10^{17}$$

$$\Rightarrow N(^1\text{H}^3) = \frac{20 \times 10^{23}}{3 \times 1.25 \times 10^{17}} = 5.33 \times 10^6$$

$$\Rightarrow kt = \ln \frac{N_0}{N} \Rightarrow \frac{\ln 2}{12.3} \times 40 = \ln \frac{5.33 \times 10^6}{N}$$

$$\Rightarrow N = 5.6 \times 10^5$$

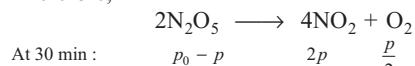
78. For the reaction :



If p_0 is the initial pressure, the total pressure after completion of reaction would be $\frac{5}{2} p_0$.

$$\Rightarrow 584.5 = \frac{5}{2} p_0 \Rightarrow p_0 = 233.8 \text{ mm}$$

Let the pressure of N_2O_5 decreases by ' p ' amount after 30 min. Therefore,



$$\text{Total pressure} = p_0 + \frac{3}{2} p = 284.5$$

$$\Rightarrow p = \frac{2}{3} (284.5 - 233.8) = 33.8$$

$$\text{Now, } kt = \ln \frac{p_0}{p_0 - p}$$

$$\Rightarrow k = \frac{1}{30} \ln \frac{233.8}{233.8 - 33.8} \text{ min}^{-1} = 5.2 \times 10^{-3} \text{ min}^{-1}$$

79. Arrhenius equation is :

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$\text{when } t_{1/2} = 10 \text{ min, } k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10 \times 60} = 1.115 \times 10^{-3} \text{ s}^{-1}$$

$$\Rightarrow \frac{E_a}{2.303 RT} = \log A - \log k = \log \frac{A}{k} = \log \frac{4 \times 10^{13}}{1.115 \times 10^{-3}}$$

$$= 16.54$$

$$\Rightarrow T = \frac{E_a}{2.303 R \times 16.54} = \frac{98.6 \times 1000}{2.303 \times 16.54 \times 8.314} = 311.34 \text{ K}$$

80. The minimum rate of decay required after 6.909 h is 346 particles min^{-1} .

$$\Rightarrow \text{Rate} = kN$$

$$\Rightarrow N = \frac{\text{Rate}}{k} = \frac{346 \times 66.6 \times 60}{0.693} = 1.995 \times 10^6 \text{ atoms}$$

$$\Rightarrow kt = \ln \frac{N_0}{N} \Rightarrow \frac{\ln 2}{66.6} \times 6.909 = \ln \frac{N_0}{N} = 0.0715$$

$$\Rightarrow \frac{N_0}{N} = 1.074$$

$$\Rightarrow N_0 = 1.074 \times N = 1.074 \times 1.995 \times 10^6$$

$$= 2.14 \times 10^6 \text{ atoms of Mo}$$

$$\Rightarrow \text{Mass of Mo required} = \frac{2.14 \times 10^6}{6.023 \times 10^{23}} \times 99 = 3.56 \times 10^{-16} \text{ g}$$

81. $k = 1.5 \times 10^{-6} \text{ s}^{-1}$

$$kt = \ln \frac{100}{100 - x}$$

$$\Rightarrow \ln \frac{100}{100 - x} = 1.5 \times 10^{-6} \text{ s}^{-1} \times 10 \times 60 \times 60 \text{ s} = 0.0054$$

$$\Rightarrow \frac{100}{100 - x} = 1.055$$

$\Rightarrow x = 5.25\%$ reactant is converted into product.

$$\text{Half-life} = \frac{\ln 2}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000 \text{ s} = 128.33 \text{ h}$$

82. For a first order process : $\ln \frac{[A]_0}{[A]} = kt \Rightarrow \ln [A] = \ln [A]_0 - kt$

If the reactant is in gaseous state

$$\text{and } kt_{1/10} - \ln \frac{[A]_0}{[A]_0 / 10} = \ln 10 \quad \dots(\text{ii})$$

$$\text{Therefore, } \frac{t_{1/8}}{t_{1/10}} = \frac{\ln 8}{\ln 10} = \log 8 = 3 \log 2 = 3 \times 0.3 = 0.9$$

$$\Rightarrow \frac{t_{1/8}}{t_{1/10}} \times 10 = 0.9 \times 10 = 9$$

$$\ln p = \ln p_0 - kt \quad \dots(\text{i})$$

where p is the partial pressure of reactant remaining unreacted at instant ' t ' and p_0 is its initial partial pressure.

Also, from equation (i), $\ln p$ vs t would give a straight line. Therefore, decomposition of N_2O_5 following first order kinetics.

$$83. k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5770} \text{ yr}^{-1} = 1.2 \times 10^{-4} \text{ yr}^{-1}$$

$$\text{Also } kt = \ln \frac{1}{f} = \frac{\ln 2}{5770} \times 11540 = \ln 4 \Rightarrow f = \frac{1}{4} = 0.25$$

84. For a first order reaction,

$$kt = \ln \frac{[A]_0}{[A]}$$

where $[A]_0$ = Initial concentration of reactant

$[A]$ = Concentration of reactant remaining unreacted at time t .

$$(i) \Rightarrow k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{10} \ln \frac{100}{100 - 20} = \frac{1}{10} \ln \frac{5}{4}$$

$$= \frac{2.303 (\log 5 - 2 \log 2)}{10} \text{ min}^{-1} = 0.023 \text{ min}^{-1}$$

$$(ii) \quad t = \frac{1}{k} \ln \frac{100}{25} = \frac{2 \ln 2}{k} = \frac{2 \times 0.693}{0.023} = 60 \text{ min}$$

85. Looking at the rate data of experiment number 1 and 2 indicates that rate is doubled on doubling concentration of A while concentration of B is constant. Therefore, order with respect to A is 1. Similarly, comparing data of experiment number 1 and 3, doubling concentration of B , while concentration of A is constant, has no effect on rate.

Therefore, order with respect to B is zero.

$$\Rightarrow \text{Rate} = k [A]$$

$$\Rightarrow k = \frac{0.005}{0.010} = 0.5 \text{ min}^{-1} = \frac{0.693}{t_{1/2}}$$

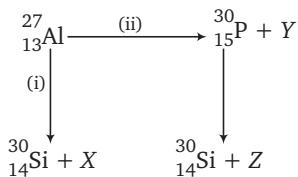
$$\Rightarrow t_{1/2} = \frac{0.693}{0.5} = 1.386 \text{ min}$$

12

Nuclear Chemistry

Objective Questions I (Only one correct option)

1. Bombardment of aluminium by α -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X , Y and Z respectively, are (2011)

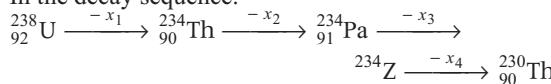


- (a) proton, neutron, positron (b) neutron, positron, proton
(c) proton, positron, neutron (d) positron, proton, neutron
2. A positron is emitted from ${}^{23}_{11}\text{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is (2007, 3M)
(a) 22/10 (b) 22/11
(c) 23/10 (d) 23/12
3. ${}^{23}_{11}\text{Na}$ is the more stable isotope of Na. Find out the process by which ${}^{24}_{11}\text{Na}$ can undergo radioactive decay. (2003, 1M)
(a) β^- -emission (b) α -emission
(c) β^+ -emission (d) K -electron capture
4. The number of neutrons accompanying the formation of ${}^{139}_{54}\text{Xe}$ and ${}^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by ${}^{235}_{92}\text{U}$, followed by nuclear fission is (1999, 2M)
(a) 0 (b) 2 (c) 1 (d) 3
5. ${}^{27}_{13}\text{Al}$ is a stable isotope. ${}^{29}_{13}\text{Al}$ is expected to decay by
(a) α -emission (b) β -emission (1996, 1M)
(c) positron emission (d) proton emission
6. The radiation from a naturally occurring radioactive substance, as seen after deflection by a magnet in one direction. (1984, 1M)
(a) definitely alpha rays (b) definitely beta rays
(c) both alpha and beta rays (d) either alpha rays or beta rays
7. An isotope of Ge^{76}_{32} is (1984, 1M)
(a) Ge^{77}_{32} (b) As^{77}_{33}
(c) Se^{77}_{34} (d) Se^{78}_{34}
8. If uranium (mass number 238 and atomic number 92) emits an α -particle, the product has mass number and atomic number (1981, 1 M)
(a) 236 and 92 (b) 234 and 90
(c) 238 and 90 (d) 236 and 90

Objective Questions II

(One or more than one correct option)

9. In the decay sequence.



x_1 , x_2 , x_3 and x_4 are particles/radiation emitted by the respective isotopes. The correct option(s) is(are) (2019 Adv.)

- (a) Z is an isotope of uranium
(b) x_2 is β^-
(c) x_1 will deflect towards negatively charged plate
(d) x_3 is γ -ray

10. A plot of the number of neutrons (n) against the number of protons (p) of stable nuclei exhibits upward deviation from linearity for atomic number, $Z > 20$. For an unstable nucleus having n/p ratio less than 1, the possible mode(s) of decay is (are) (2016 Adv.)

- (a) β^- -decay (β -emission) (b) orbital or K -electron capture
(c) neutron emission (d) β^+ -decay (positron emission)

11. In the nuclear transmutation, ${}^9_4\text{Be} + X \longrightarrow {}^8_4\text{Be} + Y$
 X and Y are (2013 Adv.)
(a) (γ, n) (b) (p, D) (c) (n, D) (d) (γ, p)

12. Decrease in atomic number is observed during (1998, 2M)
(a) alpha emission (b) beta emission
(c) positron emission (d) electron capture

13. The nuclear reactions accompanied with emission of neutron(s) are (1988, 1 M)
(a) ${}^{27}_{13}\text{Al} + {}^4_2\text{He} \longrightarrow {}^{30}_{15}\text{P}$ (b) ${}^{12}_6\text{C} + {}^1_1\text{H} \longrightarrow {}^{13}_{7}\text{N}$
(c) ${}^{30}_{15}\text{P} \longrightarrow {}^{30}_{14}\text{Si} + {}^0_1e$ (d) ${}^{241}_{96}\text{Cm} + {}^4_2\text{He} \longrightarrow {}^{244}_{97}\text{Bk} + {}^0_1e$

Numerical Answer Type Questions

14. ${}^{238}_{92}\text{U}$ is known to undergo radioactive decay to form ${}^{206}_{82}\text{Pb}$ by emitting alpha and beta particles. A rock initially contained 68×10^{-6} g of ${}^{238}_{92}\text{U}$. If the number of alpha particles that it would emit during its radioactive decay of ${}^{238}_{92}\text{U}$ to ${}^{206}_{82}\text{Pb}$ in three half-lives is $Z \times 10^{18}$, then what is the value of Z ? (2020 Adv.)

- 15.** During the nuclear explosion, one of the products is ^{90}Sr with half-life of 6.93 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby in place of Ca, how much time, in years, is required to reduce it by 90% if it is not lost metabolically (2020 Main, 7 Jan I)

Assertion and Reason

Read the following questions and answer as per the direction given below:

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
 - (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
 - (c) Statement I is true; Statement II is false
 - (d) Statement I is false; Statement II is true
- 16. Statement I** The plot of atomic number (*y*-axis) *versus* number of neutrons (*x*-axis) for stable nuclei shows a curvature towards *x*-axis from the line of 45° slope as the atomic number is increased.
Statement II Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons and neutrons in heavier nuclides. (2008)
- 17. Statement I** Nuclide $^{30}_{13}\text{Al}$ is less stable than $^{40}_{20}\text{Ca}$.
Statement II Nuclides having odd number of protons and neutrons are generally unstable. (1998)

Fill in the Blanks

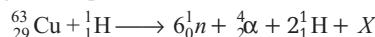
- 18.** (a) $^{92}_{92}\text{U} + {}_0n^1 \longrightarrow {}_{52}^{137}\text{A} + {}_{40}^{97}\text{B} + \dots$
 (b) $^{82}_{34}\text{Se} \longrightarrow 2 {}_{-1}e^0 + \dots$ (2005, 1M \times 2 = 2M)
- 19.** A radioactive nucleus decays by emitting one alpha and two beta particles, the daughter nucleus is.... of the parent. (1989, 1M)
- 20.** The number of neutrons in the parent nucleus which gives N^{14} on beta emission is (1985, 1M)

- 21.** Elements of the same mass number but different atomic number are known as (1983, 1M)

- 22.** An element ${}_Z M^A$ undergoes an α -emission followed by two successive β^- -emissions. The element formed is (1982, 1M)

Integer Answer Type Questions

- 23.** The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element *X* as shown below. To which group, element *X* belongs in the periodic table? (2012)



- 24.** The number of neutrons emitted when $^{235}_{92}\text{U}$ undergoes controlled nuclear fission to $^{142}_{54}\text{Xe}$ and $^{90}_{38}\text{Sr}$ is (2010)

Subjective Questions

- 25.** The total number of α and β particles emitted in the nuclear reaction $^{92}_{92}\text{U}^{238} \longrightarrow {}_{82}^{214}\text{Pb}$ is (2009)

- 26.** $^{92}_{92}X^{234} \xrightarrow[-6\beta]{-7\alpha} Y$. Find out atomic number, mass number of *Y* and identify it. (2004)

- 27.** $^{92}_{92}\text{U}^{238}$ is radioactive and it emits α and β particles to form $^{82}_{82}\text{Pb}^{206}$. Calculate the number of α and β particles emitted in this conversion.

An ore of $^{92}_{92}\text{U}^{238}$ is found to contain $^{92}_{92}\text{U}^{238}$ and $^{82}_{82}\text{Pb}^{206}$ in the weight ratio of 1 : 0.1. The half-life period of $^{92}_{92}\text{U}^{238}$ is 4.5×10^9 yr. Calculate the age of the ore. (2000)

- 28.** Write a balanced equation for the reaction of N^{14} with α -particle.

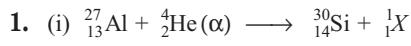
- 29.** $^{90}_{90}\text{Th}^{234}$ disintegrates to give $^{82}_{82}\text{Pb}^{206}$ as the final product. How many alpha and beta particles are emitted during this process? (1986, 2M)

Answers

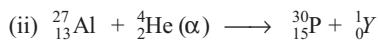
- | | | | |
|--------------|--|-------------|---------------|
| 1. (a) | 2. (c) | 3. (a) | 4. (b) |
| 5. (b) | 6. (c) | 7. (a) | 8. (b) |
| 9. (a, b, c) | 10. (b, d) | 11. (a, b) | 12. (a, c, d) |
| 13. (a, d) | 14. (1.2) | 15. (23.03) | 16. (a) |
| 17. (b) | 18. $2 {}_0^1n, {}_{36}^{82}\text{Kr}$ | | 19. isotope |

- | | | | |
|-------------------------------------|-------------|------------------------------|---------|
| 20. eight | 21. isobars | 12. ${}_Z M^{A-4}$ | 23. (8) |
| 24. 3 | 25. (8) | 26. ${}_{84}^{206}\text{Po}$ | |
| 27. $(7.12 \times 10^8 \text{ yr})$ | | 29. (13) | |

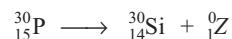
Hints & Solutions



X is proton ${}^1_1\text{H}$.

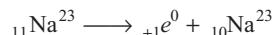


Y is neutron, 1_0n .

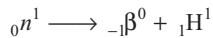


Z is positron, ${}^0_{+1}e$

2. The required nuclear reaction is



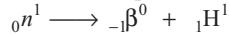
3. In stable isotope of Na, there are 11 protons and 12 neutrons. In the given radioactive isotope of sodium (Na^{24}), there are 13 neutrons, one neutron more than that required for stability. A neutron rich isotope always decay by β -emission as



4. The balanced nuclear reaction is



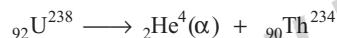
5. ${}^{29}_{13}\text{Al}$ is neutron rich isotope, will decay by β -emission converting some of its neutron into proton as



6. Both α -rays and β -rays are deflected by magnetic field.

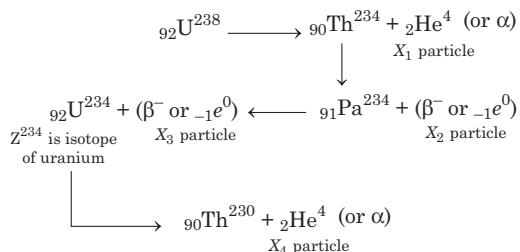
7. Isotopes have same atomic number (Z) but different mass number (A). Therefore, ${}^{76}_{32}\text{Ge}$ and ${}^{77}_{32}\text{Ge}$ are isotopes.

8. The nuclear reaction is



9. **Key Idea** The loss of one α -particle will decrease the mass number by 4 and atomic number by 2. On the other hand, loss of β -particle will increase the atomic number by 1.

In decay sequence,



X_1 particle will deflect towards negatively charged plate due to presence of positive charge on α - particles.

Hence, options (a, b, c) are correct.

10. For the elements with atomic number (Z) larger than 20,

Neutrons (n) > Protons (p); Thus, $n/p > 1$

Thus, there is upward deviation from linearity.

If $n < p$, Thus $n/p < 1$, then

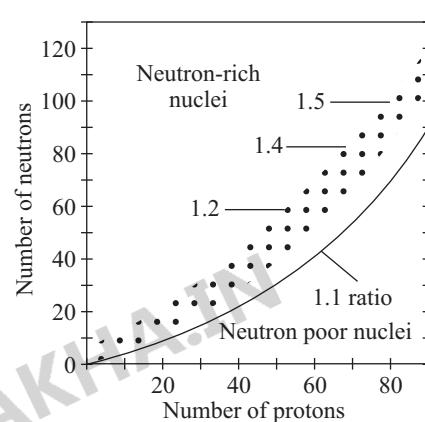
(a) By β^- - decay, ${}^1_0n \longrightarrow {}^1_1p + {}^0_{-1}e$ neutron changes to proton. Thus, (n/p) ratio further decreases below 1. Thus, this decay is not allowed.

(b) By orbital or K - electron capture, ${}^1_1p + {}^0_{-1}e \longrightarrow {}^1_0n$ proton changes to neutron, hence, (n/p) ratio increases. Thus stability increases. Thus correct.

(c) Neutron emission further decreases n/p ratio.

(d) By β^+ -emission, ${}^1_1p \longrightarrow {}^1_0n + {}^0_{+1}e$ proton changes to neutron.

Hence, n/p ratio increases. Thus correct.



Plot of the number of neutrons against the number of protons in stable nuclei (shown by dots).

11. PLAN ${}^9_4\text{Be} + {}^b_aX \longrightarrow {}^8_4\text{Be} + {}^d_cY$

$\boxed{\quad}$
Atomic number same

$$4 + a = 4 + c$$

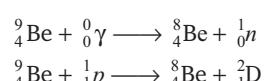
$$9 + b = 8 + d$$

$$\begin{array}{ll} \text{If } X = {}^0_0\gamma & a = 0 \\ & b = 0 \\ Z^{234} \text{ is isotope} & \\ \text{of uranium} & \end{array}$$

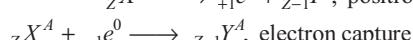
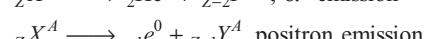
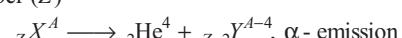
$$\begin{array}{ll} c = 0 & \\ d = 1 & \end{array}$$

$$\begin{array}{ll} \text{If } X = {}^1_1p & a = 1 \\ & b = 1 \\ Y = {}^1_0n & \\ & \end{array}$$

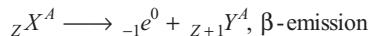
$$\begin{array}{ll} c = 1 & \\ d = 2 & \end{array}$$



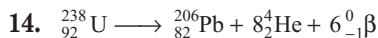
12. In the following nuclear reactions, there occur decrease in atomic number (Z)



In beta emission, increase in atomic number is observed.



13. If sum of mass number of product nuclides is less than the sum of parent nuclides, then neutron emission will occur. In both (a) and (d), sum of mass number of product nuclides is one unit less than the sum of parent nuclides, neutron emission will balance the mass number.



Number of moles of ${}_{92}^{238}\text{U}$ present initially

$$= \frac{68 \times 10^{-6}}{238}$$

After three half-lives, moles of ${}_{92}^{238}\text{U}$ decayed

$$= \frac{68 \times 10^{-6}}{238} \times \left(1 - \frac{1}{2^3}\right) = \frac{68 \times 10^{-6}}{238} \times \frac{7}{8}$$

Therefore, number of α -particles emitted

$$= \frac{68 \times 10^{-6}}{238} \times \frac{7}{8} \times 8 \times 6.023 \times 10^{23} \\ = 1.204 \times 10^{18} \approx 1.2 \times 10^{18}$$

Thus, the correct answer is 1.2.

15. Radioactive decay follows first order kinetics.

\therefore Time taken for decay from N_0 to N_t is
(N = number of nuclei)

$$t = \frac{1}{\lambda} \ln \frac{N_0}{N_t}$$

$$t = \frac{1}{\lambda} \times 2.303 \log \frac{N_0}{N_t} \quad \dots(i)$$

Also, we know λ = (decay constant) $= \frac{0.693}{t_{1/2}}$

where, $t_{1/2} = 6.93$ yr (given)

Also, we know 90% nuclei are decayed

$$\therefore \frac{N_0}{N_t} = \frac{100}{10} = 10$$

Put the values of λ and $\frac{N_0}{N_t}$ in Eq. (i), we get

$$\therefore t = \frac{6.93}{0.693} \times 2.303 \times \log 10$$

16. After atomic number 20, proton-proton repulsion increases immensely, more neutrons are required to shield this electrostatic repulsion, curve of stability incline towards neutron axis.

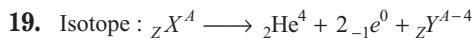
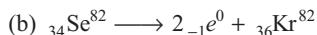
17. Upto atomic number of 20, stable nuclei possess neutron to proton ratio (n/p) = 1.

$$\frac{n}{p} ({}_{13}^{27}\text{Al}^{30}) = \frac{17}{13} = 1.3 > 1, \text{ unstable, } \beta\text{-emitter.}$$

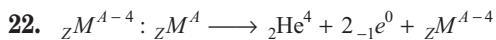
$$\frac{n}{p} ({}_{20}^{40}\text{Ca}^{40}) = \frac{20}{20} = 1, \text{ stable.}$$

Also, nuclei with both neutrons and protons odd are usually unstable but it does not explain the assertion appropriately.

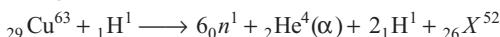
$$= 23.03 \text{ (yr)}$$



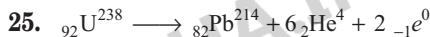
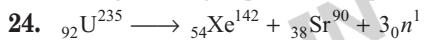
21. Isobars have same mass number but different atomic number.



23. Balancing the given nuclear reaction in terms of atomic number (charge) and mass number:



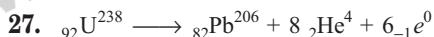
The atomic number 26 corresponds to transition metal Fe which belongs to 8th group of modern periodic table.



\Rightarrow Number of ($\alpha + \beta$) = 6 + 2 = 8



Y is ${}_{84}^{84}\text{Po}^{206}$.



Present : $N_0 - N$

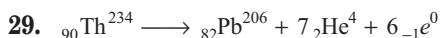
$$\text{Given, } \frac{w(\text{U})}{w(\text{Pb})} = \frac{1}{0.1} = 10$$

$$\Rightarrow \frac{N(\text{U})}{N(\text{Pb})} = \frac{10}{238} \times \frac{206}{1} = \frac{N_0 - N}{N}$$

$$\Rightarrow \frac{N}{N_0 - N} = \frac{238}{2060} \Rightarrow \frac{N_0}{N_0 - N} = 1 + \frac{238}{2060} = \frac{2298}{2060}$$

Now, applying first order rate law

$$\left(\frac{\ln 2}{t_{1/2}} \right) t = \ln \left(\frac{N_0}{N_0 - N} \right) \Rightarrow t = \frac{(t_{1/2})}{\log 2} \log \left(\frac{N_0}{N_0 - N} \right) \\ = \frac{4.5 \times 10^9}{0.3} \log \frac{2298}{2060} = 7.12 \times 10^8 \text{ yr}$$



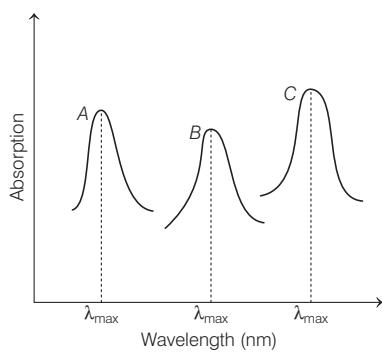
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Surface Chemistry

Objective Questions I (Only one correct option)

1. Simplified absorption spectra of three complexes [(i), (ii) and (iii)] of M^{n+} ion are provided below; their λ_{\max} values are marked as A, B and C respectively. The correct match between the complexes and their λ_{\max} values is

(2020 Main, 2 Sep II)



- (i) $[M(\text{NCS})_6]^{(-6+n)}$
(ii) $[MF_6]^{(-6+n)}$
(iii) $[M(\text{NH}_3)_6]^{n+}$
- (a) A-(iii), B-(i), C-(ii)
(b) A-(ii), B-(i), C-(iii)
(c) A-(ii), B-(iii), C-(i)
(d) A-(i), B-(ii), C-(iii)
2. Among the following, the incorrect statement about colloids is
- (2019 Main, 12 April II)
- (a) They can scatter light
(b) They are larger than small molecules and have high molar mass
(c) The osmotic pressure of a colloidal solution is of higher order than the true solution at the same concentration
(d) The range of diameters of colloidal particles is between 1 and 1000 nm
3. Peptisation is a
- (2019 Main, 12 April I)
- (a) process of bringing colloidal molecule into solution
(b) process of converting precipitate into colloidal solution
(c) process of converting a colloidal solution into precipitate
(d) process of converting soluble particles to form colloidal solution
4. The correct option among the following is
- (2019 Main, 10 April II)
- (a) colloidal medicines are more effective, because they have small surface area.

(b) brownian motion in colloidal solution is faster if the viscosity of the solution is very high.

(c) addition of alum to water makes it unfit for drinking.

(d) colloidal particles in lyophobic sols can be precipitated by electrophoresis.

5. A gas undergoes physical adsorption on a surface and follows the given Freundlich adsorption isotherm equation $\frac{x}{m} = Kp^{0.5}$

Adsorption of the gas increases with (2019 Main, 10 April I)

- (a) increase in p and increase in T
(b) increase in p and decrease in T
(c) decrease in p and decrease in T
(d) decrease in p and increase in T

6. Match the catalysts Column I with products Column II.

(2019 Main, 9 April I)

Column I (Catalyst)	Column II (Product)
(A) V_2O_5	(i) Polyethlyene
(B) $\text{TiCl}_4 / \text{Al}(\text{Me})_3$	(ii) Ethanal
(C) PbCl_2	(iii) H_2SO_4
(D) Iron oxide	(iv) NH_3

(a) (A)-(ii), (B)-(iii), (C)-(i), (D)-(iv)

(b) (A)-(iv), (B)-(iii), (C)-(ii), (D)-(i)

(c) (A)-(iii), (B)-(i), (C)-(ii), (D)-(iv)

(d) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)

7. The number of water molecule(s) not coordinated to copper ion directly in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is

(2019 Main, 9 April I)

- (a) 2
(b) 3
(c) 1
(d) 4

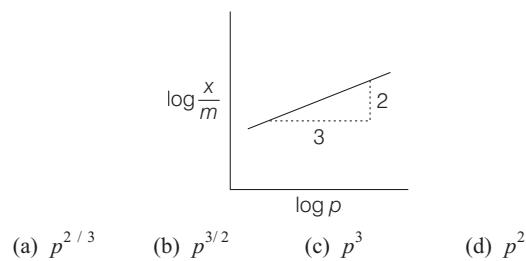
8. The aerosol is a kind of colloid in which (2019 Main, 9 April I)

- (a) gas is dispersed in liquid
(b) gas is dispersed in solid
(c) liquid is dispersed in water
(d) solid is dispersed in gas

9. Adsorption of a gas follows Freundlich adsorption isotherm. x is the mass of the gas adsorbed on mass m of the adsorbent.

The plot of $\log \frac{x}{m}$ versus $\log p$ is shown in the given graph. $\frac{x}{m}$ is proportional to

(2019 Main, 8 April I)



10. Among the following, the false statement is
(2019 Main, 12 Jan II)

- (a) Tyndall effect can be used to distinguish between a colloidal solution and a true solution
- (b) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane
- (c) Lyophilic sol can be coagulated by adding an electrolyte
- (d) Latex is a colloidal solution of rubber particles which are positively charged

11. Given, Gas : H₂, CH₄, CO₂, SO₂
Critical temperature/K 33 190 304 630
On the basis of data given above, predict which of the following gases shows least adsorption on a definite amount of charcoal?
(2019 Main, 12 Jan I)

- (a) CH₄ (b) SO₂ (c) CO₂ (d) H₂

12. Among the colloids cheese (C), milk (M) and smoke (S), the correct combination of the dispersed phase and dispersion medium, respectively is
(2019 Main, 11 Jan II)
- (a) C : liquid in solid; M : liquid in liquid; S : solid in gas
 - (b) C : solid in liquid; M : liquid in liquid; S : gas in solid
 - (c) C : liquid in solid; M : liquid in solid; S : solid in gas
 - (d) C : solid in liquid; M : solid in liquid; S : solid in gas

13. An example of solid sol is
(2019 Main, 11 Jan I)
- (a) gem stones (b) hair cream
 - (c) butter (d) paint

14. Haemoglobin and gold sol are examples of
(2019 Main, 10 Jan II)
- (a) negatively and positively charged sols, respectively
 - (b) negatively charged sols
 - (c) positively charged sols
 - (d) positively and negatively charged sols, respectively

15. Which of the following is not an example of heterogeneous catalytic reaction?
(2019 Main, 10 Jan I)
- (a) Haber's process
 - (b) Combustion of coal
 - (c) Hydrogenation of vegetable oils
 - (d) Ostwald's process

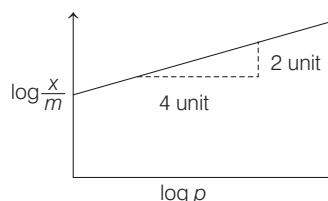
16. The correct match between item-I and Item-II is
(2019 Main, 9 Jan II)

- | | |
|-----------------|------------------|
| A. Benzaldehyde | P. Dynamic phase |
| B. Alumina | Q. Adsorbent |
| C. Acetonitrile | R. Adsorbate |
- (a) (A) → (R); (B) → (Q); (C) → (P)
 - (b) (A) → (P); (B) → (R); (C) → (Q)
 - (c) (A) → (Q); (B) → (P); (C) → (R)
 - (d) (A) → (Q); (B) → (R); (C) → (P)

17. Which of the salt-solution is most effective for coagulation of arsenious sulphide?
(2019 Main, 9 Jan II)

- (a) BaCl₂
- (b) AlCl₃
- (c) Na₃PO₄
- (d) NaCl

18. Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p . $\frac{x}{m}$ is proportional to
(2019 Main, 9 Jan I)



19. The Tyndall effect is observed only when following conditions are satisfied
(2017 Main)

1. The diameter of the dispersed particles is much smaller than the wavelength of the light used.
 2. The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
 3. The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.
 4. The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.
- (a) 1 and 4
 - (b) 2 and 4
 - (c) 1 and 3
 - (d) 2 and 3

20. For a linear plot of $\log(x/m)$ versus $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants)
(2016 Main)

- (a) $1/n$ appears as the intercept
- (b) Only $1/n$ appears as the slope
- (c) $\log\left(\frac{1}{n}\right)$ appears as the intercept
- (d) Both k and $1/n$ appear in the slope term

21. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
(2013 Adv.)

- (a) the adsorption requires activation at 25°C
- (b) the adsorption is accompanied by a decrease in enthalpy
- (c) the adsorption increases with increase of temperature
- (d) the adsorption is irreversible

22. The coagulating power of electrolytes having ions Na^+ , Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order
(2013 Main)

- (a) $\text{Al}^{3+} < \text{Ba}^{2+} < \text{Na}^+$
- (b) $\text{Na}^+ < \text{Ba}^{2+} < \text{Al}^{3+}$
- (c) $\text{Ba}^{2+} < \text{Na}^{2+} < \text{Al}^{3+}$
- (d) $\text{Al}^{3+} < \text{Na}^+ < \text{Ba}^{2+}$

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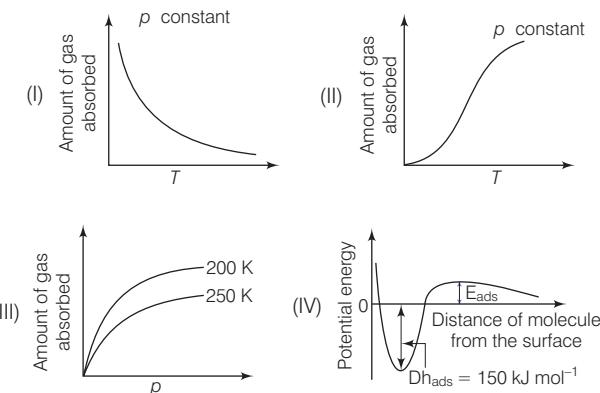
23. Among the electrolytes Na_2SO_4 , CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$ and NH_4Cl , the most effective coagulating agent for Sb_2S_3 sol is
 (a) Na_2SO_4 (b) CaCl_2
 (c) $\text{Al}_2(\text{SO}_4)_3$ (d) NH_4Cl (2009, 1M)
24. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions, is
 (a) $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 (b) $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
 (c) $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$
 (d) $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ (2008, 3M)
25. Lyophilic sols are
 (a) irreversible sols
 (b) prepared from inorganic compounds
 (c) coagulated by adding electrolytes
 (d) self-stabilising (2005, 1M)
26. Spontaneous adsorption of a gas on solid surface is an exothermic process, because
 (a) ΔH increases for system
 (b) ΔS increases for gas
 (c) ΔS decreases for gas
 (d) ΔG increases for gas (2004, 1M)
27. Rate of physisorption increases with
 (a) decrease in temperature (b) increase in temperature
 (c) decrease in pressure (d) decrease in surface area (2003, 1M)
28. When the temperature is increased, surface tension of water
 (a) increases (b) decreases
 (c) remains constant (d) shows irregular behaviour (2002, 1M)

Objective Questions II

(One or more than one correct option)

29. The correct statement(s) about surface properties is(are)
 (2017 Adv.)
 (a) The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen of same amount of activated charcoal at a given temperature
 (b) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium
 (c) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system
 (d) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution
30. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2 . The true statement(s) regarding this adsorption is (are)
 (2015 Adv.)
 (a) O_2 is physisorbed
 (b) heat is released
 (c) occupancy of π^*2p of O_2 is increased
 (d) bond length of O_2 is increased

31. The given graph/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct? (2012)



- (a) I is physisorption and II is chemisorption
 (b) I is physisorption and III is chemisorption
 (c) IV is chemisorption and II is chemisorption
 (d) IV is chemisorption and III is chemisorption
32. Choose the correct reason(s) for the stability of the lyophobic colloidal particles. (2012)
- (a) Preferential adsorption of ions on their surface from the solution
 (b) Preferential adsorption of solvent on their surface from the solution
 (c) Attraction between different particles having opposite charges on their surface
 (d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles
33. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) (2011)
- (a) Adsorption is always exothermic
 (b) Physisorption may transform into chemisorption at high temperature
 (c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature
 (d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation

Numerical Answer Type Questions

34. The mass of gas adsorbed, x per unit mass of adsorbate, m was measured at various pressures, p . A graph between $\log \frac{x}{m}$ and $\log p$ gives a straight line with slope equal to 2 and the intercept equal to 0.4771. The value of $\frac{x}{m}$ at a pressure of 4 atm is (Given, $\log 3 = 0.4771$)
 (2020 Main, 2 Sep I)

Assertion and Reason

Read the following questions and answer as per the direction given below:

- (a) Statement I is true; Statement II is true; Statement II is a correct explanation of Statement I.
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

- 35. Statement I** Micelles are formed by surfactant molecules above the critical micelle concentration (CMC).

Statement II The conductivity of a solution having surfactant molecules decreases sharply at the CMC. (2007)

Answers

- | | | | | | | | |
|---------|---------|---------|---------|---------------|---------------|------------|------------|
| 1. (a) | 2. (c) | 3. (b) | 4. (d) | 21. (b) | 22. (b) | 23. (c) | 24. (a) |
| 5. (b) | 6. (c) | 7. (c) | 8. (d) | 25. (d) | 26. (c) | 27. (a) | 28. (b) |
| 9. (a) | 10. (d) | 11. (d) | 12. (a) | 29. (a, c) | 30. (b, c, d) | 31. (a, c) | 32. (a, d) |
| 13. (a) | 14. (d) | 15. (b) | 16. (a) | 33. (a, b, d) | 34. (48) | 35. (b) | |
| 17. (b) | 18. (c) | 19. (b) | 20. (b) | | | | |

Hints & Solutions

- 1.** Here, same metal ion, M^{n+} form three homoleptic octahedral complexes (i), (ii) and (iii) on separate combination with three mono-dentate ligands $\text{N}^{\ddagger}\text{CS}^-$, F^- and NH_3 respectively.

So, we have to compare their CFSE (Δ_0) as well as wavelength (λ) values, where

$$\Delta E(\text{CFSE}) = \frac{hc}{\lambda} \text{ or, } \Delta_0 \propto \frac{1}{\lambda}$$

Again, Δ_0 value will depend on power of ligand as placed in spectrochemical series.

$$\text{Power of ligand} \propto \Delta_0 \propto \frac{1}{\lambda},$$



→ Power of Ligand ← λ

→ Δ₀

So, for the given complexes, it is evident from the plot (Absorption vs λ)

$$\begin{array}{ccc} \lambda_{\max}^{(ii)} > \lambda_{\max}^{(i)} > \lambda_{\max}^{(iii)} \\ (C) & (B) & (A) \\ [\text{F}^-] & [\text{NCS}^-] & [\text{NH}_3] \end{array}$$

- 2.** Statement (c) is incorrect about colloids. Colligative properties such as relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure of a colloidal solution is of low order than the true solution at the same concentration.

- 3.** Peptisation is a process of converting precipitate into colloidal solution. This process involves the shaking of precipitate with the dispersion medium in the presence of small amount of electrolyte. The electrolyte added is called **peptising agent**.

During peptisation, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately breakup into smaller particles of the size of a colloid.

- 4.** The explanation of the given statements are as follows :

(a) Colloidal medicines are more effective because they (dispersed phase) have larger surface area.

Thus, option (a) is incorrect.

(b) Brownian motion of dispersed phase particles in colloidal solution is faster if the viscosity of the solution is very low. Thus, option (b) is incorrect.

(c) Addition of alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$), an electrolyte to water makes it fit for drinking purposes because alum coagulates mud particles from water.

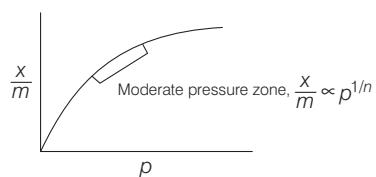
Thus, option (c) is incorrect.

(d) Precipitation of lyophobic solution particles by electrophoresis is called cottrell precipitation.

Thus, option (d) is correct.

- 5.** For physisorption or physical adsorption,

Adsorption isotherm (Temperature, $T = \text{constant}$) is shown below:



where, $x = \text{amount of adsorbate}$, $m = \text{amount of adsorbent}$,

$$\frac{x}{m} = \text{degree of adsorption}$$

$$\frac{1}{n} = \text{order of the reaction, where, } 0 < \frac{1}{n} < 1 \text{ and so, } 1 < n < \infty$$

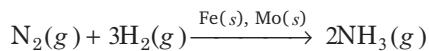
$$\text{Here, } \frac{x}{m} = Kp^{1/2},$$

$$\text{i.e., } \frac{x}{m} \propto p^{1/2}$$

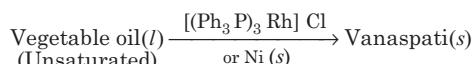
15. In heterogeneous catalytic reactions, physical state of reactants and that of catalyst(s) used are different.

Haber's process, hydrogenation of vegetable oils and Ostwald's process all are heterogeneous process. Combustion of coal is not a heterogeneous catalytic reaction.

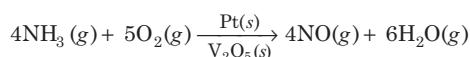
- In Haber's process



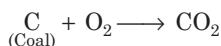
- Hydrogenation of vegetable oils,



- Ostwald's process,



- No catalyst is used in combustion of coal. The reaction is highly spontaneous in nature.



16. Using the principle of adsorption chromatography, qualitative and quantitative analysis of benzaldehyde can be done from its mixture with acetonitrile. Here, a mobile phase moves over a stationary phase (adsorbent). Adsorbents used are alumina (Al_2O_3) and silica gel. The sample solution of benzaldehyde and acetonitrile when comes in contact with the adsorbent, benzaldehyde gets adsorbed on the surface of the adsorbent. So, benzaldehyde acts as adsorbate whereas acetonitrile starts moving as mobile phase over the stationary phase of the adsorbate. Hence, act as dynamic phase.

17. Arsenious sulphide sol is a negative colloid, $As_2S_3.(S^{2-})$. So, it will be coagulated by the cation of an electrolyte.

According to the Hardy-Schulze rule, the higher the charge of the ion, the more effective it is in bringing about coagulation. Here, the cations available are Al^{3+} (from $AlCl_3$), Ba^{2+} (from $BaCl_2$) and Na^+ (from Na_3PO_4 and $NaCl$). So, their power to coagulate $As_2S_3.(S^{2-})$ will follow the order as



18. According to Freundlich adsorption isotherm,

$$\frac{x}{m} \propto p^{1/n} \Rightarrow \frac{x}{m} = Kp^{1/n}$$

On taking log on both sides, we get

$$\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n} \log p$$

On comparing with equation of straight line, $y = mx + c$, plot of $\log \frac{x}{m}$ vs $\log p$ gives,

$$\text{Slope } \frac{(y_2 - y_1)}{(x_2 - x_1)} = \frac{1}{n} \Rightarrow \frac{2}{4} = \frac{1}{2}$$

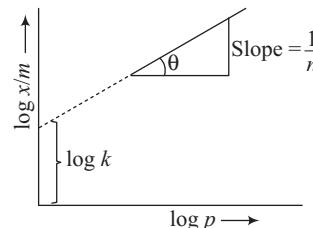
$$\therefore \frac{x}{m} \propto p^{1/2}$$

19. Colloidal solutions show Tyndall effect due to scattering of light by colloidal particles in all directions in space. It is observed only under the following conditions.

- The diameter of the colloids should not be much smaller than the wavelength of light used.

- The refractive indices of the dispersed phase and dispersion medium should differ greatly in magnitude.

20. According to Freundlich adsorption isotherm, $\frac{x}{m} = kp^{1/n}$



On taking logarithm of both sides, we get

$$\log \frac{x}{m} = \log k + \log p^{1/n}$$

$$\text{or} \quad \log \frac{x}{m} = \log k + \frac{1}{n} \log p \\ y = c + mx \\ y = \log \frac{x}{m},$$

$$c = \text{intercept} = \log k$$

$$m = \text{slope} = \frac{1}{n} \text{ and } x = \log p$$

21. Physical adsorption takes place with decrease in enthalpy thus exothermic change. It is physical adsorption and does not require activation. Thus, (a) is incorrect.

Being physical adsorption $\Delta H < 0$ thus, (b) is correct. Exothermic reaction is favoured at low temperature thus (c) is incorrect. Physical adsorption is always reversible, thus (d) is incorrect.

22. According to Hardy Schulze rule, greater the charge on oppositely charged ion, greater is its coagulating power. Since arsenic sulphide is a negatively charged sol, thus, the order of coagulating power is $Na^+ < Ba^{2+} < Al^{3+}$.

23. Sb_2S_3 is a negative (anionic) sol. According to Hardy Schulze rule, greater the valency of cationic coagulating agent, higher its coagulating power. Therefore, $Al_2(SO_4)_3$ will be the most effective coagulating agent in the present case.

24. Larger the hydrophobic fragment of surfactant, easier will be the micellisation, smaller the critical micelle concentration. Therefore, $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ will have the lowest critical micelle concentration.

25. Lyophilic sols are reversible, not easily coagulated because it is self-stabilising.

26. $\Delta G = \Delta H - T\Delta S$

As gas is adsorbed on surface of solid, entropy decreases, i.e. $\Delta S < 0$. Therefore, for $\Delta G < 0$, ΔH must be negative.

27. It is an exothermic process, according to Le-Chatelier's principle, lowering temperature drive the process in forward direction.

28. As temperature increases surface tension of liquid decreases.

29. (a) Higher the critical temperature, greater the extent of adsorption.



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As gaseous adsorbate is adsorbed on solid surface, entropy decreases, $\Delta S < 0$. Also formation of bond between P and Q results in release of energy, hence $\Delta H < 0$.

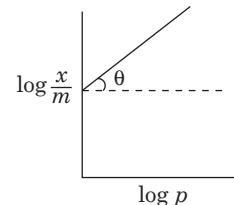
30. Since, adsorption involves electron transfer from metal to O_2 , it is chemical adsorption not physical adsorption, hence (a) is incorrect. Adsorption is spontaneous which involves some bonding between adsorbent and adsorbate, hence exothermic. The last occupied molecular orbital in O_2 is $\pi^* 2p$. Hence, electron transfer from metal to oxygen will increase occupancy of $\pi^* 2p$ molecular orbitals. Also increase in occupancy of $\pi^* 2p$ orbitals will decrease bond order and hence increase bond length of O_2 .
31. **Graph-I** represents physisorption as in physisorption, adsorbents are bonded to adsorbate through weak van der Waals' force. Increasing temperature increases kinetic energy of adsorbed particles increasing the rate of desorption, hence amount of adsorption decreases.
Graph-II represents chemisorption as it is simple activation energy diagram of a chemical reaction.
Graph-III also represents physical adsorption as extent of adsorption increasing with pressure.
Graph-IV represents chemisorption as it represents the potential energy diagram for the formation of a typical covalent bond.
32. Lyophobic sol, which is otherwise unstable, gets stabilised by preferential adsorption of ions on their surface, thus developing a potential difference between the fixed layer and the diffused layer. Thus, option (a) and (d) are correct.
33. (a) In the process of adsorption, a bond is formed between adsorbate and adsorbent, hence always exothermic.
(b) Physisorption require very low activation energy while chemisorption require high activation energy. Therefore a physisorption may transform into chemisorption but only at high temperature.

(c) It is wrong statement as at higher temperature, physically adsorbed substance starts desorbing.

(d) In physical adsorption, van der Waals' force hold the adsorbate and adsorbent together which is a weak electrostatic attraction. In chemisorption, strong chemical bond binds the adsorbate to the adsorbent. Therefore, chemisorption is more exothermic than physical adsorption.

34. From Freundlich adsorption isotherm equation,

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p$$



When we plot $\log x/m$ vs $\log p$, we get a straight line of

$$(i) \text{slope} = \frac{1}{n} = 2 \Rightarrow n = \frac{1}{2}$$

$$(ii) \text{intercept} = \log K = 0.4771$$

$$\Rightarrow \log K = \log 3 \Rightarrow K = 3$$

$$\text{So, } \frac{x}{m} = Kp^{1/n} = 3 \times 4^2 = 48.00 \quad (\because p = 4 \text{ atm})$$

35. Both statements are independently correct but Statement II does not explain Statement I. Critical micelle concentration is the minimum concentration of surfactant at which micelle formation commences first. At critical micelle concentration, several molecules of surfactant coalesce together to form one single micelle molecule. This decreases the apparent number of molecule suddenly lowering conductivity sharply.

14

s-Block Elements

Topic 1 Group I Elements

Objective Questions I (Only one correct option)

1. Which of the following liberates O₂ upon hydrolysis? (2020 Adv.)
(a) Pb₃O₄ (b) KO₂
(c) Na₂O₂ (d) Li₂O₂
2. Dihydrogen of high purity (> 99.95%) is obtained through (2020 Main, 6 Sep II)
(a) the reaction of Zn with dilute HCl
(b) the electrolysis of acidified water using Pt electrodes
(c) the electrolysis of brine solution
(d) the electrolysis of warm Ba(OH)₂ solution using Ni electrodes.
3. In the following reactions, products (A) and (B), respectively, are (2020 Main, 7 Jan II)
NaOH + Cl₂ → (A) + side products (hot and conc.)
Ca(OH)₂ + Cl₂ → (B) + side products (dry)
(a) NaClO₃ and Ca(OCl)₂ (b) NaClO₃ and Ca(ClO₃)₂
(c) NaOCl and Ca(OCl)₂ (d) NaOCl and Ca(ClO₃)₂
4. The temporary hardness of a water sample is due to compound X. Boiling this sample converts X to compound Y. X and Y, respectively, are (2019 Main, 12 April II)
(a) Mg(HCO₃)₂ and Mg(OH)₂
(b) Ca(HCO₃)₂ and Ca(OH)₂
(c) Mg(HCO₃)₂ and MgCO₃
(d) Ca(HCO₃)₂ and CaO
5. The incorrect statement is (2019 Main, 12 April II)
(a) lithium is the strongest reducing agent among the alkali metals.
(b) lithium is least reactive with water among the alkali metals.
(c) LiNO₃ decomposes on heating to give LiNO₂ and O₂.
(d) LiCl crystallise from aqueous solution as LiCl · 2H₂O.
6. The metal that gives hydrogen gas upon treatment with both acid as well as base is (2019 Main, 12 April I)
(a) magnesium (b) mercury
(c) zinc (d) iron
7. The correct statements among (a) to (d) are: (2019 Main, 8 April II)
 1. Saline hydrides produce H₂ gas when reacted with H₂O.
 2. Reaction of LiAlH₄ with BF₃ leads to B₂H₆.
 3. PH₃ and CH₄ are electron rich and electron precise hydrides, respectively.

4. HF and CH₄ are called as molecular hydrides.
(a) (1), (2), (3) and (4) (b) (1), (2) and (3) only
(c) (3) and (4) only (d) (1), (3) and (4) only
8. The strength of 11.2 volume solution of H₂O₂ is [Given that molar mass of H = 1 g mol⁻¹ and O = 16 g mol⁻¹] (2019 Main, 8 April II)
(a) 1.7% (b) 34% (c) 13.6% (d) 3.4%
9. The correct order of hydration enthalpies of alkali metal ions is (2019 Main, 8 April I)
(a) Li⁺ > Na⁺ > K⁺ > Cs⁺ > Rb⁺
(b) Na⁺ > Li⁺ > K⁺ > Rb⁺ > Cs⁺
(c) Na⁺ > Li⁺ > K⁺ > Cs⁺ > Rb⁺
(d) Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺
10. The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are (2019 Main, 12 Jan II)
 - I. They activate many enzymes.
 - II. They participate in the oxidation of glucose to produce ATP.
 - III. Along with sodium ions, they are responsible for the transmission of nerve signals.

(a) I, and III only (b) I, II and III
(c) I and II only (d) III only
11. A metal on combustion in excess air forms X. X upon hydrolysis with water yields H₂O₂ and O₂ along with another product. The metal is (2019 Main, 12 Jan I)
(a) Li (b) Mg (c) Rb (d) Na
12. The hardness of a water sample (in terms of equivalents of CaCO₃) containing is (Molar mass of CaSO₄ = 136 g mol⁻¹) (2019 Main, 12 Jan I)
(a) 100 ppm (b) 10 ppm (c) 50 ppm (d) 90 ppm
13. The hydride that is not electron deficient is (2019 Main, 11 Jan II)
(a) AlH₃ (b) B₂H₆ (c) SiH₄ (d) GaH₃
14. The correct statements among (a) to (d) regarding H₂ as a fuel are : (2019 Main, 11 Jan I)
 - I. It produces less pollutants than petrol.
 - II. A cylinder of compressed dihydrogen weights ~ 30 times more than a petrol tank producing the same amount of energy.

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- III. Dihydrogen is stored in tanks of metal alloys like NaNi_5 .
IV. On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.
- (a) I, II and III only (b) II, III and IV only
(c) II and IV only (d) I and III only
- 15.** NaH is an example of (2019 Main, 11 Jan I)
(a) metallic hydride (b) electron-rich hydride
(c) saline hydride (d) molecular hydride
- 16.** Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of (2019 Main, 10 Jan II)
(a) sodium ammonia complex
(b) sodium ion-ammonia complex
(c) sodamide
(d) ammoniated electrons
- 17.** The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are (2019 Main, 10 Jan I)
(a) 2 and 1 (b) 3 and 2
(c) 2 and 0 (d) 3 and 1
- 18.** The chemical nature of hydrogen peroxide is (2019 Main, 10 Jan I)
(a) oxidising and reducing agent in both acidic and basic medium
(b) oxidising and reducing agent in acidic medium, but not in basic medium
(c) reducing agent in basic medium, but not in acidic medium
(d) oxidising agent in acidic medium, but not in basic medium
- 19.** The metal that forms nitride by reacting directly with N_2 of air, is (2019 Main, 9 Jan II)
(a) Rb (b) K
(c) Cs (d) Li
- 20.** What is reason of temporary hardness of water? (2019 Main, 9 Jan II)
(a) Na_2SO_4 (b) CaCl_2
(c) NaCl (d) $\text{Ca}(\text{HCO}_3)_2$
- 21.** The isotopes of hydrogen are (2019 Main, 9 Jan I)
(a) deuterium and tritium only
(b) protium and deuterium only
(c) protium, deuterium and tritium
(d) tritium and protium only
- 22.** Hydrogen peroxide oxidises $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ in acidic medium but reduces $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ in alkaline medium. The other products formed are, respectively. (2018 Main)
(a) $(\text{H}_2\text{O} + \text{O}_2)$ and H_2O
(b) $(\text{H}_2\text{O} + \text{O}_2)$ and $(\text{H}_2\text{O} + \text{OH}^-)$
(c) H_2O and $(\text{H}_2\text{O} + \text{O}_2)$
(d) H_2O and $(\text{H}_2\text{O} + \text{OH}^-)$
- 23.** Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is (2017 Main)
(a) Both form basic carbonates
(b) Both form soluble bicarbonates
(c) Both form nitrides
(d) nitrates of both Li and Mg yield NO_2 and O_2 on heating
- 24.** The hottest region of Bunsen flame shown in the figure given below is (2016 Main)
-
- (a) region 2 (b) region 3 (c) region 4 (d) region 1
- 25.** Which one of the following statements about water is false? (2016 Main)
(a) Water can act both as an acid and as a base
(b) There is extensive intramolecular hydrogen bonding in the condensed phase
(c) Ice formed by heavy water sinks in normal water
(d) Water is oxidised to oxygen during photosynthesis
- 26.** The main oxides formed on combustion of Li, Na and K in excess of air respectively are (2016 Main)
(a) LiO_2 , Na_2O_2 and K_2O (b) Li_2O_2 , Na_2O_2 and KO_2
(c) Li_2O , Na_2O_2 and KO_2 (d) Li_2O , Na_2O and KO_2
- 27.** Which of the following atoms has the highest first ionisation energy? (2016 Main)
(a) Na (b) K (c) Sc (d) Rb
- 28.** Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a (2014 Adv.)
(a) reducing agent, oxidising agent
(b) reducing agent, reducing agent
(c) oxidising agent, oxidising agent
(d) oxidising agent, reducing agent
- 29.** In which of the following reactions H_2O_2 acts as a reducing agent? (2014 Main)
- I. $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \longrightarrow 2\text{H}_2\text{O}$
II. $\text{H}_2\text{O}_2 - 2e^- \longrightarrow \text{O}_2 + 2\text{H}^+$
III. $\text{H}_2\text{O}_2 + 2e^- \longrightarrow 2\text{OH}^-$
IV. $\text{H}_2\text{O}_2 + 2\text{OH}^- - 2e^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O}$
(a) I and II (b) III and IV (c) I and III (d) II and IV
- 30.** A sodium salt of an unknown anion when treated with MgCl_2 gives white precipitate only on boiling. The anion is (2004, 1M)
(a) SO_4^{2-} (b) HCO_3^- (c) CO_3^{2-} (d) NO_3^-
- 31.** A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are respectively (1996, 1M)
(a) O_2, H_2 (b) $\text{S}_2\text{O}_8^{2-}, \text{Na}$ (c) O_2, Na (d) $\text{S}_2\text{O}_8^{2-}, \text{H}_2$
- 32.** Hydrolysis of one mole of peroxodisulphuric acid produces (1996, 1M)
(a) two moles of sulphuric acid
(b) two moles of peroxomono sulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomono sulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomono sulphuric acid and one mole of hydrogen peroxide
- 33.** The species that do not contain peroxide ions, is (1992, 1M)
(a) PbO_2 (b) H_2O_2 (c) SrO_2 (d) BaO_2

- 34.** The metallic lustre exhibited by sodium metal is explained by
 (a) diffusion of sodium ions
 (b) oscillation of loose electron
 (c) excitation of free protons
 (d) existence of body centred cubic lattice (1987, 1M)
- 35.** A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at cathode and anode are respectively (1987, 1M)
 (a) H_2 , O_2 (b) O_2 , H_2 (c) O_2 , Na (d) O_2 , SO_2
- 36.** Nitrogen dioxide cannot be obtained by heating (1985, 1M)
 (a) KNO_3 (b) $Pb(NO_3)_2$ (c) $Cu(NO_3)_2$ (d) $AgNO_3$
- 37.** The oxide that gives H_2O_2 on treatment with a dilute acid is
 (a) PbO_2 (b) Na_2O_2 (1985, 1M)
 (c) MnO_2 (d) TiO_2
- 38.** Molecular formula of Glauber's salt is (1985, 1M)
 (a) $MgSO_4 \cdot 7H_2O$ (b) $CuSO_4 \cdot 5H_2O$
 (c) $FeSO_4 \cdot 7H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$
- 39.** Heavy water is (1983, 1M)
 (a) H_2O^{18}
 (b) water obtained by repeated distillation
 (c) D_2O
 (d) water at $4^\circ C$
- 40.** A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of (1981, 1M)
 (a) sodium atoms (b) sodium hydride
 (c) sodium amide (d) solvated electrons
- 41.** The temporary hardness of water is due to calcium bicarbonate can be removed by adding (1979, 1M)
 (a) $CaCO_3$ (b) $Ca(OH)_2$ (c) $CaCl_2$ (d) HCl

Objective Questions II

(One or more than one correct option)

- 42.** The pair(s) of reagents that yield paramagnetic species is/are
 (a) Na and excess of NH_3 (b) K and excess of O_2
 (c) Cu and dilute HNO_3 (d) O_2 and 2-ethylanthraquinol
- 43.** The compound(s) formed upon combustion of sodium metal in excess air is (are) (2007, 2M)
 (a) Na_2O_2 (b) Na_2O (c) NaO_2 (d) $NaOH$
- 44.** Sodium nitrate decomposes above $\approx 800^\circ C$ to give
 (a) N_2 (b) O_2 (1998, 2M)
 (c) NO_2 (d) Na_2O
- 45.** Highly pure dilute solution of sodium in liquid ammonia
 (a) shows blue colour
 (b) exhibits electrical conductivity
 (c) produces sodium amide
 (d) produces hydrogen gas (1998, 2M)
- 46.** When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with
 (a) H^+ ions (b) SO_4^{2-} ions (c) Mg^{2+} ions (d) OH^- ions (1990, 1M)
- 47.** Sodium sulphate is soluble in water, whereas barium sulphate is sparingly soluble because (1989, 1M)
 (a) the hydration energy of sodium sulphate is more than its lattice energy

- (b) the lattice energy of barium sulphate is more than its hydration energy
 (c) the lattice energy has no role to play in solubility
 (d) the hydration energy of sodium sulphate is less than its lattice energy

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
 (c) Statement I is correct; Statement II is incorrect
 (d) Statement I is incorrect; Statement II is correct

- 48.** **Statement I** Alkali metals dissolve in liquid ammonia to give blue solution.

Statement II Alkali metals in liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$ (M = alkali metals). (2007, 3M)

- 49.** **Statement I** LiCl is predominantly a covalent compound.
Statement II Electronegativity difference between Li and Cl is too small. (1998, 2M)

- 50.** **Statement I** The alkali metals can form ionic hydrides which contain the hydride ion, H^- .

Statement II The alkali metals have low electronegativity, their hydrides conduct electricity when fused and liberate hydrogen gas at the anode. (1994, 2M)

Fill in the Blanks

51. Hydrogen gas is liberated by the action of aluminium with concentrated solution of (1987, 1M)
52. Sodium dissolved in liquid ammonia conducts electricity because of (1985, 1M)
53. The adsorption of hydrogen by palladium is commonly known as (1983, 1M)
54. Iodine reacts with hot NaOH solution. The products are NaI and (1980, 1M)

True/False

55. Sodium when burnt in excess of oxygen gives sodium oxide. (1987, 1M)

Subjective Questions

56. A white solid is either Na_2O or Na_2O_2 . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
 (i) Identify the substance and explain with balanced equation.
 (ii) Explain what would happen to the red litmus if the white solid were the other compound. (1999, 4M)
57. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations. (1998, 4M)

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58. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes 'milky' on bubbling carbon dioxide gas. Identify A, B, C and D. (1997, 3M)

59. Complete and balance the following chemical reaction.
Anhydrous potassium nitrate is heated with excess of metallic potassium
 $\text{KNO}_3(s) + \text{K}(s) \longrightarrow \dots + \dots$ (1992, 1M)

Topic 2 Group II Elements

Objective Questions I (Only one correct option)

- 1.** Match the following compounds (Column -I) with their uses (Columns -II). (2020 Main, 6 Sep II)

Column - I		Column - II	
(I)	$\text{Ca}(\text{OH})_2$	(A)	Casts of statues
(II)	NaCl	(B)	White wash
(III)	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	(C)	Antacid
(IV)	CaCO_3	(D)	Washing soda preparation

- 60.** Give reasons in one or two sentences for the following:
“ H_2O_2 is a better oxidising agent than H_2O .” (1986, 1M)

61. Sodium carbonate is prepared by Solvay process but the same process is not extended to the manufacture of potassium carbonate, explain. (1981, 1M)

62. Water is a liquid, while H_2S is a gas at ordinary temperature. Explain. (1978, 1M)

7. Magnesium powder burns in air to give (2019 Main, 9 April I)

 - (a) MgO and Mg₃N₂
 - (b) Mg(NO₃)₂ and Mg₃N₂
 - (c) MgO only
 - (d) MgO and Mg(NO₃)₂

- 8.** The covalent alkaline earth metal halide ($X = \text{Cl}, \text{Br}, \text{I}$) is
(2019 Main, 8 April II)

- 9.** Match the following items in Column I with the corresponding items in Column II. (2019 Main, 11 Jan II)

Column I	Column II
(i) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	A. Portland cement ingredient
(ii) $\text{Mg}(\text{HCO}_3)_2$	B. Castner-Kellner process
(iii) NaOH	C. Solvay process
(iv) $\text{Ca}_3\text{Al}_2\text{O}_6$	D. Temporary hardness

- (a) (i) - (D); (ii) - (A); (iii) - (B); (iv) - (C)
 - (b) (i) - (B); (ii) - (C); (iii) - (A); (iv) - (D)
 - (c) (i) - (C); (ii) - (B); (iii) - (D); (iv) - (A)
 - (d) (i) - (C); (ii) - (D); (iii) - (B); (iv) - (A)

- 10.** The amphoteric hydroxide is (2019 Main, 11 Jan I)
(a) $\text{Be}(\text{OH})_2$ (b) $\text{Ca}(\text{OH})_2$ (c) $\text{Sr}(\text{OH})_2$ (d) $\text{Mg}(\text{OH})_2$

11. The metal used for making X-ray tube window is
(2019 Main, 10 Jan I)

(a) Na (b) Be (c) Mg (d) Ca

14. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order.

K₂CO₃ (I), MgCO₃ (II), CaCO₃ (III), BeCO₃ (IV)

(a) I < II < III < IV (b) IV < II < III < I (1996, 1M)
(c) IV < II < I < III (d) II < IV < III < I

- 16.** Calcium is obtained by (1980, 1M)
 (a) electrolysis of molten CaCl_2
 (b) electrolysis of solution of CaCl_2 in water
 (c) reduction of CaCl_2 with carbon
 (d) roasting of limestone

Objective Questions II

(One or more than one correct option)

- 17.** The reagent(s) used for softening the temporary hardness of water is(are) (2010)
 (a) $\text{Ca}_3(\text{PO}_4)_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) Na_2CO_3 (d) NaOCl
- 18.** MgSO_4 on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula? (2006, 3M)
 (a) $\text{Mg}(\text{NH}_4)\text{PO}_4$ (b) $\text{Mg}_3(\text{PO}_4)_3$
 (c) $\text{MgCl}_2 \cdot \text{MgSO}_4$ (d) MgSO_4
- 19.** The material used in solar cells contains (1993, 1M)
 (a) Cs (b) Si (c) Sn (d) Ti

Fill in the Blank

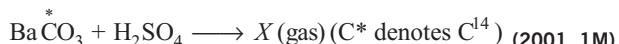
- 20.** Anhydrous MgCl_2 is obtained by heating the hydrated salt with (1980, 1M)

True/False

- 21.** $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ on heating gives anhydrous MgCl_2 . (1982, 1M)

Subjective Questions

- 22.** Identify (X) in the following synthetic scheme and write their structures.



- 23.** Give reasons for the following in one or two sentences only : “ BeCl_2 can be easily hydrolysed.” (1999, 2M)

- 24.** The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why? (1997, 2M)

- 25.** Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas A and an alkaline solution. The solution on exposure to air produces a thin solid layer of B on the surface. Identify the compounds A and B . (1996, 3M)

- 26.** Arrange the following in increasing order of basic strength : $\text{MgO}, \text{SrO}, \text{K}_2\text{O}, \text{NiO}, \text{Cs}_2\text{O}$ (1991, 1M)

Answers**Topic 1**

- | | | | |
|---------|---------------|------------|---------------|
| 1. (b) | 2. (d) | 3. (a) | 4. (a) |
| 5. (c) | 6. (c) | 7. (a) | 8. (d) |
| 9. (d) | 10. (b) | 11. (c) | 12. (a) |
| 13. (c) | 14. (a) | 15. (c) | 16. (d) |
| 17. (d) | 18. (a) | 19. (d) | 20. (d) |
| 21. (c) | 22. (c) | 23. (a) | 24. (a) |
| 25. (b) | 26. (c) | 27. (c) | 28. (a) |
| 29. (d) | 30. (b) | 31. (a) | 32. (c) |
| 33. (a) | 34. (b) | 35. (a) | 36. (a) |
| 37. (b) | 38. (d) | 39. (c) | 40. (d) |
| 41. (b) | 42. (a, b, c) | 43. (a, b) | 44. (a, b, d) |

- | | | | |
|--------------------------|------------|-----------------|-----------------------|
| 45. (a, b) | 46. (a, d) | 47. (a, b) | 48. (b) |
| 49. (c) | 50. (a) | 51. NaOH | |
| 52. (solvated electrons) | | 53. (occlusion) | 54. (NaIO_3) |
| 55. (F) | | | |

Topic 2

- | | | | |
|---------------|---------|---------|-------------|
| 1. (b) | 2. (d) | 3. (b) | 4. (b) |
| 5. (d) | 6. (c) | 7. (a) | 8. (d) |
| 9. (d) | 10. (a) | 11. (b) | 12. (c) |
| 13. (b) | 14. (b) | 15. (d) | 16. (a) |
| 17. (b, c, d) | 18. (a) | 19. (b) | 20. dry HCl |
| 21. F | | | |

Hints & Solutions**Topic 1 Group I Elements**

1. (a) $\text{Pb}_3\text{O}_4 + \text{H}_2\text{O} \longrightarrow$ No reaction

Pb_3O_4 is insoluble in water or do not react with water.

- (b) $\text{KO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2\text{O}_2 + 1/2 \text{ O}_2$

Potassium superoxide is a strong oxidant, able to convert oxides into peroxides or molecular oxygen. Hydrolysis gives oxygen gas, hydrogen peroxide and potassium hydroxide.

- (c) $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$

When sodium peroxide dissolves in water, it is hydrolysed and forms sodium hydroxide and hydrogen peroxide. The reaction is highly exothermic.

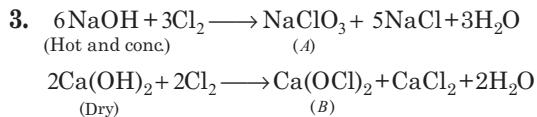
- (d) $\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{LiOH} + \text{H}_2\text{O}_2$

The reactivity of Li_2O_2 toward water differs from LiO_2 , in Li_2O_2 results in H_2O_2 as a product. Hence, the correct option is (b).

2. Electrolysis of warm aqueous $\text{Ba}(\text{OH})_2$ solution between nickel electrodes is a commercial method to obtain highly pure (> 99.95%) dihydrogen.

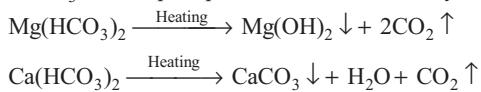
In the presence of $\text{Ba}(\text{OH})_2$, water dissociates into ions easily and quickly and H^+ ions are produced, which go on cathode, gets discharged there and liberate hydrogen gas.

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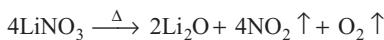


Thus, A : NaClO_3
B : $\text{Ca}(\text{OCl})_2$

4. The temporary hardness of a water sample is due to compound X [i.e. $\text{Mg}(\text{HCO}_3)_2$]. Boiling of this sample converts X[i.e. $\text{Mg}(\text{HCO}_3)_2$] to compound Y[i.e. $\text{Mg}(\text{OH})_2$]. Generally, temporary hardness is due to presence of magnesium and calcium hydrogen carbonates. It can be removed by boiling. During boiling, the soluble $\text{Mg}(\text{HCO}_3)_2$ is converted into insoluble $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{HCO}_3)_2$ changed to insoluble CaCO_3 . These precipitates can be removed by filtration.



5. Statement (c) is incorrect. LiNO_3 (Lithium nitrate) on heating gives a mixture of Li_2O , NO_2 and O_2 .



Among the alkali metals, lithium is the strongest reducing agent.

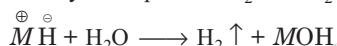
6. Metal that gives hydrogen gas upon treatment with both acid as well as base is zinc. Hence, it is amphoteric in nature.

Reactions involved are as follows:

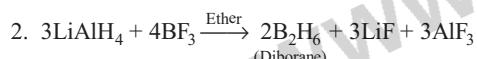


7. The explanation of given statements are as follows :

1. Saline or ionic hydrides produce H_2 with H_2O .



Thus, statement (1) is correct.



Thus, statement (2) is correct.

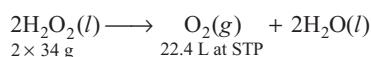
3. PH_3 and CH_4 are covalent hydrides and in both of the hydrides, octet of P and C have been satisfied. But P in PH_3 has one lone pair of electrons and C in CH_4 does not have so PH_3 (group 15) and CH_4 (group 14) are electron rich and electron precise hydrides, respectively.

Thus, statement (3) is correct.

4. HF and CH_4 are called as molecular hydrides because of their discrete and sterically symmetrical structure.

Thus, statement (4) is also correct.

8. 11.2 volume of H_2O_2 means that 1 mL of this H_2O_2 will give 11.2 mL of oxygen at STP.



22.4 L of O_2 at STP is produced from $\text{H}_2\text{O}_2 = 68 \text{ g}$

$\therefore 11.2 \text{ L of O}_2$ at STP is produced from

$$\text{H}_2\text{O}_2 = \frac{68}{22.4} \times 11.2 = 34 \text{ g}$$

$\therefore 34 \text{ g of H}_2\text{O}_2$ is present in 1000 g of solution

$$\therefore \% w/w = \frac{34}{1000} \times 100 = 3.4\%$$

9. **Key Idea** The amount of energy released when one mole of gaseous ions combine with water to form hydrated ions is called hydration enthalpy.

The correct order of hydration enthalpies of alkali metal ions is



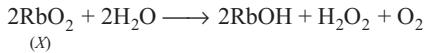
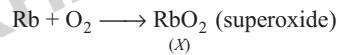
Li^+ possesses the maximum degree of hydration due to its small size. As a consequence of hydration enthalpy, their mobility also get affected. Cs^+ has highest and Li^+ has lowest mobility in aqueous solution.

10. All the statements are correct. K^+ being metallic unipositive ions work as enzyme activators. These also participate in many reactions of glycolysis and Kreb's cycle to produce ATP from glucose.

Being unipositive these are also equally responsible for nerve signal transmission along with Na^+ . (Na^+ ion-pump theory)

11. Metal (A) is rubidium (Rb). In excess of air, it forms $\text{RbO}_2(X)$. X is a superoxide that have O_2^- ion. It is due to the stabilisation of large anion by large cations through lattice energy effects. $\text{RbO}_2(X)$ gets easily hydrolysed by water to form the hydroxide, H_2O_2 and O_2 .

The reaction involved are as follows:



12. Hardness of water sample can be calculated in terms of ppm concentration of CaCO_3 .

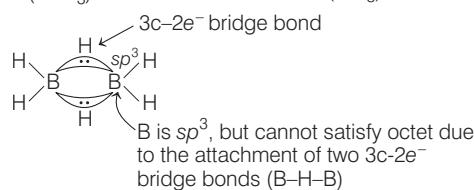
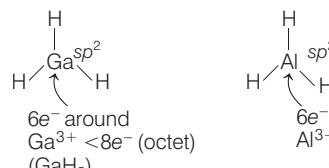
Given, molarity = 10^{-3}M

i.e. 1000 mL of solution contains 10^{-3} mole of CaCO_3 .

\therefore Hardness of water = ppm of CaCO_3

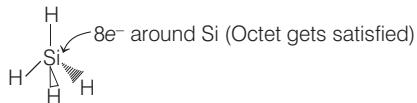
$$= \frac{10^{-3} \times 1000}{1000} \times 10^6 = 100 \text{ ppm}$$

13. GaH_3 , AlH_3 and B_2H_6 are the hydrides of group-13 (ns^2np^1), whereas SiH_4 is an hydride of group 14.



So, B_2H_6 , AlH_3 and GaH_3 are electron deficient hydrides.

But, SiH_4 is an electron precise hydride of group-14 (ns^2np^2), i.e. these hydrides can have the required number of electrons to write their conventional Lewis structures.



14. (I) H_2 is a 100% pollution free fuel. So, statement (I) is correct.
 (II) Molecular weight of H_2 (2u).

$$= \frac{1}{29} \times \text{molecular weight of butane},$$

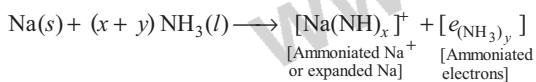
C_4H_{10} (LPG) [58u].

So, compressed H_2 weighs ~30 times more than a petrol tank and statement (II) is correct.

- (III) NaNi_5 , Ti-TiH_2 etc. are used for storage of H_2 in small quantities. Thus, statement (III) is correct.
 (IV) On combustion values of energy released per gram of liquid dihydrogen (H_2) : 142 kJ g⁻¹, and for LPG : 50 kJ g⁻¹. So, statement (IV) is incorrect.

15. $\overset{\oplus}{\text{Na}}\text{H}$ is an example of ionic or saline hydride. These hydrides are formed when hydrogen combines with metals having less electronegativity and more electropositive character with respect to hydrogen.
 Except Be and Mg, all s-block metals form saline hydrides.
 Hydrides of p-block elements are covalent in nature, viz., electron deficient hydrides (by group-13 elements), electron-precise hydrides (by group-14 elements), and electron-rich hydrides (by group 15-17 elements). Hydrides of d, f-block metals are called interstitial or metallic hydrides.

16. Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of ammoniated electrons. The reaction is represented as follows:



Ammoniated (solvated) electrons show electronic transition in visible region and the solution becomes deep blue coloured.

This deep blue solution also shows the following properties due to the presence of ammoniated electrons.

- (i) It is strongly reducing in nature.
- (ii) It is paramagnetic.
- (iii) It is a good conductor of electricity.

17. Hydrogen has three isotopes:

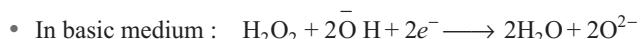
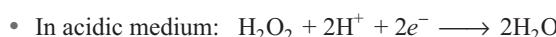
${}^1\text{H}$	${}^2\text{H}$	${}^3\text{H}$
Protium (P)	Deuterium (D)	Tritium (T)
p	1	1
n	0	2
$\frac{n}{p}$	0	2

Only tritium (T) is radioactive, because of its very high $\frac{n}{p}$ value,

$$\left(\frac{n}{p} = 2 \right).$$

18. H_2O_2 can act as both oxidising and reducing agents in both acidic and basic medium.

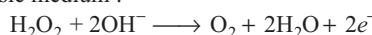
H_2O_2 as oxidising agent



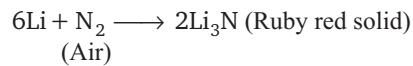
H_2O_2 as reducing agent



In basic medium :



19. Among the group-1 metals, only Li is able to form its nitride, Li_3N . [All alkaline earth metals of group-2 form their nitride, $M_3\text{N}_2$]



Li^{\oplus} is the smallest metal ion of group-1. Smaller size of Li^{\oplus} and larger size of nitride ion, N^{3-} , enable Li^{\oplus} to polarise the spherical electron cloud of N^{3-} and it gives higher stability to Li_3N .

20. Temporary hardness of water is due to presence of soluble $\text{Ca}(\text{HCO}_3)_2$ or $\text{Mg}(\text{HCO}_3)_2$.

Permanent hardness of water is due to the presence of CaCl_2 or CaSO_4 or MgCl_2 or MgSO_4 .

Temporary hardness of water is also called carbonate hardness which can be easily removed by boiling or by treatment with $\text{Ca}(\text{OH})_2$ (Clark's method).

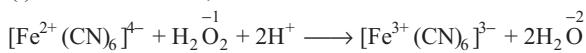
21. There are three known isotopes of hydrogen, each possessing an atomic number 1 and atomic masses 1, 2 and 3 respectively. These are named as protium (${}^1\text{H}$), deuterium (${}^2\text{H}$ or D) and tritium (${}^3\text{H}$ or T)

The most common isotope is the ordinary hydrogen usually called protium. It consists of one proton in the nucleus and an electron revolving around it.

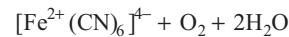
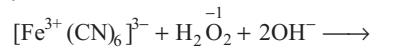
The second isotope of hydrogen is called heavy hydrogen or deuterium. It consists of one proton and one neutron in the nucleus and an electron revolving around it. The third isotope of hydrogen is called tritium. It consists of one proton and two neutrons in the nucleus and an electron revolving around it.

22. Both reactions in their complete format are written below

(i) In acidic medium,



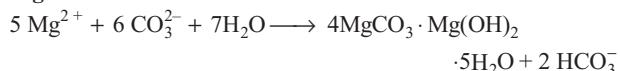
(ii) In alkaline medium,



Hence, H_2O (for reaction (i)) and $\text{O}_2 + \text{H}_2\text{O}$ (for reaction (ii)) are produced as by product.

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23. Mg can form basic carbonate while Li cannot.



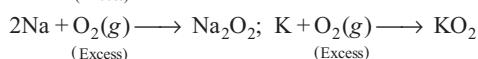
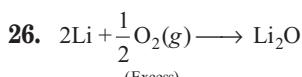
24. Region 1 (Pre-heating zone)

Region 2 (Primary combustion zone, hottest zone)

Region 3 (Internal zone)

Region 4 (Secondary reaction zone)

25. There is extensive intermolecular H-bonding in the condensed phase.



27. Order of first ionisation energy is Sc > Na > K > Rb.

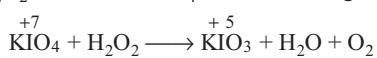
Due to poor shielding effect, removal of one electron from $4s$ orbital is difficult as compared to $3s$ -orbital.

28. **PLAN** This problem can be solved by using concept of oxidant and reductant.

Oxidant Oxidant increases the oxidation number of the species with which it is reacted.

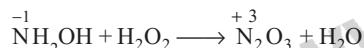
Reductant Reductant decreases the oxidation number of the species with which it is reacted.

H_2O_2 reacts with KIO_4 in the following manner:



On reaction of KIO_4 with H_2O_2 , oxidation state of I varies from +7 to +5, i.e. decreases. Thus, KIO_4 gets reduced hence, H_2O_2 is a reducing agent here.

With NH_2OH , it given following reaction:



In the above reaction, oxidation state of N varies from -1 to +3. Here, oxidation number increases, hence H_2O_2 is acting as an oxidising agent here.

Hence, (a) is the correct choice.

29. Release of electron is known as reduction. So, H_2O_2 acts as reducing agent when it releases electrons.

Here, in reaction (II) and (IV), H_2O_2 releases two electron, hence reaction (II) and (IV) is known as **reduction**.

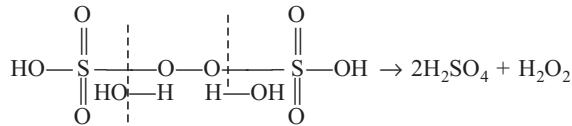
In reaction (I) and (III), two electrons are being added, so (I) and (III) represents **oxidation**.

30. $\text{Mg}(\text{HCO}_3)_2$ on boiling decomposes to give white precipitate of MgCO_3 as:

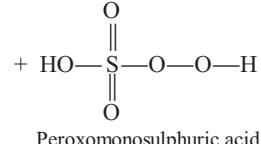
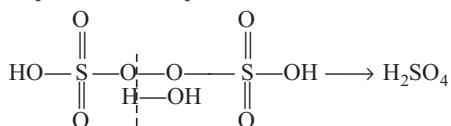


31. Electrolysis of aqueous Na_2SO_4 gives $\text{H}_2(g)$ at cathode and $\text{O}_2(g)$ at anode.

32. Peroxodisulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) on complete hydrolysis gives two moles of H_2SO_4 and one mole of H_2O_2 as



On partial hydrolysis, it gives one mole of H_2SO_4 and one mole of peroxomonosulphuric acid as



33. In PbO_2 , Pb is in +4 oxidation state and oxygen is in -2 oxidation state. In all other case, peroxide ion (O_2^{2-}) is present.

34. Metallic lustre of any metal is due to oscillation of free electrons present in the metal.

35. H_2O is reduced as well as oxidised giving $\text{H}_2(g)$ at cathode and $\text{O}_2(g)$ at anode.

36. KNO_3 and other nitrates of alkali metals (except LiNO_3) are thermally stable.

37. Sodium peroxide on treatment with dilute acid gives H_2O_2



38. Glauber's salt is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

39. D_2O is commonly known as heavy water.

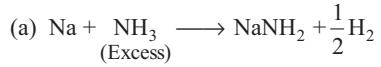
40. Presence of solvated electrons makes solution of alkali metal in liquid ammonia makes them strongly reducing agent.

41. Lime treatment remove bicarbonate hardness by forming insoluble CaCO_3 as



42. **PLAN** Paramagnetic character of species can be easily explained on the basis of presence of unpaired electrons, i.e. compounds containing unpaired electron(s) is/are paramagnetic.

Reaction of alkali metals with ammonia depends upon the physical state of ammonia whether it is in gaseous state or liquid state. If ammonia is considered as a gas then reaction will be

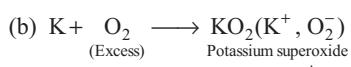


($\text{NaNH}_2 + 1/2 \text{H}_2$ are diamagnetic)

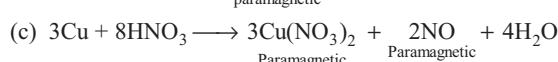
If ammonia is considered as a liquid then reaction will be

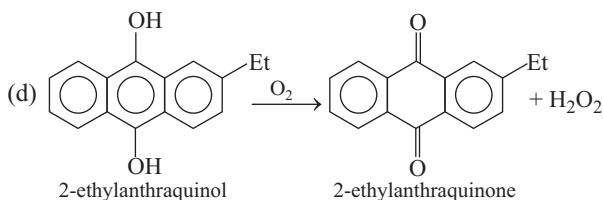


- Ammoniated electron
- Blue colour
- Paramagnetic
- Very strong reducing agent



Potassium superoxide
paramagnetic

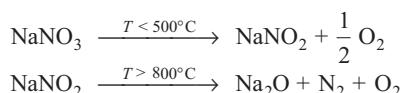




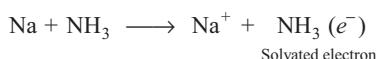
Hence, option (a), (b) and (c) are correct choices.

43. When sodium metal is burnt in excess of air, mainly sodium peroxide (Na_2O_2) with little sodium oxide (Na_2O) are formed.

44. NaNO_2 when heated, it decomposes in two stages as:



- 45.** In dilute solution of Na in liquid ammonia, solvated electrons are present whose emission spectrum gives blue colouration to solution.



Also, presence of solvated electrons and solvated Na^+ ion makes solution highly conducting.

- 46.** Zeolite acts as ion exchange resin and its Na^+ is exchanged with H^+ and Mg^{2+} ions present in hard water.

47. Solubility of a salt is influenced by two major factors, lattice energy and hydration energy. For greater solubility, there should be smaller lattice energy and greater hydration energy.

48. Both statements are correct but blue colour is due to presence of solvated electron $\text{NH}_3(e^-)$.

49. Statement I is correct. Small size of Li^+ makes it highly polarising, introduces predominant covalency in LiCl . Statement II is incorrect, there is very large difference in electronegativity of Li and Cl.

50. Alkali metal forms MH in which hydrogen is in -1 oxidation state. Both statements are correct and statement -2 is correct explanation of statement I.

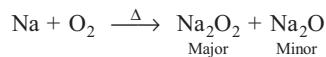
51. $\text{Al} + \text{conc. NaOH} \longrightarrow \text{NaAlO}_2 + \text{H}_2 \uparrow$

52. Na in liquid ammonia contain $\text{NH}_3(e^-)$ which possesses charge and conduct electricity.

53. Occlusion is a phenomena in which particles are physically trapped in voids.

54. I_2 disproportionate in alkali giving NaI and NaIO_3 .

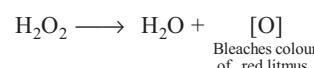
55. Sodium when burnt in excess of oxygen, gives sodium peroxide as major product.



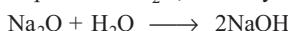
- 56.** The substance is Na_2O_2 . When Na_2O_2 is dissolved in water, it forms NaOH and H_2O_2 . In this case, NaOH is a strong base while H_2O_2 is a weak acid.

(i) $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$

H_2O_2 decolourises red litmus paper due to its bleaching action which is due to its oxidising character.

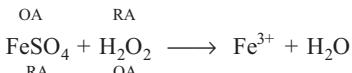


- (ii) If the compound is Na_2O , it will hydrolyse to form NaOH .

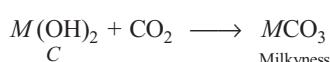
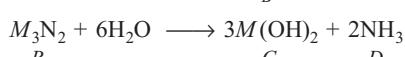


NaOH solution formed above will change colour of red litmus paper into blue.

- 57.** $\text{KMnO}_4 + \text{H}_2\text{O}_2 \longrightarrow \text{MnO}_2 + \text{KOH} + \text{O}_2$



- 58.** $3M + N_2 \xrightarrow{A} M_3N_2$



M can be either Ca or Ba but essentially not Mg because $Mg(OH)_2$ is very sparingly soluble in water.

- 59.** $2\text{KNO}_3(s) + 10\text{K}(s) \longrightarrow 6\text{K}_2\text{O}(s) + \text{N}_2(g)$

- 60.** In H_2O_2 , the peroxide ion (O_2^{2-}) is unstable, has tendency to pass into stable oxide state (O^{2-}). Hence, H_2O_2 is a good oxidising agent while H_2O is stable.

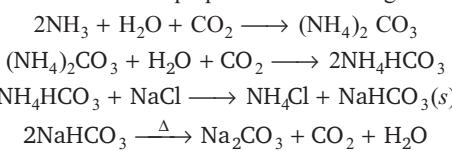
- 61.** In Solvay process, NaHCO_3 is extracted from the solution by fractional crystallisation, which is then heated to convert it into $\text{Na}_2\text{CO}_3 \cdot \text{KHCO}_3$, being more soluble than NaHCO_3 , cannot be extracted by fractional crystallisation. Hence, Solvay process fails in production of K_2CO_3 .

- 62.** Water forms stronger intermolecular H-bonds, therefore it is liquid at room temperature while H_2S cannot form such strong intermolecular bonds, gas at room temperature.

Topic 2 Group II Elements

1. Correct match is I → (B), II → (D), III → (A), IV → (C)
(I) $\text{Ca}(\text{OH})_2$ used in white wash.

(II) NaCl is used in the preparation of washing soda.



- (III) $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ (plaster of Paris) is used for making casts of statues.

- (IV) CaCO_3 is used as an antacid.

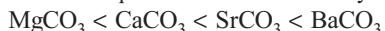
- 2.** In comparison to boron, beryllium has lesser nuclear charge and greater first ionisation enthalpy.

Electronic configuration of Be(4) = $1s^2$, $2s^2$.

It possess completely filled s -orbitals. Hence, high amount of energy is required to pull the electron from the gaseous atom. Beryllium (4) lies left to the boron (5) and on moving from left to right an electron is added due to which nuclear charge increases from Be to B.

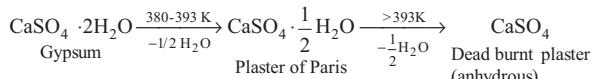
216 s-Block Elements

3. The correct sequence of thermal stability of carbonates is

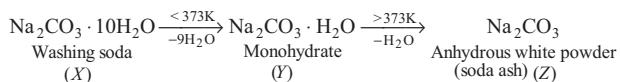


On moving down the group, i.e. from Mg to Ba, atomic radius generally increases. It is due to the addition of shell. As a result, the atomic size increases. CO_3^{2-} is a large anion. Hence, more stabilised by Ba^{2+} (large cation) and less stabilised by Mg^{2+} . Therefore, BaCO_3 has highest thermal stability followed by SrCO_3 , CaCO_3 and MgCO_3 .

4. Baking soda (NaHCO_3) is not a hydrated solid. Thus, (X) is not baking soda. Thus, option (a) and (c) are incorrect. Dead burnt plaster (CaSO_4) is obtained from gypsum via the formation of plaster of Paris.



Therefore, the reaction takes place as follows :

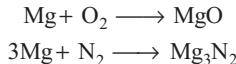


5. Names of magnesium alloys are given by two letters followed by two numbers. The common alloying elements are *A* (Aluminium), *Z* (zinc), *T* (tin), *M* (manganese) etc. Numbers indicate respective nominal compositions of main alloying elements, e.g. 'AZ 91' implies the composition of the alloy as : Al = 9%, Zn = 1% and Mg = 100 - (9 + 1) = 90%

Among the alloys given, Mg – Al (Magnalium ; Mg = 5%, Al = 95%) is being light, tough and strong, hence it is used in aircrafts.

6. The structures of beryllium chloride in the solid state and vapour phase, respectively are dimeric and chain. In vapour phase at above 900°C , BeCl_2 is monomeric having a linear structure Cl—Be—Cl. The bonding in BeCl_2 is covalent and Be atom accommodates $2 + 2 = 4$ electrons in the two sp -hybrid orbitals. Below 900°C , beryllium chloride in vapour phase exists as a mixture of monomer BeCl_2 and dimer Be_2Cl_4 .

7. Magnesium powder burns in air to give MgO and Mg_3N_2 . MgO does not combine with excess oxygen to give any superoxide. Mg reacts with nitrogen to form magnesium nitride (Mg_3N_2).



8. **Key Idea** According to Fajan's rule, degree of covalency (ionic potential), $\phi \propto$ polarisation power of the cation \propto charge on the cation

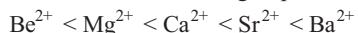
$$\propto \frac{1}{\text{size of the cation}}$$

Alkaline earth metals contains bipositive (H^{2+}) ions in their compounds.

So, here

- (i) Charge on cation, i.e. + 2 is constant.
(ii) Halide present (X^-) is also constant.

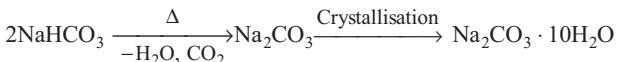
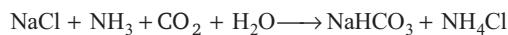
So, the covalent character depends on the size of alkaline earth metal. As we move down the group, size of metal ion increases.



So, Be^{2+} readily forms covalent compounds like BeX_2 , because of very high positive charge density over its small size, so that it readily polarises anionic spherical electron cloud.

9. (i) Washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) is manufactured in Solvay process. In this method, CO_2 gas is passed through a conc. solution of NaCl saturated with NH_3 . It gives ammonium carbonate followed by ammonium hydrogen carbonate.

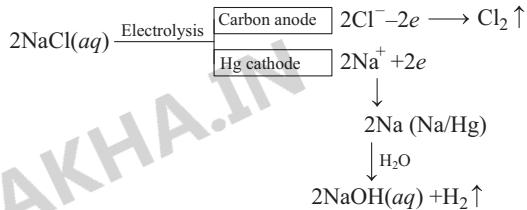
The obtained NH_4HCO_3 is treated with solution of NaCl which result in the formation of NaHCO_3 . The crystal obtained are heated to obtain Na_2CO_3 .



- (ii) $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$ cause temporary hardness to water that can be easily removed by boiling.

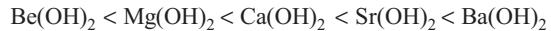
- (iii) NaOH is manufactured by Castner-Kellner process.

In this reaction, Na amalgam flows out and treated with water to give NaOH and H_2 gas. During electrolysis, hydrogen is evolved at cathode and chlorine is evolved at anode, which are the by product of this process.



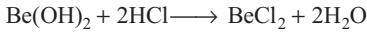
- (iv) Portland cement constitutes, tricalcium aluminosilicate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, i.e. $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{SiO}_2$.

10. For group-2 metal hydroxides, basicity increases down the group, as:

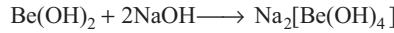


This is because as the size of metal atom increases, $M-\text{OH}$ bond length increases or $M-\text{OH}$ bond become weaker thus readily breaks to release OH^- ions which are responsible for the basicity of these solutions.

But $\text{Be}(\text{OH})_2$ shows amphoteric (basic as well as acidic) character as it reacts with acid and alkali both which is shown in the following reactions. $\text{Be}(\text{OH})_2$ as a base :



$\text{Be}(\text{OH})_2$ as an acid :



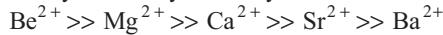
11. Among the four elements given, Na, Be, Mg and Ca, Be has highest IE value because of its smallest size and $2s^2$ valence shell configuration.

So, X-ray cannot cause ionisation from the material used, i.e. Be in the tube window, which may cause interference in the study.

12. A saturated aqueous solution of $M(\text{NO}_3)_2$ on crystallisation will produce hydrated crystal, $M(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ only when hydration enthalpy ($\Delta H_{\text{hyd}}^\circ$) of M^{2+} ion will be appreciably more negative.

Hydration of an ion depends on its size. Smaller the size of an ion, higher will be its charge density and as a result it will remain more solvated (hydrated) through ion dipole interaction.

Size of group-2 metal ions increases on going down the group. So, their ability to form hydrated crystals follows the order:

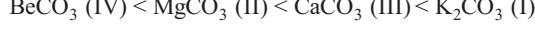


Thus, $\text{Ba}(\text{NO}_3)_2$ is slightly or almost insoluble in water.

13. As we move down the group, size of metal increases. Be has lower size while SO_4^{2-} has bigger size, that's why BeSO_4 breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases. On the other hand, rest of the metals, i.e. Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time saving technique In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy. Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence, BeSO_4 is the right response.

14. Thermal stability of salts with common anion depends on polarising power of cation. Greater the polarising power, lower be their thermal stability. Hence,

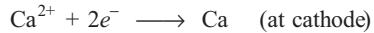


15. The reaction involved is



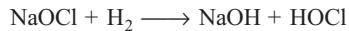
The most electronegative atom, oxygen, in BaSO_4 and H_2O_2 has -2 and -1 oxidation state respectively.

16. Electrolysis of molten CaCl_2 gives calcium at cathode

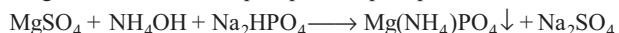


In case of electrolysis in aqueous medium, less electropositive H^+ is reduced at cathode rather than Ca^{2+} .

17. $\text{Ca}(\text{OH})_2 + \text{Ca}(\text{HCO}_3)_2 \longrightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$
(Clark's method)



18. Magnesium ammonium phosphate is precipitated out.



19. Si is used in solar cells, because of its semi-conductor properties.

20. Anhydrous MgCl_2 is obtained by heating hydrated salt in stream of dry HCl.

21. Heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ brings about partial dehydration as



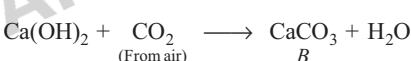
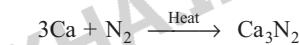
22. $\text{Ba}^*\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$ (${}^*\text{C} = \text{C}^{14}$)

23. Be in BeCl_2 is electron deficient, short of two lone pair of electrons from stable octet. H_2O has lone pair of electrons, reacts with BeCl_2 .

24. Alkaline earth metal salts have M^{2+} ions which has very high polarising power compared to polarising power of monovalent metal ion (M^+) of alkali metal. Due to high polarising power of M^{2+} , it associate more water than M^+ .

25. $A = \text{NH}_3, B = \text{CaCO}_3$,

Reactions involved are :



26. Basic strength (i) decreases from left to right in period and (ii) increases from top to bottom in group. Therefore,



15

p-Block Elements-I

Topic 1 Group 13 Elements

Objective Questions I (Only one correct option)

1. The reaction of $\text{H}_3\text{N}_3\text{B}_3\text{Cl}_3$ (*A*) with LiBH_4 in tetrahydrofuran gives inorganic benzene (*B*). Further, the reaction of (*A*) with (*C*) leads to $\text{H}_3\text{N}_3\text{B}_3(\text{Me})_3$. Compounds (*B*) and (*C*) respectively, are
(2020 Main, 9 Jan II)
- (a) diborane and MeMgBr
 - (b) boron nitride and MeBr
 - (c) borazine and MeBr
 - (d) borazine and MeMgBr

2. The green colour produced in the borax bead test of a chromium (III) salt is due to
(2019 Adv.)
- (a) Cr_2O_3
 - (b) CrB
 - (c) $\text{Cr}(\text{BO}_2)_3$
 - (d) $\text{Cr}_2(\text{B}_4\text{O}_7)_3$

3. The correct statements among I to III regarding group 13 element oxides are:
(2019 Main, 9 April II)

- I. Boron trioxide is acidic.
 - II. Oxides of aluminium and gallium are amphoteric.
 - III. Oxides of indium and thallium are basic.
- (a) I, II and III
 - (b) I and III only
 - (c) I and II only
 - (d) II and III only

4. Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively.
(2019 Main, 8 April I)
- (a) B_2O_3 and H_3BO_3
 - (b) B_2O_3 and $[\text{BH}_4]^-$
 - (c) H_3BO_3 and B_2O_3
 - (d) HBO_2 and H_3BO_3

5. The relative stability of +1 oxidation state of group 13 elements follows the order
(2019 Main, 11 Jan II)
- (a) $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$
 - (b) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
 - (c) $\text{Tl} < \text{In} < \text{Ga} < \text{Al}$
 - (d) $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$

6. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6 , respectively, are
(2019 Main, 10 Jan II)
- (a) 4 and 2
 - (b) 2 and 4
 - (c) 2 and 2
 - (d) 2 and 1

7. The electronegativity of aluminium is similar to
(2019 Main, 10 Jan I)
- (a) lithium
 - (b) carbon
 - (c) beryllium
 - (d) boron

8. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to
(2019 Main, 9 Jan I)

- (a) lattice effect
- (b) lanthanoid contraction
- (c) inert pair effect
- (d) diagonal relationship

9. The increasing order of atomic radii of the following Group 13 elements is
(2016 Adv.)

- (a) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
- (b) $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$
- (c) $\text{Al} < \text{In} < \text{Ga} < \text{Tl}$
- (d) $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$



How can this reaction proceed in forward direction?
(2006, 3M)

- (a) Addition of *cis* 1, 2-diol
- (b) Addition of borax
- (c) Addition of *trans* 1, 2-diol
- (d) Addition of Na_2HPO_4

11. H_3BO_3 is

(2003, 1M)

- (a) monobasic acid and weak Lewis acid
- (b) monobasic and weak Bronsted acid
- (c) monobasic and strong Lewis acid
- (d) tribasic and weak Bronsted acid

12. In compounds of type $E\text{Cl}_3$, where $E = \text{B}, \text{P}, \text{As}$ or Bi , the angles $\text{Cl}-E-\text{Cl}$ for different E are in the order

(1999, 2M)

- (a) $\text{B} > \text{P} = \text{As} = \text{Bi}$
- (b) $\text{B} > \text{P} > \text{As} > \text{Bi}$
- (c) $\text{B} < \text{P} = \text{As} = \text{Bi}$
- (d) $\text{B} < \text{P} < \text{As} < \text{Bi}$

13. Moderate electrical conductivity is shown by

(1982, 1M)

- (a) silica
- (b) graphite
- (c) diamond
- (d) None of these

Objective Questions II

(One or more than one correct option)

14. Among the following, the correct statement(s) is(are)

(2017 Adv.)

- (a) $\text{Al}(\text{CH}_3)_3$ has the three-centre two-electron bonds in its dimeric structure
- (b) The Lewis acidity of BCl_3 is greater than that of AlCl_3

- (c) AlCl_3 has the three-centre two-electron bonds in its dimeric structure
 (d) BH_3 has the three-centre two-electron bonds in its dimeric structure
- 15.** The crystalline form of borax has (2016 Adv.)
 (a) tetrานuclear $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ unit
 (b) all boron atoms in the same plane
 (c) equal number of sp^2 and sp^3 hybridised boron atoms
 (d) one terminal hydroxide per boron atom
- 16.** The correct statement(s) for orthoboric acid is/are (2014 Adv.)
 (a) It behaves as a weak acid in water due to self ionisation
 (b) Acidity of its aqueous solution increases upon addition of ethylene glycol
 (c) It has a three-dimensional structure due to hydrogen bonding
 (d) It is a weak electrolyte in water
- 17.** In the reaction, $2X + \text{B}_2\text{H}_6 \longrightarrow [\text{BH}_2(X)_2]^+[\text{BH}_4]^-$ the amine(s) X is/are (2009)
 (a) NH_3
 (b) CH_3NH_2
 (c) $(\text{CH}_3)_2\text{NH}$
 (d) $(\text{CH}_3)_3\text{N}$

Numerical Answer Type Question

- 18.** Among B_2H_6 , $\text{B}_3\text{N}_3\text{H}_6$, N_2O , N_2O_4 , $\text{H}_2\text{S}_2\text{O}_3$ and $\text{H}_2\text{S}_2\text{O}_8$, the total number of molecules containing covalent bond between two atoms of the same kind is(2019 Adv.)

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I
 (b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I
 (c) Statement I is correct; Statement II is incorrect
 (d) Statement I is incorrect; Statement II is correct
- 19.** **Statement I** Boron always forms covalent bond.
Statement II The small size of B^{3+} favours formation of covalent bond. (2007, 3M)
- 20.** **Statement I** In water, orthoboric acid behaves as a weak monobasic acid.
Statement II In water, orthoboric acid acts as a proton donor. (2007, 3M)
- 21.** **Statement I** $\text{Al}(\text{OH})_3$ is amphoteric in nature.
Statement II Al—O and O—H bonds can be broken with equal ease in $\text{Al}(\text{OH})_3$. (1998 , 2M)

Match the Column

- 22.** Match the following. (2006, 6M)

Column I	Column II
A. $\text{Bi}^{3+} \rightarrow (\text{BiO})^+$	p. Heat
B. $[\text{AlO}_2]^- \rightarrow \text{Al}(\text{OH})_3$	q. Hydrolysis
C. $\text{SiO}_4^{4-} \rightarrow \text{Si}_2\text{O}_7^{6-}$	r. Acidification
D. $(\text{B}_4\text{O}_7^{2-}) \rightarrow [\text{B}(\text{OH})_3]$	s. Dilution by water

Fill in the Blank

- 23.** The two types of bonds present in B_2H_6 are covalent and(1994, 1M)

True/False

- 24.** The basic nature of hydroxide of group 13 (group IIIA) decreases progressively down the group. (1993, 1M)
- 25.** All the Al—Cl bonds in Al_2Cl_6 are equivalent. (1989, 1M)

Integer Answer Type Questions

- 26.** Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is(2015 Adv.)
- 27.** The value of n in the molecular formula $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ is(2010)

Subjective Questions

- 28.** AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3 , AlF_3 is precipitated. Write the balanced chemical equations. (2004, 2M)
- 29.** (i) How is boron obtained from borax? Give chemical equations with reaction conditions.
 (ii) Write the structure of B_2H_6 and its reaction with HCl. (2002)
- 30.** Compound X on reduction with LiAlH_4 gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y . Give balanced reactions involved in the formation of Y and its reaction with air.
 Draw the structure of Y . (2001, 5M)
- 31.** Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. (1997, 2M)
- 32.** Anhydrous AlCl_3 is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution.
 (Ionisation energy for Al = 5137 kJ mol⁻¹
 $\Delta H_{\text{hydration}}$ for $\text{Al}^{3+} = -4665 \text{ kJ mol}^{-1}$
 $\Delta H_{\text{hydration}}$ for $\text{Cl}^- = -381 \text{ kJ mol}^{-1}$) (1997, 2M)

Topic 2 Group 14 Elements

Objective Questions I (Only one correct option)

1. The C—C bond length is maximum in (2019 Main, 12 April II)
 - (a) graphite
 - (b) C_{70}
 - (c) C_{60}
 - (d) diamond
2. The basic structural unit of feldspar, zeolites, mica and asbestos is (2019 Main, 12 April I)
 - (a) $(SiO_3)^{2-}$
 - (b) SiO_2
 - (c) $(SiO_4)^{4-}$
 - (d) $\begin{array}{c} R \\ | \\ -(Si-O)_n- \\ | \\ R \end{array}$ ($R = Me$)
3. The correct order of catenation is (2019 Main, 10 April I)
 - (a) $C > Sn > Si \approx Ge$
 - (b) $Si > Sn > C > Ge$
 - (c) $C > Si > Ge \approx Sn$
 - (d) $Ge > Sn > Si > C$
4. The amorphous form of silica is (2019 Main, 9 April II)
 - (a) tridymite
 - (b) kieselguhr
 - (c) cristobalite
 - (d) quartz
5. C_{60} an allotrope of carbon contains (2019 Main, 9 April I)
 - (a) 16 hexagons and 16 pentagons
 - (b) 20 hexagons and 12 pentagons
 - (c) 12 hexagons and 20 pentagons
 - (d) 18 hexagons and 14 pentagons
6. The element that does not show catenation is (2019 Main, 12 Jan II)
 - (a) Ge
 - (b) Sn
 - (c) Si
 - (d) Pb
7. The element that shows greater ability to form $p\pi-p\pi$ multiple bonds, is (2019 Main, 12 Jan II)
 - (a) Ge
 - (b) Si
 - (c) Sn
 - (d) C
8. The chloride that cannot get hydrolysed is (2019 Main, 11 Jan I)
 - (a) $SnCl_4$
 - (b) CCl_4
 - (c) $PbCl_4$
 - (d) $SiCl_4$
9. Correct statements among (I) to (IV) regarding silicones are: (2019 Main, 9 Jan I)
 - I. They are polymers with hydrophobic character.
 - II. They are biocompatible.
 - III. In general, they have high thermal stability and low dielectric strength.
 - IV. Usually, they are resistant to oxidation and used as greases.
 - (a) I and II only
 - (b) I, II, III only
 - (c) I, II, III and IV
 - (d) I, II and IV only
10. Name the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is (2005, 1M)
 - (a) pyrosilicate
 - (b) sheet silicate
 - (c) linear chain silicate
 - (d) three-dimensional silicate
11. Me_2SiCl_2 on hydrolysis will produce (2003, 1M)
 - (a) $(Me)_2Si(OH)_2$
 - (b) $(Me)_2Si=O$
 - (c) $[-O-(Me)_2Si-O-]_n$
 - (d) $Me_2SiCl(OH)$

12. Identify the correct order of acidic strength of CO_2 , CuO , CaO , H_2O . (2002, 3M)
 - (a) $CaO < CuO < H_2O < CO_2$
 - (b) $H_2O < CuO < CaO < CO_2$
 - (c) $CaO < H_2O < CuO < CO_2$
 - (d) $H_2O < CO_2 < CaO < CuO$
13. Which one of the following oxides is neutral? (1996, 1M)
 - (a) CO
 - (b) SnO_2
 - (c) ZnO
 - (d) SiO_2
14. Which of the following halides is least stable and has doubtful existence? (1996, 1M)
 - (a) CCl_4
 - (b) GeI_4
 - (c) SnI_4
 - (d) PbI_4

Objective Question II

(One or more than one correct option)

15. Choose the correct statement(s) among the following: (2020 Adv.)
 - (a) $SnCl_2 \cdot 2H_2O$ is a reducing agent.
 - (b) SnO_2 reacts with KOH to form $K_2[Sn(OH)_6]$.
 - (c) A solution of $PbCl_2$ in HCl contains Pb^{2+} and Cl^- ions.
 - (d) The reaction of Pb_3O_4 with hot dilute nitric acid to give PbO_2 is a redox reaction.
16. With respect to graphite and diamond, which of the statement(s) given below is/are correct? (2012)
 - (a) Graphite is harder than diamond
 - (b) Graphite has higher electrical conductivity than diamond.
 - (c) Graphite has higher thermal conductivity than diamond.
 - (d) Graphite has higher C—C bond order than diamond

Assertion and Reason

- (a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I
- (b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I
- (c) Statement I is correct; Statement II is incorrect
- (d) Statement I is incorrect; Statement II is correct

17. **Statement I** Pb^{4+} compounds are stronger oxidising agents than Sn^{2+} compounds.

Statement II The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to ‘inert pair effect’. (2008, 3M)

18. **Statement I** Between $SiCl_4$ and CCl_4 , only $SiCl_4$ reacts with water.

Statement II $SiCl_4$ is ionic and CCl_4 is covalent. (2001, S, 1M)

Fill in the Blanks

19. A liquid which is permanently supercooled is frequently called (1997, 1M)

20. The recently discovered allotrope of carbon (e.g. C_{60}) is commonly known as (1994, 1M)
21. The hydrolysis of trialkyl chlorosilane R_3SiCl , yields (1994, 1M)
22. The hydrolysis of alkyl substituted chlorosilanes gives (1991, 1M)

True/False

23. The tendency for catenation is much higher for C than for Si. (1993, 1M)
24. Diamond is harder than graphite. (1993, 1M)
25. Graphite is a better lubricant on the moon than on the earth. (1987, 1M)
26. Carbon tetrachloride burns in air when lighted to give phosgene gas. (1983, 1M)

Subjective Questions

27. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (give reactions only).
- Silicon
 - Linear silicon containing methyl group only
 - Na_2SiO_3 (2001, 5M)

28. Draw the structure of a cyclic silicate, $(Si_3O_9)^{6-}$ with proper labelling. (1998, 4M)
29. Write the balanced equation for the preparation of crystalline silicon from $SiCl_4$. (1990, 1M)
30. Each entry in column X is in some way related to the entries in columns Y and Z. Match the appropriate entries.

X	Y	Z
Yeast	Fermentation	Ethanol
Mica	Graphite	Abrasive
Superphosphate	Crystalline cubic	Insulator
Carbon fibres	Layer structure	Fertiliser
Rock salt	Diamond structure	Reinforced plastics
Carborundum	Bone ash	Preservative

(1989, 3M)

31. Give reasons for the following in one or two sentences : “Graphite is used as a solid lubricant.” (1985, 1M)
32. Give reason for the following in one or two sentences : “Solid carbon dioxide is known as dry ice.” (1983, 1M)
33. Carbon acts as an abrasive and also as a lubricant, explain. (1981, 1M)

Answers

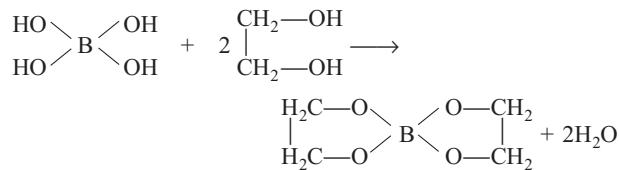
Topic 1

- | | | | |
|---|--------------------------------------|---------------|------------|
| 1. (d) | 2. (c) | 3. (a) | 4. (a) |
| 5. (b) | 6. (a) | 7. (c) | 8. (c) |
| 9. (b) | 10. (a) | 11. (a) | 12. (b) |
| 13. (b) | 14. (a, b, c) | 15. (a, c, d) | 16. (b, d) |
| 17. (a, b, c) | 18. (4.00) | 19. (a) | 20. (a) |
| 21. (a) | 22. (A → q; B → r; C → p ; D → q, r) | | |
| 23. (Three centre two electron bond or banana bond) | | | |
| 24. (F) | 25. (F) | 27. (3) | |

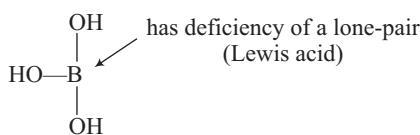
Topic 2

- | | | | |
|-------------------|---------|--------------------|-----------------|
| 1. (d) | 2. (c) | 3. (c) | 4. (b) |
| 5. (b) | 6. (d) | 7. (d) | 8. (b) |
| 9. (d) | 10. (a) | 11. (c) | 12. (a) |
| 13. (a) | 14. (d) | 15. (a,c) | 16. (b, d) |
| 17. (a) | 18. (c) | 19. (glass) | |
| 20. (Buckminster) | | 21. (R_3SiO_2) | 22. (silicones) |
| 23. (T) | 24. (T) | 25. (T) | 26. (F) |

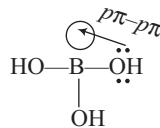
9. Due to poor shielding of *d*-orbital in Ga, atomic radius of Ga is smaller than that of Al. Thus, Ga < Al < In < Tl.
10. Orthoboric acid is a very weak acid, direct neutralisation does not complete. However, addition of *cis*-diol allow the reaction to go to completion by forming a stable complex with $[\text{B}(\text{OH})_4]^-$ as:



11. Orthoboric acid is a weak, monobasic, Lewis acid.



$p\pi-p\pi$ backbonding between 'B' and 'O' decreases acid strength greatly :



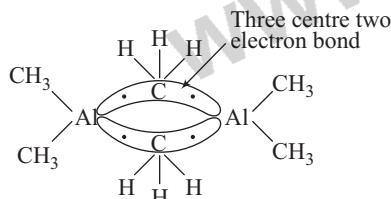
12. In BCl_3 , bond angle = 120° .

In PCl_3 , AsCl_3 and BiCl_3 , central atom is sp^3 hybridised. Since P, As and Bi are from the same group, bond angle decreases down the group. Hence, overall order of bond angle is :



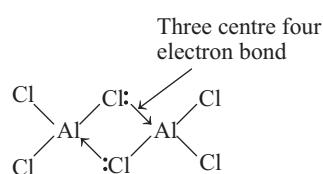
13. Graphite has layered structure and conducted electricity moderately. Silica and diamond have 3-dimensional network structures and non-conducting.

14. (a)

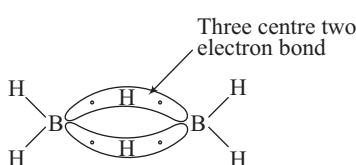


- (b) BCl_3 is stronger Lewis acid than AlCl_3 due to greater extent of $p\pi-p\pi$ back bonding in AlCl_3 .

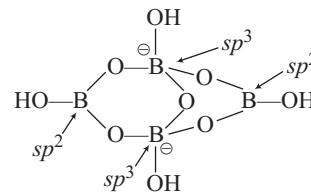
- (c)



- (d)

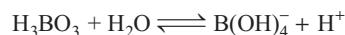


15. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (borax) is actually made of two tetrahedral and two triangular units, and is actually written as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 5\text{H}_2\text{O}$.



- (a) Thus, correct.
- (b) Boron atoms are in different planes thus, incorrect.
- (c) Two sp^2 and two sp^3 -hybridised B atoms thus, correct.
- (d) Each boron has one —OH group thus, correct.

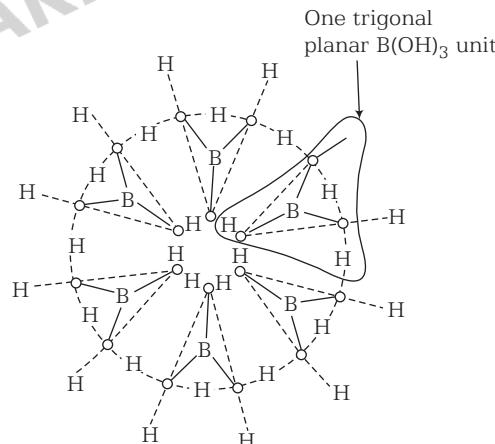
16. (a) It does not undergo self ionisation in water but accepts an electron pair from water, so it behaves as weak monobasic acid.



Hence, (a) is incorrect.

- (b) When treated with 1, 2-dihydroxy or polyhydroxy compounds, they form chelate (ring complex) which effectively remove $[\text{B}(\text{OH})_4]^-$ species from solution and thereby produce maximum number of H_3O^+ or H^+ ions, i.e. results in increased acidity.

- (c) Boric acid crystallises in a layer structure in which planar triangular BO_3^{3-} ions are bonded together through hydrogen bonds.

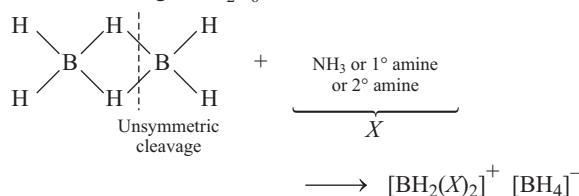


- (d) In water the pK_a value of H_3BO_3 is 9.25.

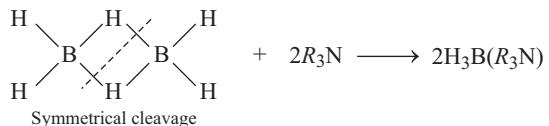


So, it is a weak electrolyte in water.

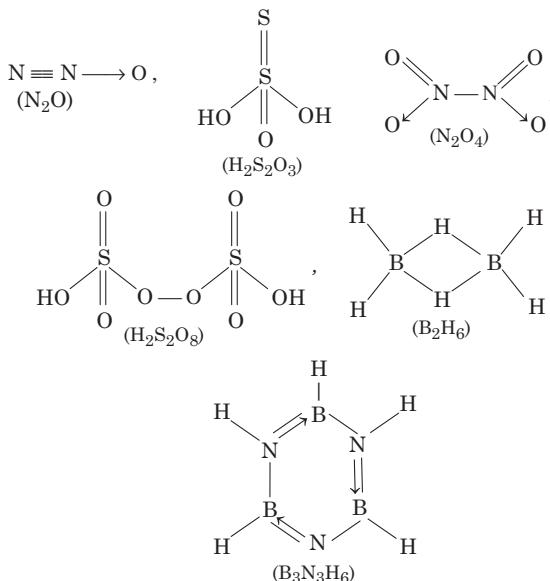
17. Diborane (B_2H_6) undergoes unsymmetric cleavage with NH_3 , primary and secondary amine while tertiary amine brings about symmetrical cleavage of B_2H_6 as :



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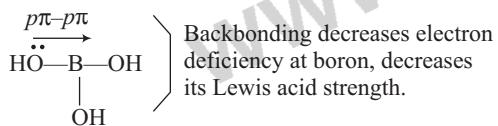
18. N_2O , N_2O_4 , $\text{H}_2\text{S}_2\text{O}_3$ and $\text{H}_2\text{S}_2\text{O}_8$ molecules are containing covalent bond between two atoms.



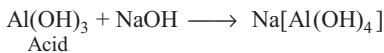
B_2H_6 and $\text{B}_3\text{N}_3\text{H}_6$ have polar bond, but do not have same kind of atom.

19. Small size and high charge on B^{3+} makes it highly polarising. Therefore, in most of its compounds, boron forms covalent bonds. Hence, both statement I and statement II are correct and statement II is a correct explanation of statement I.

20. Orthoboric acid is a weak, monobasic, Lewis acid and the poor acidic character is due to $p\pi-p\pi$ backbonding as:



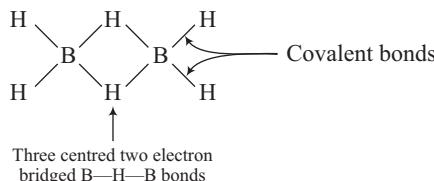
21. Due to small size and high charge on Al in $\text{Al}(\text{OH})_3$ the fission ability of Al—O and O—H bonds become comparable and compound can give both H^+ and HO^- under appropriate reaction conditions as:



Therefore, both statements are correct and statement II is a correct explanation of statement I.

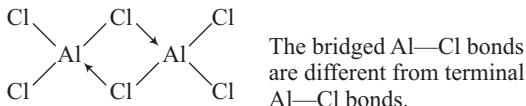
22. (A) Bi^{3+} hydrolysis to $(\text{BiO})^+$ — q.
 (B) $[\text{AlO}_2^-]$ exist in basic medium, on acidification gives $\text{Al}(\text{OH})_3$ — r.
 (C) Orthosilicate (SiO_4^{4-}) on heating changes into pyrosilicate $\text{Si}_2\text{O}_7^{6-}$ — p.
 (D) Tetraborate ion $[\text{B}_4\text{O}_7^{2-}]$ on treatment with dil. acid hydrolysis gradually to orthoboric acid — q, r.

23. Three centred two electron bonds.



24. The basic nature of hydroxide of group-13 increases from top to bottom due to increase in electropositive character.

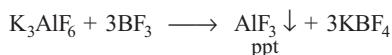
25. In Al_2Cl_6 , Al—Cl bonds are not equivalent :



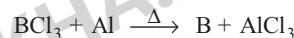
26. $\text{B}_2\text{H}_6 + 6 \text{CH}_3\text{OH} \longrightarrow 2[\text{B}(\text{OCH}_3)_3] + 6\text{H}_2$
 Therefore, from 3 moles of B_2H_6 , 6 moles of $\text{B}(\text{OCH}_3)_3$ will be

27. $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$, $2n + 6 + 24 - 36 = 0 \Rightarrow n = 3$

28. $3\text{KF} + \text{AlF}_3 \longrightarrow \text{B}_2\text{H}_5\text{Cl} + \text{H}_2$



29. (i) $\text{Na}_2\text{B}_4\text{O}_7 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_3\text{BO}_3$

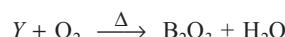


- (ii) B_2H_6 :
-

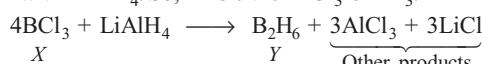
It has 4 terminal B—H bonds. There are two B—H—B, three centred two electron bridged bonds.



30. Compound X $\xrightarrow{\text{LiAlH}_4} Y$ a hydride + other compound. Hydride Y contains 21.72% hydrogen.

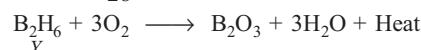


Therefore, Y is a hydride of boron and it is obtained by reduction of X with LiAlH_4 . So, X is either BCl_3 or BF_3 .

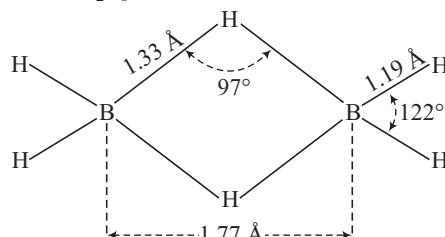


Molar mass of $\text{B}_2\text{H}_6 = 2 \times 11 + 6 = 28$

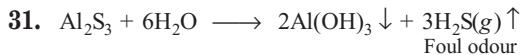
% of H in $\text{B}_2\text{H}_6 = \frac{6}{28} \times 100 = 21.5 \approx 21.72$



Structure of Y (B_2H_6)



- (a) There are 4 terminal B—H bonds.
- (b) There are two 3-centre-2-electron B—H—B bridged bonds.
- (c) Terminal H—B—H planes are perpendicular to bridged B—H—B bonds.



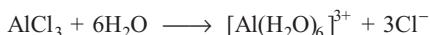
Foul odour on damping of Al_2S_3 is due to the formation of H_2S gas as shown above.

32. The total hydration energy of AlCl_3

$$\begin{aligned} &= \text{Hydration energy of } \text{Al}^{3+} + 3 \times \text{Hydration energy of } \text{Cl}^- \\ &= -4665 + 3(-381) \text{ kJ/mol} \\ &= -5808 \text{ kJ/mol} \end{aligned}$$

The above hydration energy is more than the energy required for ionisation of AlCl_3 into Al^{3+} and 3Cl^- .

Due to this reason, AlCl_3 becomes ionic in aqueous solution. In aqueous solution, it is ionised completely as

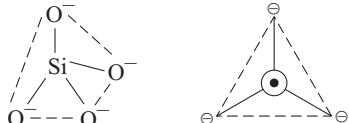


Topic 2 Groups 14 Elements

1. The C—C bond length is maximum in diamond having value 154 pm. Here, each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. It has a rigid three-dimensional network of carbon atoms.

C—C bond length within the layers of graphite is 141.5 pm. In C_{60} , C—C distances between single and double bonds are 143.5 pm and 138.3 pm respectively.

2. The basic structural unit of feldspar, zeolites, mica and asbestos is $(\text{SiO}_4)^{4-}$. These all are silicates. All silicates involve two types of Si—O bonds.
 (i) Terminal Si—O bonds in which oxygen is bonded to a silicon and not other atom.
 (ii) Bridging Si—O—Si bonds in which oxygen is bonded to two silicon atoms.

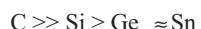


In SiO_4^{4-} ion, each Si atom is bonded to four oxygen atoms tetrahedrally.

3. Catenation property is an unique property of group 14 elements. Down the group 14, catenation power decreases as:
 $\text{C} > \text{Si} > \text{Ge} \approx \text{Sn}$
 Pb does not show catenation.
4. Silica occurs in nature in several amorphous and crystalline forms. Kieselguhr is the amorphous form of silica. Quartz, tridymite and cristobalite are crystalline forms of silica.
5. C_{60} is aromatic allotrope of carbon containing 12 pentagons and 20 hexagons. It is a fullerene having a shape like soccer ball and called Buckminster fullerene.

6. The property of self-linking of atoms of an element through covalent bonds to form straight or branched chains and rings of different sizes is called catenation. Down the group, catenation tendency decreases due to decrease in element bond strength. Carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) are group-14 elements.

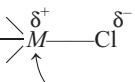
Catenation tendency is highest in carbon while silicon has second highest tendency of catenation among all elements of family due to higher bond energy. The decreasing tendency of catenation among group 14 elements is as follows:



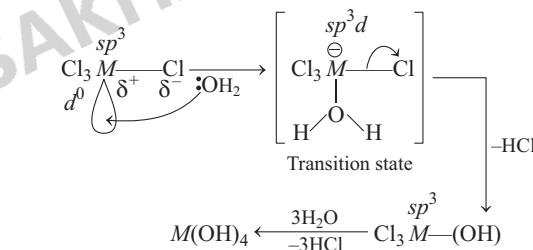
However, Pb does not show catenation.

7. Carbon (C) has greatest ability to form stable $p\pi-p\pi$ multiple bonds. $2p$ -orbitals of this element participate in the process. The stability of multiple bonds of C is attributed to their closeness with C-nucleus. Thus, the smaller size of C plays a significant role in the process.

8. The compounds given are the tetrahalides ($M\text{Cl}_4$) of group 14 elements. For the hydrolysis, (nucleophilic substitution) of $M\text{Cl}_4$ the nature of the $M—\text{Cl}$ bond should be as:



It must expand its covalency beyond 4 by the use of its vacant d -orbital which will accommodate the lone pair of electrons of H_2O (the nucleophile).



Here, M can be Si, Sn and Pb because they have vacant nd -orbital. But, carbon is a member of second period ($n = 2$, $l = 0, 1$), it does not have d -orbital ($l = 2$). So, CCl_4 will not be hydrolysed and correct option is (b).

9. Silicones are polysiloxanes with general chemical formula, $[R_2\text{SiO}]_n$, where R is an organic group such as:
 $-\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_6\text{H}_5$ etc.
- Silicones have many useful properties:
- (i) They repel water and form watertight seals.
 - (ii) They are heat resistant because of constancy of properties over a wide range of temperature (-100° to 250° C).
 - (iii) Silicones are non-toxic.
 - (iv) Silicones are biocompatible because these do not support microbiological growth and these have high gas permeability at room temperature.
 - (v) They are resistant to O_2, O_3 and UV-radiation.
 - (vi) Silicones are formulated to be electrically insulative.

226 p-Block Elements-I

- (vii) Silicone grease is typically used as a lubricant for brake components in automobiles, since it is stable at high temperature, is not water soluble and is a odourless viscous liquid.
10. In sheet silicates, three out of four oxygen of SiO_4^{4-} unit are shared as shown below :
-
- In pyrosilicates, there is only one shared oxygen, in linear chain silicates, two oxygen per tetrahedra are shared while in three-dimensional silicates, all four oxygens are shared.
11. Me_2SiCl_2 on hydrolysis yields a linear chain silicone as :
- $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{Cl}-\text{Si}-\text{Cl} + 2\text{H}_2\text{O} \longrightarrow \text{HO}-\text{Si}-\text{OH} + 2\text{HCl} \\ | \\ \text{CH}_3 \end{array}$$
- $$n\text{HO}-\text{Si}-\text{OH} \xrightarrow{\text{Polymerisation}} \left[-\text{O}-\text{Si}-\text{O}- \right]_n$$
- $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{Si}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$$
12. CO_2 is acidic oxide, H_2O is neutral, CaO is strongly basic and CuO is weakly basic. Therefore, order of acid strength is :
- $$\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$$
13. Carbon monoxide is a neutral oxide, all others are amphoteric :
- $$\begin{array}{l} \text{SnO}_2 + 4\text{HCl} \longrightarrow \text{SnCl}_4 + 2\text{H}_2\text{O} \\ \text{ZnO} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\text{O} \\ \text{SiO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \end{array}$$
- SnO_2 and ZnO also react with NaOH . SiO_2 is also attacked by H_3PO_4 .
14. PbI_4 is least stable, has doubtful existence. It is due to inert pair effect, the stable oxidation state of lead is + 2.
15. (a) Sn^{2+} of stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) tends to convert into Sn^{4+} .
Hence, statement (a) is correct.
- (b) SnO_2 reacts with KOH and gives $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{K}_2[\text{Sn}(\text{OH})_6]$ because it is amphoteric in nature.

$$\text{SnO}_2 + \text{KOH} \longrightarrow \text{K}_2\text{SnO}_3 + \text{H}_2\text{O}$$
 or $\text{K}_2[\text{Sn}(\text{OH})_6]$
Hence, statement (b) is correct.
- (c) In conc. HCl , PbCl_2 exists as chloroplumbous acid, $\text{H}_2[\text{PbCl}_4]$
- $$\overset{\text{II}}{\text{PbCl}_2} + 2\text{HCl} \longrightarrow \overset{\text{II}}{\text{H}_2[\text{PbCl}_4]}$$
- Hence, statement (c) is incorrect.
- (d) Pb_3O_4 is a mixture of ($\overset{+2}{\text{PbO}} + \overset{+4}{\text{PbO}_2}$)
- $$\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \longrightarrow 2\overset{+2}{\text{Pb}}(\text{NO}_3)_2 + \overset{+4}{\text{PbO}_2} + 2\text{H}_2\text{O}$$
- It is not a redox reaction. Thus, the statement (d) is incorrect.
16. Diamond has a three-dimensional network structure, a hard substance where graphite is soft due to layered structure. In graphite, only three valence electrons are involved in bonding and one electron remain free giving electrical conductivity. In diamond, all the four valence electrons are covalently bonded hence, insulator.
- Diamond is better thermal conductor than graphite. Electrical conductivity is due to availability of free electrons, thermal conduction is due to transfer of thermal vibrational energy from one atom to another atom. A compact and precisely aligned crystals like diamond thus facilitate better movement of heat.
- In graphite C—C bond acquire some double bond character, hence, higher bond order than in diamond.
17. In group 13, 14, 15 as we descend down in group, the higher oxidation state becomes less tenable due to inert pair effect. Therefore, lead show +2 as stable oxidation state. Hence, Pb^{4+} act as a strong oxidising agent, itself reduced to Pb^{2+} very easily. Both statement I and statement II are correct and statement II is a correct explanation of statement I.
18. SiCl_4 reacts with water due to vacant d -orbitals available with Si as:
-
- No such vacant d -orbitals are available with carbon, hence CCl_4 does not react with water. Otherwise, both SiCl_4 and CCl_4 are covalent.
- Statement I is correct but statement II is incorrect.
19. Glass is commonly known as supercooled liquid.
20. Buckminster fullerene is the name of recently discovered allotrope of carbon.
21. After dimerisation, no reactive function group remains.
- $$\begin{array}{c} R \\ | \\ \text{R}-\text{Si}-\text{OH} \\ | \\ R \end{array} \xrightarrow{-\text{HCl}} \begin{array}{c} R \\ | \\ \text{R}-\text{Si}-\text{O}-\text{Si}-\text{R} \\ | \\ R \end{array}$$
- Dimeric silicone

22. Silicones are organosilicon polymers, obtained by hydrolysis of alkyl substituted chlorosilanes.

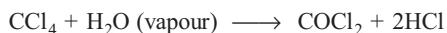
23. Due to smaller size of carbon than silicon, C—C bond is stronger than Si—Si bond, hence former is more likely to extend than latter.

24. Graphite has a layered structure of hexagonal carbon rings stacked one over other which makes it slippery.

On the other hand, in diamond, each carbon is tetrahedrally bonded to other four carbons extended in three dimensional space, giving a giant, network structure. Due to this reason, diamond is harder than graphite.

25. Graphite is better lubricant on moon than on earth because of absence of gravitational pull on the moon.

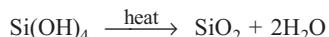
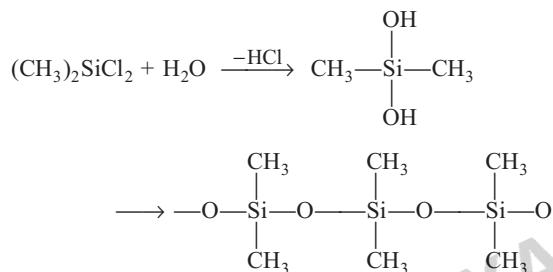
26. Phosgene gas is obtained by treatment of CCl_4 with superheated steam :



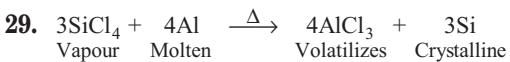
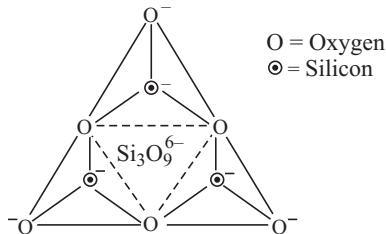
27. (i) $3\text{SiCl}_4 + 4\text{Al} \xrightarrow{\Delta} 3\text{Si} + 4\text{AlCl}_3$;

Mg or Zn can also be used.

(ii) $\text{SiCl}_4 + 2\text{CH}_3\text{MgCl} \longrightarrow (\text{CH}_3)_2\text{SiCl}_2 + 2\text{MgCl}_2$



28.



30.

X	Y	Z
Yeast	Fermentation	Ethanol
Mica	Layered structure	Insulator
Superphosphate	Bone ash	Fertiliser
Carbon fibres	Graphite	Reinforced plastics
Rock salt	Crystalline cubic	Preservative
Carborundum	Diamond structure	Abrasives

31. Graphite has layered structure and the adjacent layers are weakly associated giving slippery nature, used as solid lubricant.

32. Carbon dioxide solidifies at very low temperature, hence solid CO_2 is very cold, commonly known as dry ice. Also solid carbon dioxide sublime, without passing through liquid state.

33. The two common allotropes of carbon are diamond and graphite. Diamond is the hardest, natural, substance, used as an abrasive while graphite is soft, used as a lubricant.

16

p-Block Elements-II

Topic 1 Elements and Compounds of Group 15 and 16

Objective Questions I (Only one correct option)

1. The correct statement among the following is
(2019 Main, 12 April I)
(a) $(\text{SiH}_3)_3\text{N}$ is planar and less basic than $(\text{CH}_3)_3\text{N}$.
(b) $(\text{SiH}_3)_3\text{N}$ is pyramidal and more basic than $(\text{CH}_3)_3\text{N}$.
(c) $(\text{SiH}_3)_3\text{N}$ is pyramidal and less basic than $(\text{CH}_3)_3\text{N}$.
(d) $(\text{SiH}_3)_3\text{N}$ is planar and more basic than $(\text{CH}_3)_3\text{N}$.
2. The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are
(2019 Main, 10 April II)
(a) 20 and 3
(b) 12 and 4
(c) 20 and 4
(d) 12 and 3
3. The oxoacid of sulphur that does not contain bond between sulphur atoms is
(2019 Main 10 April I)
(a) $\text{H}_2\text{S}_2\text{O}_3$
(b) $\text{H}_2\text{S}_2\text{O}_4$
(c) $\text{H}_2\text{S}_2\text{O}_7$
(d) $\text{H}_2\text{S}_4\text{O}_6$
4. The correct order of the oxidation states of nitrogen in NO , NO_2 , NO_3 and N_2O_3 is
(2019 Main, 9 April I)
(a) $\text{NO}_2 < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}$
(b) $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{NO}_2$
(c) $\text{O}_2 < \text{N}_2\text{O}_3 < \text{NO} < \text{N}_2\text{O}$
(d) $\text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{NO} < \text{NO}_2$
5. The pair that contains two P—H bonds in each of the oxoacids is
(2019 Main, 10 Jan II)
(a) $\text{H}_4\text{P}_2\text{O}_5$ and $\text{H}_4\text{P}_2\text{O}_6$
(b) H_3PO_3 and H_3PO_2
(c) $\text{H}_4\text{P}_2\text{O}_5$ and H_3PO_3
(d) H_3PO_2 and $\text{H}_4\text{P}_2\text{O}_5$
6. When the first electron gain enthalpy ($\Delta_{e_g} H$) of oxygen is -141 kJ/mol , its second electron gain enthalpy is
(2019 Main, 9 Jan II)
(a) a positive value
(b) a more negative value than the first
(c) almost the same as that of the first
(d) negative, but less negative than the first
7. Good reducing nature of H_3PO_2 is attributed to the presence of
(2019 Main, 9 Jan II)
(a) two P—H bonds
(b) one P—H bond
(c) two P—OH bonds
(d) one P—OH bond
8. The compound that does not produce nitrogen gas by the thermal decomposition is
(2018 Main)
(a) $\text{Ba}(\text{N}_3)_2$
(b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
(c) NH_4NO_2
(d) $(\text{NH}_4)_2\text{SO}_4$
9. The order of the oxidation state of the phosphorus atom in H_3PO_2 , H_3PO_4 , H_3PO_3 and $\text{H}_4\text{P}_2\text{O}_6$ is
(2017 Adv.)
(a) $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$
(b) $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
(c) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$
(d) $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$
10. The species in which the N-atom is in a state of sp hybridisation is
(2016 Main)
(a) NO_2^-
(b) NO_3^-
(c) NO_2
(d) NO_2^+
11. The pair in which phosphorus atoms have a formal oxidation state of +3 is
(2016 Main)
(a) pyrophosphorous and hypophosphoric acids
(b) orthophosphorous and hypophosphoric acids
(c) pyrophosphorous and pyrophosphoric acids
(d) orthophosphorous and pyrophosphorous acids
12. The product formed in the reaction of SOCl_2 with white phosphorus is
(2014 Adv.)
(a) PCl_3
(b) SO_2Cl_2
(c) SCl_2
(d) POCl_3
13. Which of the following properties is not shown by NO ?
(2014 Main)
(a) It is paramagnetic in liquid state
(b) It is a neutral oxide
(c) It combines with oxygen to form nitrogen dioxide
(d) Its bond order is 2.5
14. Concentrated nitric acid upon long standing, turns yellow-brown due to the formation of
(2013 Main)
(a) NO
(b) NO_2
(c) N_2O
(d) N_2O_4

- 15.** Which of the following is the wrong statement? (2013 Main)
 (a) ONCl and ONO^- are not isoelectronic
 (b) O_3 molecule is bent
 (c) Ozone is violet-black in solid state
 (d) Ozone is diamagnetic gas
- 16.** The reaction of white phosphorus with aqueous NaOH gives phosphine alongwith another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product respectively are (2012)
 (a) redox reaction, -3 and -5
 (b) redox reaction, 3 and +5
 (c) disproportionation reaction, -3 and +5
 (d) disproportionation reaction, -3 and +3
- 17.** Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? (2012)
 (a) $\text{HNO}_3, \text{NO}, \text{NH}_4\text{Cl}, \text{N}_2$ (b) $\text{HNO}_3, \text{NO}, \text{N}_2, \text{NH}_4\text{Cl}$
 (c) $\text{HNO}_3, \text{NH}_4\text{Cl}, \text{NO}, \text{N}_2$ (d) $\text{NO}, \text{HNO}_3, \text{NH}_4\text{Cl}, \text{N}_2$
- 18.** Extra pure N_2 can be obtained by heating (2011)
 (a) NH_3 with CuO (b) NH_4NO_3
 (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (d) $\text{Ba}(\text{N}_3)_2$
- 19.** The reaction of P_4 with X leads selectively to P_4O_6 . The X , is (2009)
 (a) dry O_2
 (b) a mixture of O_2 and N_2
 (c) moist O_2
 (d) O_2 in the presence of aqueous NaOH
- 20.** The percentage of p -character in the orbitals forming P—P bonds in P_4 is (2007, 3M)
 (a) 25 (b) 33 (c) 50 (d) 75
- 21.** Which of the following is not oxidised by O_3 ? (2005, 1M)
 (a) KI (b) FeSO_4
 (c) KMnO_4 (d) K_2MnO_4
- 22.** Which gas is evolved when PbO_2 is treated with concentrated HNO_3 ? (2005)
 (a) NO_2 (b) O_2
 (c) N_2 (d) N_2O
- 23.** A pale blue liquid obtained by equimolar mixture of two gases at -30°C is (2005, 1M)
 (a) N_2O (b) N_2O_3
 (c) N_2O_4 (d) N_2O_5
- 24.** Which of the following isomers of phosphorus is thermodynamically most stable? (2005, 1M)
 (a) Red (b) White
 (c) Black (d) Yellow
- 25.** Which of the following has —O—O— linkage? (2004, 3M)
 (a) $\text{H}_2\text{S}_2\text{O}_6$ (b) $\text{H}_2\text{S}_2\text{O}_8$
 (c) $\text{H}_2\text{S}_2\text{O}_3$ (d) $\text{H}_2\text{S}_4\text{O}_6$
- 26.** For H_3PO_3 and H_3PO_4 , the correct choice is (2003, 1M)
 (a) H_3PO_3 is dibasic and reducing
 (b) H_3PO_3 is dibasic and non-reducing
 (c) H_3PO_4 is tribasic and reducing
 (d) H_3PO_3 is tribasic and non-reducing
- 27.** Polyphosphates are used as water softening agents because they (2002, 3M)
 (a) form soluble complexes with anionic species
 (b) precipitate anionic species
 (c) form soluble complexes with cationic species
 (d) precipitate cationic species
- 28.** The number of S—S bonds in sulphur trioxide trimer, (S_3O_9) is (2001, 1M)
 (a) three (b) two
 (c) one (d) zero
- 29.** Ammonia can be dried by (2000, 1M)
 (a) conc. H_2SO_4 (b) P_4O_{10}
 (c) CaO (d) anhydrous CaCl_2
- 30.** Amongst $\text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{Se}$ and H_2Te , the one with the highest boiling point is (2000, 1M)
 (a) H_2O because of hydrogen bonding
 (b) H_2Te because of higher molecular weight
 (c) H_2S because of hydrogen bonding
 (d) H_2Se because of lower molecular weight
- 31.** The correct order of acidic strength is (2000, 1M)
 (a) $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$ (b) $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$
 (c) $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$ (d) $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
- 32.** The number of P—O—P bonds in cyclic metaphosphoric acid is (2000, 1M)
 (a) zero (b) two (c) three (d) four
- 33.** One mole of calcium phosphide on reaction with excess water gives (1999, 2M)
 (a) one mole of phosphine
 (b) two moles of phosphoric acid
 (c) two moles of phosphine
 (d) one mole of phosphorus pentaoxide
- 34.** Sodium thiosulphate is prepared by (1996, 1M)
 (a) reducing Na_2SO_4 solution with H_2S
 (b) boiling Na_2SO_3 solution with S in alkaline medium
 (c) neutralising $\text{H}_2\text{S}_2\text{O}_3$ solution with NaOH
 (d) boiling Na_2SO_3 solution with S in acidic medium
- 35.** There is no S—S bond in (1991, 1M)
 (a) $\text{S}_2\text{O}_4^{2-}$ (b) $\text{S}_2\text{O}_5^{2-}$ (c) $\text{S}_2\text{O}_3^{2-}$ (d) $\text{S}_2\text{O}_7^{2-}$
- 36.** Which one of the following is the strongest base? (1989, 2M)
 (a) AsH_3 (b) NH_3 (c) PH_3 (d) SbH_3
- 37.** Amongst the trihalides of nitrogen, which one is least basic? (1987, 1M)
 (a) NF_3 (b) NCl_3
 (c) NBr_3 (d) NI_3
- 38.** Which of the following oxides of nitrogen is a coloured gas? (1987, 1M)
 (a) N_2O (b) NO
 (c) N_2O_4 (d) NO_2
- 39.** The bonds present in N_2O_5 are (1986, 1M)
 (a) only ionic (b) covalent and coordinate
 (c) only covalent (d) covalent and ionic
- 40.** A gas that cannot be collected over water is (1985, 1M)
 (a) N_2 (b) O_2 (c) SO_2 (d) PH_3

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Objective Questions II

(One or more than one correct option)

Integer Answer Type Question

- 51.** The total number of compounds having at least one bridging oxo group among the molecules given below is

N_2O_3 , N_2O_5 , P_4O_6 , P_4O_7 , $\text{H}_4\text{P}_2\text{O}_5$, $\text{H}_5\text{P}_3\text{O}_{10}$, $\text{H}_2\text{S}_2\text{O}_3$,
 $\text{H}_2\text{S}_2\text{O}_5$

(2018 Adv.)

Assertion and Reason

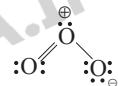
Read the following questions and answer as per the direction given below:

- (a) Statement I is correct, Statement II is correct, Statement II is the correct explanation of Statement I
 - (b) Statement I is correct, Statement II is correct, Statement II is not the correct explanation of Statement I
 - (c) Statement I is correct, Statement II is incorrect
 - (d) Statement I is incorrect, Statement II is correct

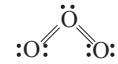
- 52. Statement I** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Statement II The reaction between nitrogen and oxygen requires high temperature. (1998, 2M)

- 53. Statement I** The electronic structure of O_3 is



Statement II The following structure is not allowed because octet around O cannot be expanded.



- 54.** Statement I HNO_3 is a stronger acid than HNO_2 .

Statement II In HNO_3 , there are two nitrogen to oxygen bonds whereas in HNO_2 , there is only one. (1998, 2M)

- 55. Statement I** Although PF_5 , PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.

Statement II Phosphorus has lower electronegativity than nitrogen. (1994. 2M)

Passage Based Questions

Passage 1

Upon heating KClO_3 in presence of catalytic amount of MnO_2 , a gas W is formed. Excess amount of W reacts with white phosphorus to give X . The reaction of X with pure HNO_3 gives Y and Z . (2017 Adv.)

- 56.** Y and Z are, respectively
 (a) N_2O_4 and HPO_3
 (b) N_2O_4 and H_3PO_3
 (c) N_2O_3 and H_3PO_4
 (d) N_2O_5 and HPO_3

57. W and X are, respectively
 (a) O_2 and P_4O_{10}
 (b) O_2 and P_4O_6
 (c) O_3 and P_4O_6
 (d) O_3 and P_4O_{10}

Passage 2

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of NH_3 and PH_3 . Phosphine is a flammable gas and is prepared from white phosphorus.

(2008, 3 × 4M = 12M)

- 58.** Among the following, the correct statement is

 - (a) Phosphates have no biological significance in humans
 - (b) Between nitrates and phosphates, phosphates are less abundant in earth's crust
 - (c) Between nitrates and phosphates, nitrates are less abundant in earth's crust
 - (d) Oxidation of nitrates is possible in soil

59. Among the following, the correct statement is

 - (a) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
 - (b) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 -orbital and is more directional
 - (c) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 -orbital and is more directional
 - (d) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

60. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a

 - (a) dimerisation reaction
 - (b) disproportionation reaction
 - (c) condensation reaction
 - (d) precipitation reaction

Match the Column

- 61.** The unbalanced chemical reactions given in Column I show missing reagent or condition (?) which are provided in Column II. Match Column I with Column II and select the correct answer using the codes given below the Columns.

(2013 Adv.)

	Column I		Column II
P.	$\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{other product}$	1.	NO
Q.	$\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{other product}$	2.	I_2
R.	$\text{N}_2\text{H}_4 \xrightarrow{?} \text{N}_2 + \text{other product}$	3.	Warm
S.	$\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{other product}$	4.	Cl_2

Codes

	P	Q	R	S		P	Q	R	S
(a)	4	2	3	1		3	2	1	4
(c)	1	4	2	3		3	4	2	1

Fill in the Blanks

62. The lead chamber process involves oxidation of SO_2 by atomic oxygen under the influence ofas catalyst. (1992, 1M)

63. In P_4O_{10} , the number of oxygen atoms bonded to each phosphorus atom is (1992, 1M)

64. The basicity of phosphorus acid (H_3PO_3) is (1990, 1M)

65. phosphorus is reactive because of its highly strained tetrahedral structure. (1987, 1M)

True/False

- 66.** Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. (1991, 1M)

67. The H—N—H bond angle in NH_3 is greater than the H—As—H bond angle in AsH_3 . (1984, 1M)

68. In aqueous solution, chlorine is a stronger oxidising agent than fluorine. (1984, 1M)

69. Dilute HCl oxidises metallic Fe to Fe^{2+} . (1983, 1M)

Numerical Answer Type Questions

70. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc. HNO_3 to a compound with the highest oxidation state of sulphur is (Given data : Molar mass of water = 18 g mol^{-1}) (2019 Adv.)

71. The total number of lone pair of electrons in N_2O_3 is (2015 Adv.)

72. Among the following, the number of compounds that can react with PCl_5 to give POCl_3 is O_2 , CO_2 , SO_2 , H_2O , H_2SO_4 , P_4O_{10} . (2011)

73. The total number of diprotic acids among the following is

H_3PO_4	H_2SO_4	H_3PO_3
H_2CO_3	$\text{H}_2\text{S}_2\text{O}_7$	H_3BO_3
H_2PO_4	H_2CrO_4	H_2SO_3

(2010)

Subjective Questions

74. Draw the structure of P_4O_{10} . (2005)

75. Arrange the following oxides in the increasing order of Bronsted basicity.
 Cl_2O_7 , BaO , SO_3 , CO_2 , B_2O_3 (2004)

76. Identify the compounds A , B , C , D

$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{Elemental S}} C \xrightarrow{I_2} D$$

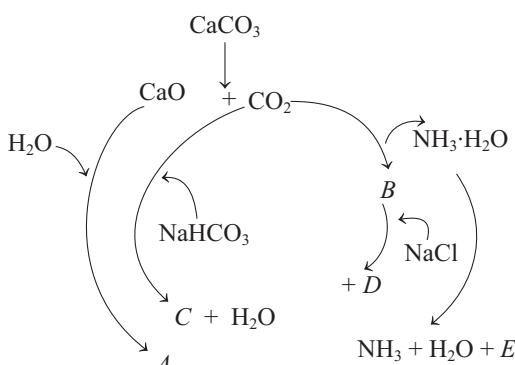
and give oxidation state of sulphur in each compounds. (2003, 4M)

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77. Write the balanced equations for the reactions of the following compounds with water:
 (i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4 (2002, 5M)

78. Give reason(s), why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule? (2000, 2M)

79. The Haber's process can be represented by the following scheme.



Identify A, B, C, D and E . (1999, 5M)

80. (a) In the following equation

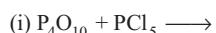


(A = HNO_2 , B = H_2SO_3 , C = NH_2OH).

Identify D. Draw the structures of A, B, C and D.

- (b) In the contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2 ? (1999, 10M)

81. Complete and balance the following chemical equations.



82. (a) Thionyl chloride can be synthesised by chlorinating SO_2 using PCl_5 . Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2,2-dimethoxypropane. Discuss all this using balanced chemical equations.
 (b) Reaction of phosphoric acid with $\text{Ca}_3(\text{PO}_4)_2$ yields a fertiliser "triple superphosphate" represent the same through balanced chemical equation. (1998, 5M)

83. A soluble compound of a poisonous element M, when heated with $\text{Zn}/\text{H}_2\text{SO}_4$, gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N. (1997, 2M)

84. Write balanced equations for the following.

- (i) Phosphorus is treated with concentrated nitric acid.
 (ii) Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.

- (iii) Manufacture of phosphoric acid from phosphorus.

- (iv) Reaction of aluminium with aqueous sodium hydroxide. (1997, $1\text{M} \times 4 = 4\text{M}$)

85. Draw the structure of P_4O_{10} and identify the number of single and double P—O bonds. (1996, 3M)

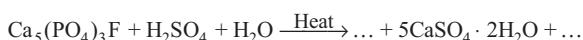
86. Account for the following. Write the answers in four or five sentences only.

- (i) The experimentally determined N—F bond lengths in NF_3 is greater than the sum of the single bond covalent radii of N and F.

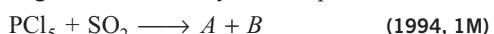
- (ii) Mg_3N_2 when reacted with water gives of NH_3 but HCl is not obtained from MgCl_2 on reaction with water at room temperature.

- (iii) $(\text{SiH}_3)_3\text{N}$ is a weaker base than $(\text{CH}_3)_3\text{N}$. (1995, $2\text{M} \times 3 = 6\text{M}$)

87. Complete and balance the following reactions. (1994, 1M)



88. In the following reaction, identify the compounds A and B



89. Complete and balance the following reaction.

Red phosphorus is reacted with iodine in the presence of water.



90. Give reasons in two or three sentences only. Sulphur dioxide is a more powerful reducing agent in the alkaline medium than in acidic medium. (1992, 2M)

91. Draw the two resonance structures of ozone which satisfy the octet rule. (1991, 1M)

92. Give reasons in one or two sentences.

Ammonium chloride is acidic in liquid ammonia solvent. (1991, 1M)

93. Write the balanced chemical equations for the following.

- (i) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda.

- (ii) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate.

- (iii) Elemental phosphorus reacts with concentrated HNO_3 to give phosphoric acid.

- (iv) Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution.

- (v) Carbon dioxide is passed through a suspension of limestone in water. (1991, $1 \times 5 = 5\text{M}$)

94. Write the balanced chemical equation for the following reactions.

- (i) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution.

- (ii) Sodium iodate is added to a solution of sodium bisulphite. (1990, 2M)

95. Write the two resonance structures of N_2O that satisfy the octet rule. (1990, 2M)

- 96.** Draw balanced equations for
 (i) the preparation of phosphine from CaO and white phosphorus.
 (ii) the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. (1990, 2M)
- 97.** Explain the following (1989, 2M)
 (i) H_3PO_3 is a dibasic acid.
 (ii) Phosphine has lower boiling point than ammonia.
- 98.** Write the balanced chemical equations for the following.
 (i) Hypophosphorous acid is heated.
 (ii) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium.
- 99.** Arrange the following as indicated. CO_2 , N_2O_5 , SiO_2 , SO_3 in the order of increasing acidic character.
- 100.** Give balanced equations for the following.
 (i) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
 (ii) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. (1988, 3M)
- 101.** Give reason for “valency of oxygen is generally two, whereas sulphur shows valency of two, four and six.” (1988, 1M)
- 102.** Explain the following in one or two sentences.
 (i) Magnesium oxide is used for the lining of steel making furnace.
 (ii) The mixture of hydrazine and hydrogen peroxide with a copper (II) catalyst is used as a rocket fuel.
 (iii) Orthophosphorous acid is not tribasic acid.
 (iv) The molecule of magnesium chloride is linear, whereas that of stannous chloride is angular. (1987, 4M)
- 103.** Write balanced equations for the following. (1987, 2M)
 (i) Phosphorus is reacted with boiling aqueous solution of sodium hydroxide in an inert atmosphere.
 (ii) Dilute nitric acid is slowly reacted with metallic tin.
- 104.** Complete and balance the following reactions.
 (i) $S + OH^- \longrightarrow S^{2-} + S_2O_3^{2-} + \dots$
 (ii) $ClO_3^- + I^- + H_2SO_4 \longrightarrow Cl^- + HSO_4^- + \dots + \dots$ (1986, 2M)
- 105.** Write down the balanced equation for the reactions when
 (i) calcium phosphate is heated with a mixture of sand and carbon.
 (ii) ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. (1985, 2M)
- 106.** Draw the resonance structures of nitrous oxide. (1985, 90, 2M)
- 107.** Show with balanced chemical reaction what happens when following are mixed?
 Aqueous solution of ferric sulphate and potassium iodide. (1984, 1M)
- 108.** Write the matched set (of three) for each entry in Column A
- | A | B | C |
|---------------|------------------------|----------------|
| Asbestos | Paramagnetic | Air pollutant |
| Lithium metal | Silicates of Ca and Mg | Electron donor |
| Nitric oxide | Reducing agent | |
- (1984, 2M)
- 109.** Complete and balance the following reactions.
 (i) $HNO_3 + HCl \longrightarrow NO + Cl_2$
 (ii) $Ce^{3+} + S_2O_8^{2-} \longrightarrow SO_4^{2-} + Ce^{4+}$
 (iii) $Cl_2 + OH^- \longrightarrow Cl^- + ClO^-$ (1983, 3M)
- 110.** Explain, “orthophosphoric acid, H_3PO_4 is tribasic but phosphorous acid, H_3PO_3 is dibasic”. (1982, 1M)
- 111.** Give structural formula for the following.
 (i) Phosphorous acid, H_3PO_3
 (ii) Pyrophosphoric acid, $H_4P_2O_7$ (1981, 2M)
- 112.** Sulphur melts to a clear mobile liquid at $119^\circ C$, but on further heating above $160^\circ C$, it becomes viscous, explain. (1981, 1M)
- 113.** Explain the following in not more than two sentences .
 (i) Conc. HNO_3 turns yellow in sunlight.
 (ii) Bleaching powder loses its bleaching properties when it is kept in an open bottle for a long time. (1980, 2M)

Topic 2 Elements and Compounds of Group 17 and 18

Objective Questions I (Only one correct option)

- The electron gain enthalpy (in kJ/mol) of fluorine, chlorine, bromine and iodine, respectively, are (2020 Main, 7 Jan I)
 (a) -333, -325, -349 and -296
 (b) -296, -325, -333 and -349
 (c) -333, -349, -325 and -296
 (d) -349, -333, -325 and -296
- The number of bonds between sulphur and oxygen atoms in $S_2O_8^{2-}$ and the number of bonds between sulphur and sulphur atoms in rhombic sulphur, respectively, are (2020 Main, 8 Jan I)
 (a) 4 and 6 (b) 8 and 8 (c) 4 and 8 (d) 8 and 6
- The noble gas that does not occur in the atmosphere is (2019 Main, 10 April II)
 (a) Ra (b) Kr (c) He (d) Ne

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- 4.** Chlorine on reaction with hot and concentrated sodium hydroxide gives (2019 Main, 12 Jan II)
 (a) Cl^- and ClO^- (b) Cl^- and ClO_3^-
 (c) ClO_3^- and ClO_2^- (d) Cl^- and ClO_2^-
- 5.** Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y , is (2019 Main, 12 Jan I)
 (a) 1 (b) 3 (c) 7 (d) 5
- 6.** Among the following reactions of hydrogen with halogens, the one that requires a catalyst is (2019 Main, 10 Jan II)
 (a) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ (b) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$
 (c) $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$ (d) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$
- 7.** The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF_4 , respectively, are (2019 Main, 10 Jan I)
 (a) sp^3d^2 and 1 (b) sp^3d and 2
 (c) sp^3d and 1 (d) sp^3d^2 and 2
- 8.** Which of the following reactions is an example of a redox reaction? (2017 Main)
 (a) $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$
 (b) $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ \text{PF}_6^-$
 (c) $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$
 (d) $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$
- 9.** The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are (2017 Main)
 (a) ClO^- and ClO_3^- (b) ClO_2^- and ClO_3^-
 (c) Cl^- and ClO^- (d) Cl^- and ClO_2^-
- 10.** Which among the following is the most reactive? (2015 Main)
 (a) Cl_2 (b) Br_2 (c) I_2 (d) ICl
- 11.** Which one has highest boiling point? (2015 Main)
 (a) He (b) Ne (c) Kr (d) Xe
- 12.** Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is (2014 Adv.)
- $$\begin{array}{ccc}
 \text{XeF}_6 & \xrightarrow{\text{Complete hydrolysis}} & P + \text{Other product} \\
 & \downarrow & \\
 & \text{HO}^-/\text{H}_2\text{O} & \\
 & \downarrow & \\
 & Q & \\
 & \downarrow & \\
 & \text{Slow disproportionation} & \\
 & \text{in HO}^-/\text{H}_2\text{O} & \\
 & \downarrow & \\
 & \text{Products} &
 \end{array}$$
- (a) 0 (b) 1 (c) 2 (d) 3
- 13.** Among the following oxoacids, the correct decreasing order of acidic strength is (2014 Main)
 (a) $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
 (b) $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$
 (c) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$
 (d) $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$
- 14.** The shape of XeO_2F_2 molecule is (2012)
 (a) trigonal bipyramidal (b) square planar
 (c) tetrahedral (d) see-saw
- 15.** Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives (2008, 3M)
 (a) $\text{Na}_2\text{S}_4\text{O}_6$ (b) NaHSO_4
 (c) NaCl (d) NaOH
- 16.** When Γ^- is oxidised by KMnO_4 in alkaline medium, Γ^- converts into (2004, 1M)
 (a) IO_3^- (b) I_2
 (c) IO_4^- (d) IO^-
- 17.** The set with correct order of acidic strength is (2001, 1M)
 (a) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 (b) $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$
 (c) $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$
 (d) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
- 18.** Which one of the following species is not a pseudo halide? (1997, 1M)
 (a) CNO^- (b) RCOO^- (c) OCN^- (d) NNN^-
- 19.** The following acids have been arranged in the order of decreasing acidic strength. Identify the correct order. ClOH (I), BrOH (II), IOH (III) (1996, 1M)
 (a) I > II > III (b) II > I > III
 (c) III > II > I (d) I > III > II
- 20.** KF combines with HF to form KHF_2 . The compound contains the species (1996, 1M)
 (a) K^+ , F^- and H^+ (b) K^+ , F^- and HF
 (c) K^+ and $[\text{HF}_2]^-$ (d) $[\text{KHF}]^+$ and F^-
- 21.** Bromine can be liberated from potassium bromide solution by the action of (1987, 1M)
 (a) iodine solution (b) chlorine water
 (c) sodium chloride (d) potassium iodide
- 22.** Chlorine acts as a bleaching agent only in the presence of (1983, 1M)
 (a) dry air (b) moisture
 (c) sunlight (d) pure oxygen
- 23.** HBr and HI reduce sulphuric acid, HCl can reduce KMnO_4 and HF can reduce (1981, 1M)
 (a) H_2SO_4 (b) KMnO_4
 (c) $\text{K}_2\text{Cr}_2\text{O}_7$ (d) None of these

Objective Questions II

(One or more than one correct option)

- 24.** With respect to hypochlorite, chlorate and perchlorate ions, choose the correct statement(s). (2020 Adv.)
 (a) The hypochlorite ion is the strongest conjugate base.
 (b) The molecular shape of only chlorate ion is influenced by the lone pair of electrons of Cl.
 (c) The hypochlorite and chlorate ions disproportionate to give rise to identical set of ions.
 (d) The hypochlorite ion oxidises the sulphite ion.

25. The correct statement(s) about the oxoacids, HClO_4 and HClO , is (are) (2017 Adv.)
 (a) The central atom in both HClO_4 and HClO is sp^3 -hybridised
 (b) HClO_4 is formed in the reaction between Cl_2 and H_2O
 (c) The conjugate base of HClO_4 is weaker base than H_2O
 (d) HClO_4 is more acidic than HClO because of the resonance stabilisation of its anion
26. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to (2017 Adv.)
 (a) decrease in $\pi^* - \sigma^*$ gap down the group
 (b) decrease in ionisation energy down the group
 (c) the physical state of X_2 at room temperature changes from gas to solid down the group
 (d) decreases in HOMO-LUMO gap down the group
27. The compound(s) with two lone pairs of electrons on the central atom is (are) (2016 Adv.)
 (a) BrF_5 (b) ClF_3 (c) XeF_4 (d) SF_4
28. The correct statement(s) regarding,
 (i) HClO , (ii) HClO_2 , (iii) HClO_3 and (iv) HClO_4 is (are)
 (a) the number of $\text{Cl} = \text{O}$ bonds in (ii) and (iii) together is two
 (b) the number of lone pair of electrons on Cl in (ii) and (iii) together is three
 (c) the hybridisation of Cl in (iv) is sp^3
 (d) amongst (i) to (iv), the strongest acid is (i)

Passage Based Questions

Passage 1

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, P and Q , respectively. The Cl_2 gas reacts with SO_2 gas in the presence of charcoal, to give a product R . R reacts with white phosphorus to give a compound S . On hydrolysis, S gives an oxoacid of phosphorus T . (2013 Adv.)

29. P and Q respectively, are the sodium salts of
 (a) hypochlorous and chloric acids
 (b) hypochlorous and chlorous acids
 (c) chloric and perchloric acids
 (d) chloric and hypochlorous acids
30. R , S and T , respectively, are
 (a) SO_2Cl_2 , PCl_5 and H_3PO_4 (b) SO_2Cl_2 , PCl_3 and H_3PO_3
 (c) SOCl_2 , PCl_3 and H_3PO_2 (d) SOCl_2 , PCl_5 and H_3PO_4

Passage 2

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. (2012)

31. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution is
 (a) 0.48 M (b) 0.96 M (c) 0.24 M (d) 0.024 M

32. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is
 (a) Cl_2O (b) Cl_2O_7 (c) ClO_2 (d) Cl_2O_6

Passage 3

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to give XeO_3 . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. (2007, 3 × 4M = 12M)

33. Argon is used in arc welding because of its
 (a) low reactivity with metal
 (b) ability to lower the melting point of metal
 (c) flammability
 (d) high calorific value
34. The structure of XeO_3 is
 (a) linear (b) planar
 (c) pyramidal (d) T-shaped
35. XeF_4 and XeF_6 are expected to be
 (a) oxidising (b) reducing
 (c) unreactive (d) strongly basic

Match the Column

36. All the compounds listed in Column I react with water. Match the result of the respective reactions with the appropriate options listed in Column II. (2010)

Column I	Column II
A. $(\text{CH}_3)_2\text{SiCl}_2$	p. Hydrogen halide formation
B. XeF_4	q. Redox reaction
C. Cl_2	r. Reacts with glass
D. VCl_5	s. Polymerisation
	t. O_2 formation

Fill in the Blank

37. The increase in solubility of iodine in aqueous solution of KI is due to the formation of (1982, 94, 1M)

True/False

38. HBr is a stronger acid than HI because of hydrogen bonding. (1993, 1M)

Numerical Answer Type Questions

39. At 143 K, the reaction of XeF_4 with O_2F_2 produces a xenon compound Y . The total number of lone pair(s) of electrons present on the whole molecule of Y is (2019 Adv.)

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- 40.** Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is (2011)

Subjective Questions

- 41.** Write the balanced equation for the reaction of the following compound with water.



- 42.** Draw molecular structures of XeF_2 , XeF_4 and XeO_2F_2 , indicating the locations of lone pair(s) of electrons. (2000, 3M)

- 43.** Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. (2000, 2M)

- 44.** Work out the following using chemical equations
“Chlorination of calcium hydroxide produces bleaching powder.” (1998, 2M)

- 45.** Complete the following chemical equations:
(i) $\text{KI} + \text{Cl}_2 \longrightarrow$ (ii) $\text{KClO}_3 + \text{I}_2 \longrightarrow$ (1996, 2M)

- 46.** Give reasons in two or three sentences only for
(i) Bond dissociation energy of F_2 is less than that of Cl_2 .
(ii) Sulphur dioxide is a more powerful reducing agent in the alkaline medium than in acidic medium. (1992, 2M)

- 47.** Write the balanced chemical equation for the following:
Sodium bromate reacts with fluorine in the presence of alkali.

- 48.** Arrange the following as indicated. HOCl , HOClO_2 , HOClO_3 , HOClO in increasing order of thermal stability (1988, 2M)

- 49.** Give balanced equation for the following:
Iodate ion reacts with bisulphite ion to liberate iodine. (1988, 3M)

- 50.** Mention the products formed in the following
“Chlorine gas is bubbled through a solution of ferrous bromide.” (1986, 2M)

- 51.** Complete and balance the following reaction:
 $\text{ClO}_3 + \text{I}^- + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}^- + \text{HSO}_4^- + \dots + \dots$ (1986, 2M)

- 52.** Arrange the following in the order of
(i) increasing bond strength HCl , HBr , HF , HI
(ii) increasing oxidation number of iodine
 I_2 , HI , HIO_4 , ICl (1986, 2M)

- 53.** Give reason in one or two sentences.
Fluorine cannot be prepared from fluorides by chemical reduction method. (1985, 1M)

- 54.** Complete and balance the following reaction.
 $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}^-$ (1983, 3M)

- 55.** Explain the following in not more than two sentences.
Bleaching powder loses its bleaching properties when it is kept in an open bottle for a long time. (1980, 2M)

- 56.** Give reasons for the following in one or two sentences.
(i) Hydrogen bromide cannot be prepared by the action of conc. sulphuric acid on sodium bromide.
(ii) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised. (1979, 2M)

- 57.** Write the balanced equations involved in the preparation of
(i) bleaching powder from slaked lime (1979, 10M)
(ii) nitric oxide from nitric acid
(iii) chlorine from sodium chloride
(iv) anhydrous aluminium chloride from alumina

Answers

Topic 1

- | | | | |
|---------------|-----------------------|---------------|-------------|
| 1. (a) | 2. (b) | 3. (c) | 4. (b) |
| 5. (d) | 6. (a) | 7. (a) | 8. (d) |
| 9. (b) | 10. (d) | 11. (d) | 12. (a) |
| 13. (a) | 14. (b) | 15. (c) | 16. (c) |
| 17. (b) | 18. (d) | 19. (b) | 20. (d) |
| 21. (c) | 22. (b) | 23. (b) | 24. (c) |
| 25. (b) | 26. (a) | 27. (c) | 28. (d) |
| 29. (c) | 30. (a) | 31. (a) | 32. (c) |
| 33. (c) | 34. (b) | 35. (d) | 36. (b) |
| 37. (a) | 38. (d) | 39. (b) | 40. (c) |
| 41. (d) | 42. (a) | 43. (b,c) | 44. (a,b,c) |
| 45. (b, d) | 46. (a, c, d) | 47. (a, b, c) | 48. (c) |
| 49. (a, c, d) | 50. (a, d) | 51. (6) | 52. (a) |
| 53. (a) | 54. (a) | 55. (b) | 56. (a) |
| 57. (b) | 58. (c) | 59. (c) | 60. (b) |
| 61. (d) | 62. (NO_2) | 63. (Four) | 64. (Two) |

- | | | | |
|-------------|-----------|---------|---------|
| 65. (white) | 66. (T) | 67. (T) | 68. (F) |
| 69. (T) | 70. (288) | 71. (8) | 72. (4) |
| 73. (6) | | | |

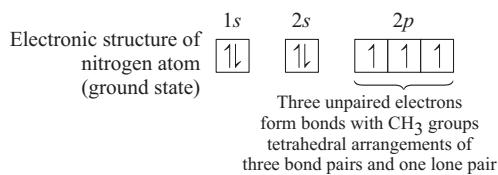
Topic 2

- | | | | |
|-----------------------|----------------|-------------|-------------|
| 1. (c) | 2. (b) | 3. (a) | 4. (b) |
| 5. (d) | 6. (b) | 7. (a) | 8. (a) |
| 9. (c) | 10. (d) | 11. (d) | 12. (c) |
| 13. (c) | 14. (a) | 15. (a) | 16. (a) |
| 17. (a) | 18. (b) | 19. (a) | 20. (c) |
| 21. (b) | 22. (b) | 23. (d) | 24. (a,b,d) |
| 25. (a, c, d) | 26. (b, c) | 27. (b, c) | 28. (b, c) |
| 29. (a) | 30. (a) | 31. (c) | 32. (a) |
| 33. (a) | 34. (c) | 35. (a) | |
| 36. (A → p, s) | B → p, q, r, t | C → p, q, t | D → p) |
| 37. (KI_3) | 38. (F) | 39. (19) | 40. (5) |

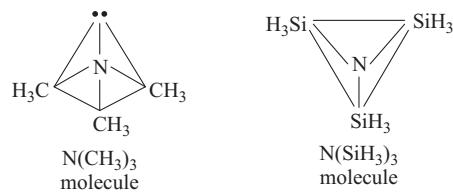
Hints & Solutions

Topic 1 Elements and Compounds of Group 15 and 16

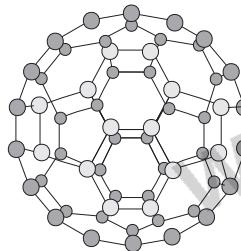
1. The correct statement is that $(\text{SiH}_3)_3\text{N}$ is planar and less basic than $(\text{CH}_3)_3\text{N}$. The compounds trimethylamine $(\text{CH}_3)_3\text{N}$ and trisilylamine $(\text{SiH}_3)_3\text{N}$ have similar formulae, but have totally different structures. In trimethylamine the arrangement of electrons is as follows :



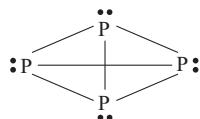
In trisilylamine, three sp^2 orbitals are used for σ -bonding, giving a plane triangular structure.



2. In C_{60} (Buckminster fullerene) twenty hexagons and twelve pentagons are present which are interlocked resulting a shape of soccer ball. Every ring in this structure is aromatic.

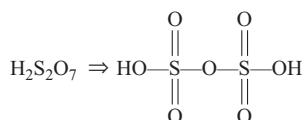


Phosphorus has large atomic size and less electronegativity, so it forms single bond instead of $p\pi-p\pi$ multiple bond. So, it consists of discrete tetrahedral P_4 molecule as shown below :



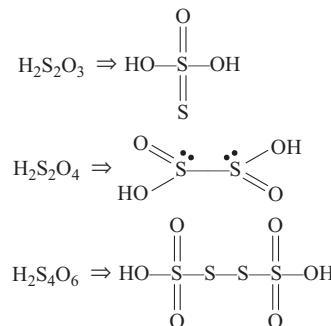
∴ Number of trigons (triangles) = 4

3. S—S bond is not present in $\text{H}_2\text{S}_2\text{O}_7$ (pyrosulphuric acid or oleum).

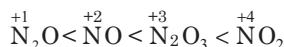


While the other given oxoacids of sulphur, i.e.

$\text{H}_2\text{S}_2\text{O}_3$ (thiosulphuric acid), $\text{H}_2\text{S}_2\text{O}_4$ (hyposulphurous or dithionous acid) and $\text{H}_2\text{S}_4\text{O}_6$ (tetrathionic acid) contains S—S bonds.



4. The correct increasing order of oxidation state of nitrogen for nitrogen oxides is



- Oxidation state of N in N_2O is

$$2(x) - 2 = 0 \\ x = +\frac{2}{2} = +1$$

- Oxidation state of N in NO is

$$x - 2 = 0 \\ x = +2$$

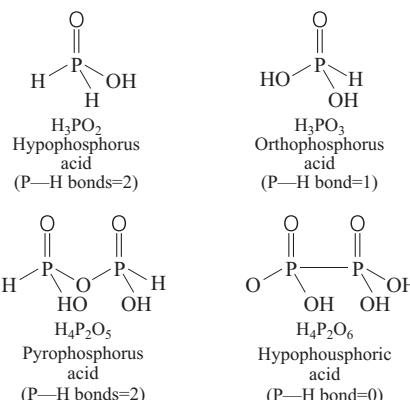
- Oxidation state of N in N_2O_3 is

$$2x + 3(-2) = 0 \\ x = \frac{6}{2} = 3$$

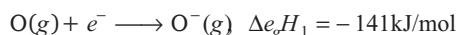
- Oxidation state of N in NO_2 is

$$x + 2(-2) = 0 \\ x - 4 = 0 \\ x = +4$$

5. Let us consider the structure of the phosphorus oxyacids,

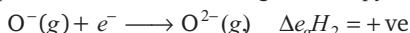


6. As given, the first electron gain enthalpy of oxygen can be shown as,



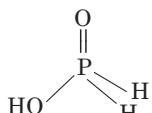
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The expression of second electron gain enthalpy of oxygen will be,



$\Delta e_g H_2$ of oxygen is positive, i.e. endothermic, because a strong electrostatic repulsion will be observed between highly negative O^- and the incoming electron (e^-). A very high amount of energy will be consumed (endothermic) by the system to overcome the electrostatic repulsion.

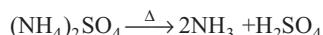
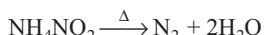
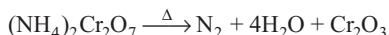
7. The structure of H_3PO_2 (hypophosphorous) acid is



Due to the presence of two P—H bonds, H_3PO_2 acts as a strong reducing agent. e.g.



8. The thermal decomposition of given compounds is shown below



Thus, only $(NH_4)_2SO_4$ does not give N_2 on heating (It gives NH_3). While rest of the given compounds gives N_2 on their thermal decomposition.

9. $H_3PO_4^{+5} > H_4P_2O_6^{+4} > H_3PO_3^{+3} > H_3PO_2^{+1}$

10.

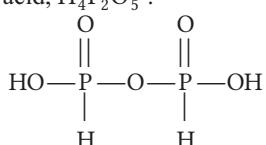
Species	Hybridisation
	sp^2
	sp^2
	sp

11. Orthophosphorous acid, H_3PO_3 : $HO-P(OH)_2$



$$H_3PO_3^x = 3 + x + 3(-2) = 0 \text{ or } x = +3$$

Pyrophosphorous acid, $H_4P_2O_5$:



$$H_4P_2O_5^x = 4 + 2x + 5(-2) = 0$$

$$4 + 2x - 10 = 0, x = +3$$

12. **PLAN** This problem is based on chemical properties of phosphorus.

White phosphorus on reaction with thionyl chloride ($SOCl_2$) produces phosphorus trichloride.



But if amount of thionyl chloride ($SOCl_2$) is in excess then it produces phosphorus pentachloride.

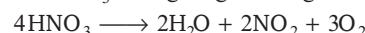


13. NO is paramagnetic in gaseous state because in gaseous state, it has one unpaired electron.

$$\text{Total number of electrons present} = 7 + 8 = 15e^-$$

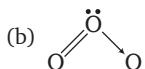
Hence, there must be the presence of unpaired electron in gaseous state while in liquid state, it dimerises due to unpaired electron.

14. NO_2 is a brown coloured gas and imparts this colour to concentrated HNO_3 during long standing.



15. (a) $ONCl = 8 + 7 + 17 = 32e^-$

$$ONO^- = 8 + 7 + 8 + 1 = 24e^- \text{ (correct)}$$

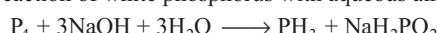


Central O-atom is sp^2 -hybridised with 1 lone pair, so bent shape (correct).

- (c) In solid state, ozone is violet-black. Ozone does not exist in solid state, thus incorrect.

- (d) O_3 has no unpaired electrons, so diamagnetic (correct). Hence, (c) is the correct.

16. The reaction of white phosphorus with aqueous alkali is



In the above reaction, phosphorus is simultaneously oxidised [$P_4(0) \longrightarrow NaH_2\overset{+1}{P}O_2$] as well as reduced

[$P_4(0) \longrightarrow \overset{-3}{PH}_3$] Therefore, this is an example of disproportionation reaction. Oxidation number of phosphorus in PH_3 is -3 and in NaH_2PO_2 is $+1$. However, $+1$ oxidation number is not given in any option, one might think that NaH_2PO_2 has gone to further decomposition on heating.



17. Let oxidation number of N be x .

$$\text{In } HNO_3, +1 + x + 3(-2) = 0 \Rightarrow x = +5$$

$$\text{In } NO, \quad x - 2 = 0 \Rightarrow x = +2$$

$$\text{In } N_2, \quad x = 0$$

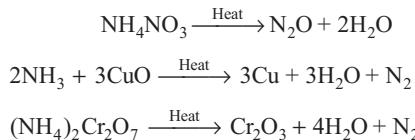
$$\text{In } NH_4Cl, \quad x + 4 - 1 = 0 \Rightarrow x = -3$$

18. $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

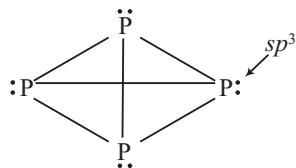
Azide salt of barium can be obtained in purest form as well as the decomposition product contains solid Ba as by product

alongwith gaseous nitrogen, hence no additional step of separation is required.

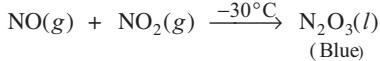
Other reactions are



19. In limited supply of oxygen, phosphorus is oxidised to its lower oxide P_4O_6 while excess of oxygen gives P_4O_{10} . A mixture of O_2 and N_2 is used for controlled oxidation of phosphorus into P_4O_6 .
20. In P_4 , all phosphorus are sp^3 -hybridised and has 75% p -character.

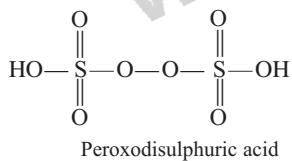


21. In KMnO_4 , Mn is already in its highest oxidation state (+7), cannot be oxidised by any oxidising agent.
22. $\text{PbO}_2 + \text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{O}_2$
23. Equimolar amounts of NO and NO_2 at -30°C gives $\text{N}_2\text{O}_3(l)$ which is a blue liquid.

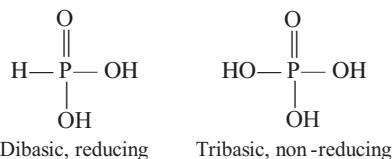


24. Black phosphorus is thermodynamically most stable allotrope of phosphorus.
It is due to three dimensional, network structure of polymeric black phosphorus.

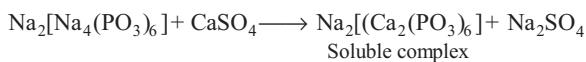
25. $\text{H}_2\text{S}_2\text{O}_8$ is a peroxy acid, has $\text{O}-\text{O}$ linkage



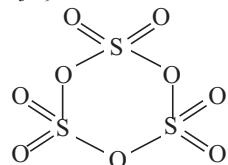
26. H_3PO_3 is a dibasic, reducing acid. H_3PO_4 is tribasic, non-reducing acid.



27. Polyphosphates are used as water softening agents because they form soluble complexes with cationic species of hard water.



28. The structure of S_3O_9 is

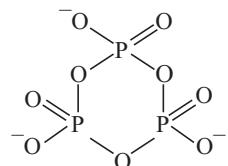


It has no S—S linkage.

29. CaO , a basic oxide, is most suitable for drying of basic ammonia.
30. H_2O , due to its ability to form intermolecular H-bonds.
31. Corresponding acids are HClO_4 , H_2SO_3 and H_3PO_4 . Hence, the order of acidic strength is

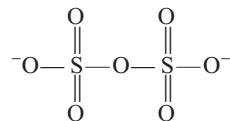


32. The structure of cyclic metaphosphate is



There is three P—O—P bonds.

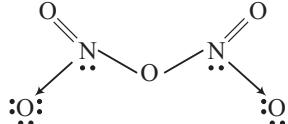
33. $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
34. $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow[\Delta]{\text{OH}^-} \text{Na}_2\text{S}_2\text{O}_3$
35. $\text{S}_2\text{O}_7^{2-}$ has no S—S linkage.



All others have atleast one S—S linkage.

36. Amongst $X\text{H}_3$ where 'X' is group-15 elements, basic strength decreases from top to bottom. Hence, NH_3 is strongest base.
37. The electron withdrawing inductive effect of halogen decreases electron density on nitrogen, lowers basic strength. Since, fluorine is most electronegative, NF_3 is least basic.
38. $\text{NO}_2(g)$ is deep brown coloured.

39. In N_2O_5 , there are σ (sigma) covalent bonds, π (pi) bonds and coordinate covalent bonds as



40. SO_2 cannot be collected over water because it reacts with water forming H_2SO_3 .
- $$\text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_3$$
41. Quicklime (CaO) is used for drying NH_3 gas because both are basic, do not react. On the other hand, H_2SO_4 and P_2O_5 are acidic, reacts with ammonia forming salts. CaCl_2 forms complex with ammonia.

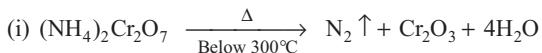
240 p-Block Elements-II

42. NO is lighter than O₂.

D₂O is commonly known as heavy water.

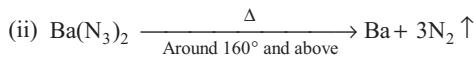
N₂ is lighter than O₂, effuse at faster rate under identical experimental conditions. NH₃ liquefies at very low temperature. Therefore, liquid NH₃ is used as a refrigerant.

43. Among the given compounds, those which generate N₂ on thermal decomposition below 300°C are **ammonium dichromate** i.e., (NH₄)₂Cr₂O₇ and **barium azide** or nitride i.e., Ba(N₃)₂. Reactions of their thermal decomposition are given below

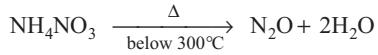


It is an exothermic reaction with

$$\Delta H = -429.1 \pm 3 \text{ kcal/mol.}$$

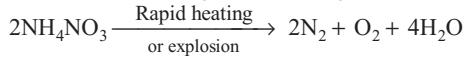


Ammonium nitrate (NH₄NO₃) on heating below 300°C gives N₂O as

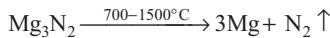


However, on rapid heating or explosion

(i.e. above 300°C) it gives off nitrogen as



Magnesium nitride (Mg₃N₂) does not decompose at lower temperatures being comparatively more stable. Its thermal decomposition requires a minimum temperature of 700°C and proceeds as



44. Statement wise explanation is

(i) **Statement (a)** Bi₂O₅ is a metallic oxide while N₂O₅ is a non-metallic oxide.

Metallic oxides being **ionic** are **basic in nature** while non metallic oxides being **covalent** are **acidic in nature**. This confirms more basic nature of Bi₂O₅ in comparison to N₂O₅. Hence, this is a correct statement.

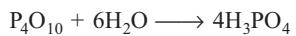
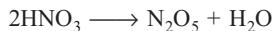
(ii) **Statement (b)** The electronegativity difference between N(3) and F(4) is less as compared to the electronegativity difference between Bi (1.7) and F(4). More electronegativity difference leads to ionic compounds. Thus, NF₃ must be more covalent in nature as compared to BiF₃. Hence, this statement is also correct.

(iii) **Statement (c)** In NH₃ intermolecular hydrogen bonding is present, which is altogether absent in PH₃. Thus, PH₃ boils at lower temperature than NH₃.

Hence, this is also a correct statement.

(iv) **Statement (d)** Due to smaller size of N the lone pair-lone pair repulsion is more in N—N single bond as compared to O—P single bond. This results to weaker N—N single bond as compared to P—P single bond. Hence, this statement is incorrect.

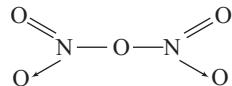
45. P₄O₁₀ is a dehydrating agent and converts HNO₃ into N₂O₅



Thus, (a) is incorrect.

(b) N₂O₅ has no unpaired electron and is thus, diamagnetic thus, (b) is correct.

(c)



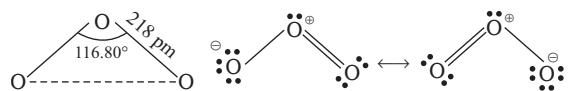
There is no N—N bond, thus, (c) is incorrect.



N₂O₅ vapours are of brownish colour. Thus, (d) is correct.

46. **Plan** Due to resonance, bond lengths between two atoms are equal. Species is said to be diamagnetic if all electrons are paired.

Process is endothermic if it takes place with absorption of heat.



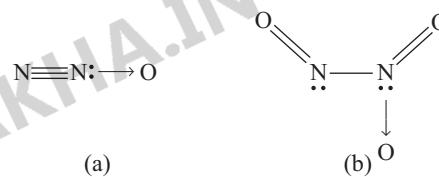
bent molecule all electrons paired thus, diamagnetic



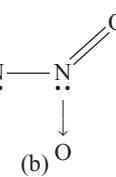
Exothermic

Thus, (b) is incorrect. (a, c, d) are correct.

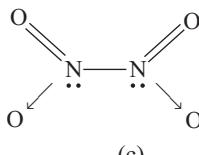
47. The structures of these oxides are



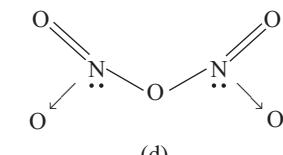
(a)



(b)

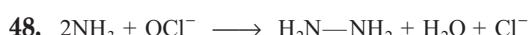


(c)

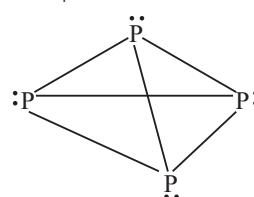


(d)

(a), (b), (c) have N—N bonds.



49. The structure of P₄ is



It has six P—P single bonds.

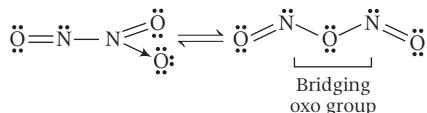
There are four lone pairs on four phosphorus. P—P—P bond angles are of 60°.



However, NH₄NO₂ on heating gives N₂.

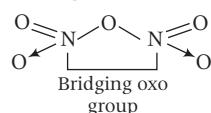
51. The structures of various molecules given in problem are discussed below—

1. N_2O_3 It is the tautomeric mixture of following two structures—



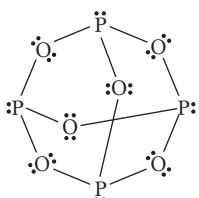
Conclusion 1 bridging oxo group is present in the compound.

2. N_2O_5 It has following structure.



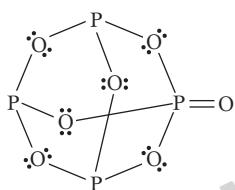
Conclusion 1 bridging oxo group is present in the compound.

3. P_4O_6



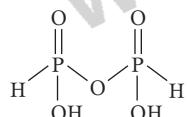
Conclusion 6 bridging oxo groups are present in the compound.

4. P_4O_7



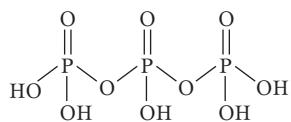
Conclusion 6 bridging oxo groups are present in the compound.

5. $\text{H}_4\text{P}_2\text{O}_5$



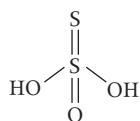
Conclusion 1 bridging oxo group is present in the compound.

6. $\text{H}_5\text{P}_3\text{O}_{10}$



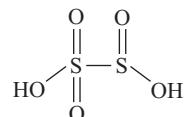
Conclusion 2 bridging oxo groups are present in the compound.

7. $\text{H}_2\text{S}_2\text{O}_3$



Conclusion This compound does not contain any bridging oxo group.

8. $\text{H}_2\text{S}_2\text{O}_5$

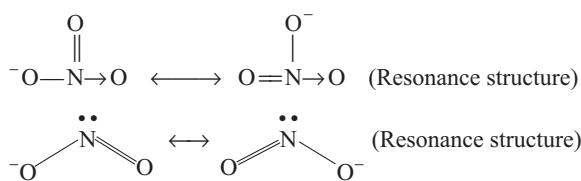


Conclusion This compound also does not contain any bridging oxo group.

52. Both Statement I and Statement II are true and Statement II is correct explanation of Statement I.

53. Both Statement I and Statement II are true and Statement II is correct explanation of Statement I.

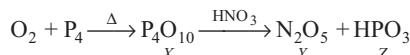
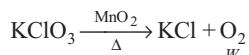
54. Both Statement I and Statement II are true and Statement II explains the Statement I appropriately. Nitrate ion (NO_3^-) is more stable than nitrite ion :



55. Both Statement I and Statement II are independently correct but reason is not the correct explanation of Statement I. Nitrogen does not have any vacant d-orbitals, it cannot expand its valence shell beyond eight electrons, i.e. it cannot violate octet. Therefore, nitrogen forms only trihalides (NX_3 with eight electrons in valence shell of N).

Phosphorus has vacant 3d-orbitals, it can expand its valence shell beyond eight electrons, its both trihalides and pentahalides exist.

Passage 1



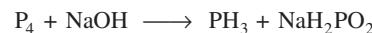
56. (a) 57. (b)

Passage 2

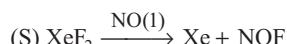
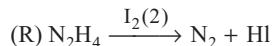
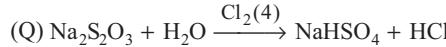
58. Due to greater solubility in water and prone to microbial attack, nitrates are less abundant in earth's crust.

59. NH_3 is stronger Lewis base than PH_3 . In a group of hydrides, basic strength decreases down the group.

60. White phosphorus undergo disproportionation in alkaline medium.

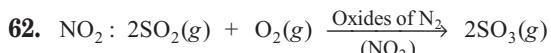


Warm (3)

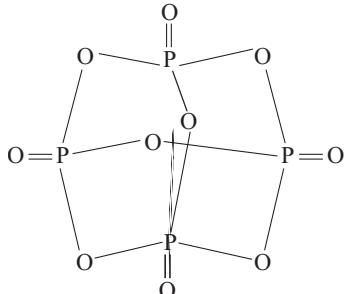


Thus, P—(3), Q—(4), R—(2), S—(1)

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63.

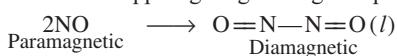


Here four oxygen atoms are bonded to each phosphorus atom.

64. H_3PO_3 [$\text{O}=\text{PH(OH)}_2$] is a dibasic acid.

65. White phosphorus has highly strained, tetrahedral structure, therefore highly reactive.

66. In liquid state, nitric oxide (NO) dimerises into $(\text{NO})_2$ and odd electrons disappear giving diamagnetic property.



67. Both 'N' and 'As' in corresponding hydrides are sp^3 -hybridised. If central atoms are from same group, bond angle decreases from top to bottom if all other things are similar. Hence, $\text{H}-\text{N}-\text{H}$ bond angle in NH_3 is greater than $\text{H}-\text{As}-\text{H}$ bond angle in AsH_3 .

68. Halogens are all good oxidising agent and their oxidising power decreases from top to bottom (F_2 to I_2) in group. Any halogen above in group oxidises halides down in group from their aqueous solution. Hence, Cl_2 can oxidise Br^- to Br_2 , I^- to I_2 but cannot oxidise F^- to F_2 rather F_2 can oxidise Cl^- to Cl_2 .

69. Fe is more electropositive than hydrogen, displaces H^+ ions from acid solution as :



70. **Key Idea** Rhombic sulphur (S_8) gets oxidised into sulphuric acid and water, NO_2 gas is released on reaction with conc. HNO_3 .

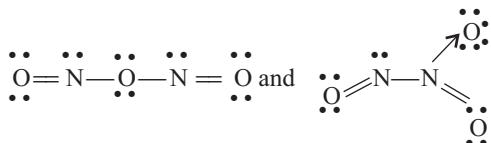
When rhombic sulphur (S_8) is oxidised by conc. HNO_3 then H_2SO_4 is obtained and NO_2 gas is released.



1 mole of rhombic sulphur produces = 16 moles of H_2O

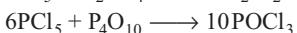
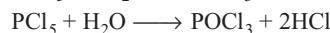
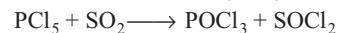
\therefore Mass of water = 16×18 (molar mass of H_2O) = 288 g

71. N_2O_3 has two proposed structures.

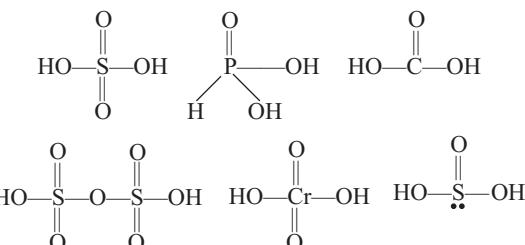


In both cases, number of lone pair of electrons are eight.

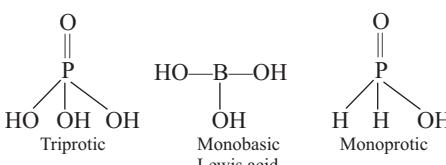
72. PCl_5 produces POCl_3 with the following reagents



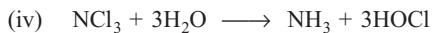
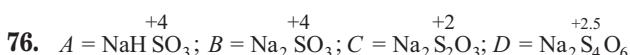
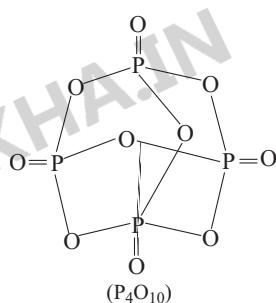
73. Diprotic acids = 6



Others are

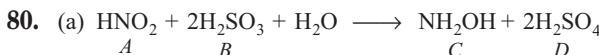
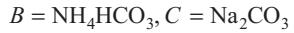


74.

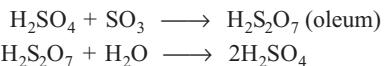


78. Nitrogen in N_2 are bonded by one sigma and two pi bonds. Phosphorus and other elements of this period, due to larger size, are very less likely to form pi bonds, hence P_4 is formed in which there is no pi bonds.

79. In given scheme : $A = \text{Ca}(\text{OH})_2$



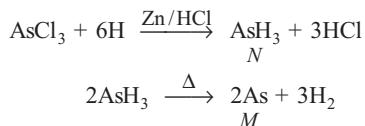
(b) In $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$, sulphuric acid is obtained in misty form and the reaction is explosive. By adding H_2SO_4 , above reaction is prevented :



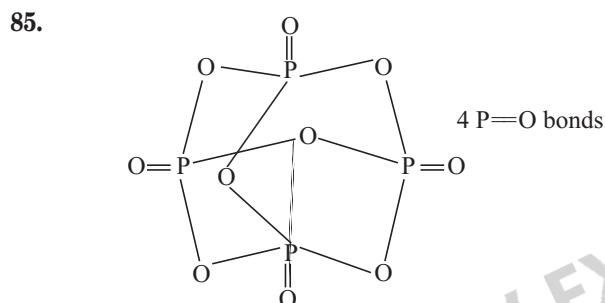
In the contact process, V_2O_5 is used as catalyst.

81. (i) $\text{P}_4\text{O}_{10} + 6\text{PCl}_5 \longrightarrow 10 \text{POCl}_3$
(ii) $\text{SnCl}_4 + 2\text{C}_2\text{H}_5\text{Cl} + 2\text{Na} \longrightarrow \text{Na}_2\text{SnCl}_4 + \text{C}_4\text{H}_{10}$
82. (a) $\text{PCl}_5 + \text{SO}_2 \longrightarrow \text{POCl}_3 + \text{SOCl}_2$
(b) $\text{Ca}_3(\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4 \longrightarrow 3\text{Ca}(\text{H}_2\text{PO}_4)_2$
triple superphosphate

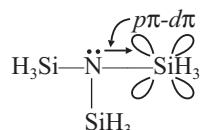
83. The poisonous element M may be As. On the basis of given information



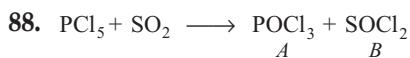
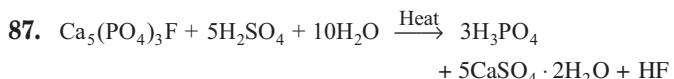
84. (i) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$
(ii) $3\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{O}_2 + 8\text{H}_2\text{O}$
(iii) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$
(iv) $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$



86. (i) The size of both nitrogen and fluorine are very small as well as they have very high electron density. Thus in NF_3 , N and F repel each other stretching the N—F bond. Hence, in NF_3 , N—F bond lengths are greater than the sum of their single bond covalent radii.
(ii) $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$
 MgCl_2 is a salt of strong acid HCl and strong base $\text{Mg}(\text{OH})_2$ and therefore, not hydrolysed in aqueous solution.
(iii) In $(\text{SiH}_3)_3\text{N}$, the lone pair of nitrogen is involved in $p\pi-d\pi$ bonding, less available on nitrogen for donation to a Lewis acid, a weaker Lewis base



Carbon does not have any vacant d -orbitals, no such $p\pi-d\pi$ bonding occur in trimethyl amine, lone pair of nitrogen is available for donation to Lewis acid, hence a stronger Lewis base.

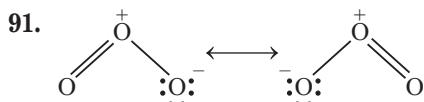


89. Red phosphorus reacts with iodine in the presence of water to form H_3PO_3 and HI as—
 $2\text{P} + 3\text{I}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{PO}_3 + 6\text{HI}$

90. SO_2 acts as reducing agent on account of following reaction :



Hence, the above reaction proceeds in forward direction on increasing concentration of HO^- ion. H^+ is on product side, adding H^+ retards the reaction by sending it in backward direction.



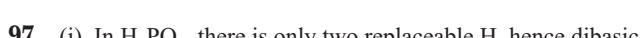
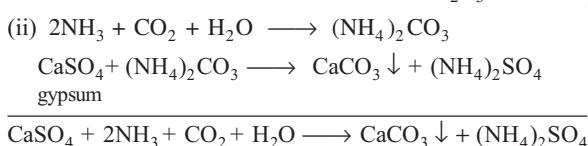
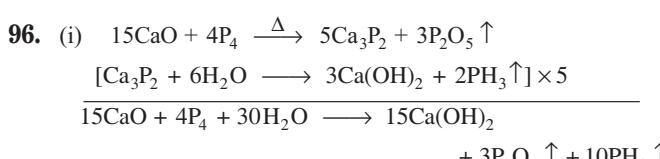
92. Ammonia, in liquid state undergo self-ionisation as :



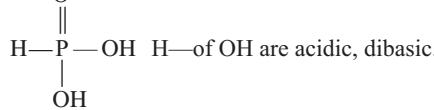
Thus, addition of NH_4Cl to liquid ammonia increases concentration of NH_4^+ in solution and NH_4Cl act as acid.

93. (i) $\text{Na}_2\text{CO}_3 + \text{NO} + \text{NO}_2 \longrightarrow 2\text{NaNO}_2 + \text{CO}_2$
(ii) $2\text{KMnO}_4 + 2\text{NH}_3 \longrightarrow 2\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O} + \text{N}_2$
(iii) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$
(iv) $2\text{H}_2\text{S} + \text{NaHSO}_3 + \text{H}^+ \longrightarrow 3\text{S} + 3\text{H}_2\text{O} + \text{Na}^+$
(v) $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{HCO}_3)_2$

94. (i) $\text{NaNO}_2 + \text{Zn} + \text{NaOH} \longrightarrow 3\text{Na}_2\text{ZnO}_2 + \text{NH}_3 + \text{H}_2\text{O}$
(ii) $2\text{NaIO}_3 + 5\text{NaHSO}_3 \longrightarrow 3\text{NaHSO}_4 + 2\text{Na}_2\text{SO}_4 + \text{I}_2 + \text{H}_2\text{O}$

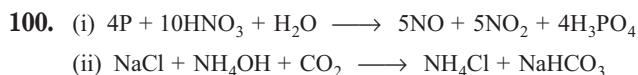
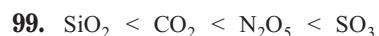
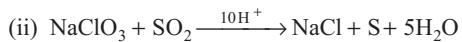
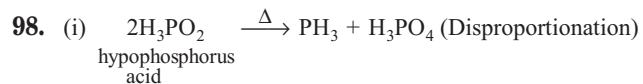


97. (i) In H_3PO_3 , there is only two replaceable H, hence dibasic



- (ii) NH_3 molecules are associated by intermolecular H—bonds.

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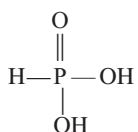


101. Oxygen lacks empty d -orbitals in its valence shell, cannot violate octet rule, hence in most of its compound it shows only divalency. On the other hand, sulphur has vacant $3d$ -orbitals in its valence shell, can violate octet rule, show di, tetra and hexa valency.

102. (i) MgO is used for the lining of steel making furnace because it forms slag with impurities, and thus helps in removing them from iron.

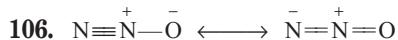
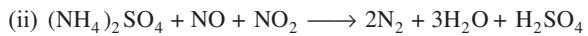
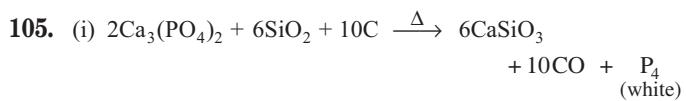
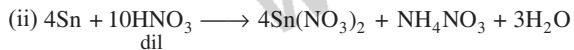
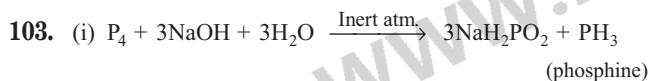
(ii) The mixture of N_2H_4 and H_2O_2 (in presence of Cu(II) catalyst) is used as a rocket propellant because the reaction is highly exothermic and large volumes of gases are evolved.
 $\text{N}_2\text{H}_4(l) + 2\text{H}_2\text{O}_2(l) \longrightarrow \text{N}_2(g) + 4\text{H}_2\text{O}(g)$

(iii) In orthophosphorus acid (H_3PO_3) only two of the three H are replaceable as



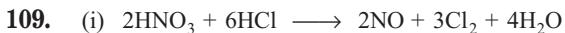
(Only H of —OH are acidic)

(iv) In MgCl_2 , Mg is sp -hybridised while in SnCl_2 , Sn is sp^2 -hybridised with a lone pair at Sn. Hence, MgCl_2 is linear while SnCl_2 is angular.

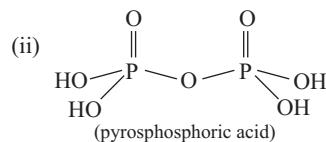
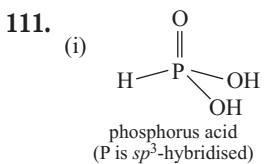
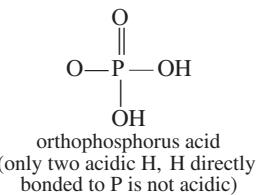
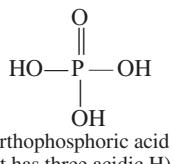


In the above reaction, strong reducing agent, iodide, reducing ferric salt into ferrous salt.

A	B	C
Asbestos	Silicates of Ca and Mg	Donor
Lithium metal	Reducing agent	Electron donor
Nitric oxide	Paramagnetic	Air pollutant

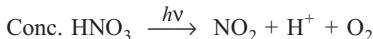


110. Orthophosphoric acid (H_3PO_4) has three replaceable (acidic) hydrogen while orthophosphorus acid (H_3PO_3) has only two replaceable hydrogen.



112. Rhombic sulphur has an eight membered puckered ring structure. On heating ring tends to break and linear chain sulphur is formed. When sulphur melts, the S_8 rings slip and roll over one another very easily. It gives rise to a clear mobile liquid. When liquid sulphur is further heated to higher temperature, rings are broken giving long chain sulphur molecules. This long chain molecules of sulphur get entangled into one another increasing viscosity of melt.

113. (i) In the presence of sunlight, concentrated nitric acid decomposes partially as



It is the NO_2 which impart yellow colouration to nitric acid.

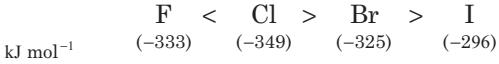
(ii) The bleaching action of bleaching powder is due to presence of available chlorine, but in contact of moisture, it releases chlorine decreasing the amount of available chlorine. Hence, bleaching property decreases gradually as bleaching powder is kept in open container for long time.

Topic 2 Elements and Compounds of Group 17 and 18

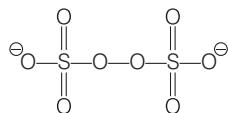
1. Electron gain enthalpy ($\Delta_{eg}H$) is the enthalpy change for converting 1 mol of isolated atoms to anions by adding electrons. All halogens have negative $\Delta_{eg}H$ (exothermic) values. Generally, $\Delta_{eg}H$ becomes less negative when comparing elements of the same group from top to bottom.

But among fluorine and chlorine there is an anomaly because inter-electron repulsion is stronger in fluorine due to its extra small size.

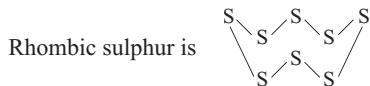
$\therefore \Delta_{eg}H$ is less exothermic than expected for F-atom. Thus, the correct values of electron gain enthalpies



2. $\text{S}_2\text{O}_8^{2-}$ is



Total number of S—O or $\text{S}=\text{O}$ bond = 8



Total number of S—S bond = 8

Thus, the correct answer is (b).

3. Radium (Ra) is a radioactive element. Ra belongs to group 2 (alkaline earth metals), it is not a noble gas.

Note In question noble gas which does not exist in the atmosphere is asked and answer is Ra. But Ra (radium) is an alkaline earth metal and not noble gas. It can be Rn (radon) and is misprint in JEE Main Paper.

4. Halogens form halates and halides with hot and concentrated solution of NaOH as :



So, Cl_2 will also give Cl^- (as NaCl) and ClO_3^- (as NaClO_3) in the above reaction.

Thus, option (b) is correct.

Note When halogens react with cold and dilute solution of NaOH, hypohalites and halides are produced as:



5. Iodine reacts with concentrated HNO_3 to yield HIO_3 along with NO_2 and H_2O . The reaction involved in as follows :



The oxidation state of 'I' in HIO_3 is + 5 as calculated below :

$$1 + x + 3(-2) = 0$$

$$x - 5 = 0, x = + 5$$

6. Chemical reactivity of halogens decreases down the group. The chemical reactivity follows the order.



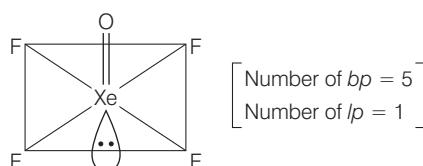
The highest reactivity of fluorine is attributed to two factors:

- The low dissociation energy of F—F bond (which results in low attraction energy for the reaction).
- Very strong bonds which are formed. Both properties arise from, small size of fluorine. I_2 is being the least reactive halogen, it requires a catalyst for the reaction.



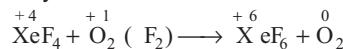
7. In XeOF_4 , Xe is sp^3d^2 -hybridised. Geometry of the molecule is octahedral, but shape of the molecule is square pyramidal.

According to VSEPR, theory it has one π bond. Remaining six electron pairs form an octahedron with one position occupied by a lone pair.



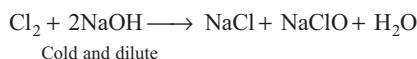
Here, Xe contains one lone pair of electrons.

8. The reaction in which oxidation and reduction occur simultaneously are termed as redox reaction.



Since, Xe undergoes oxidation while O undergoes reduction. So, it is an example of redox reaction.

9. Cl_2 , Br_2 and I_2 form a mixture of halide and hypohalites when react with cold dilute alkalis while a mixture of halides and haloate when react with concentrated cold alkalis.



$\therefore \text{Cl}^-$ and ClO^- are obtained as products when chlorine gas reacts with cold and dilute aqueous NaOH.

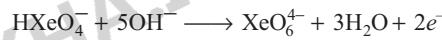
10. Interhalogen compounds are generally more reactive than halogens (except fluorine).

11. Xe has highest boiling point.

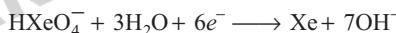
12. **PLAN** This problem can be solved by using concept involved in chemical properties of xenon oxide and xenon fluoride. XeF_6 on complete hydrolysis produces XeO_3 .

XeO_3 on reaction with OH^- produces HXeO_4^- which on further treatment with OH^- undergo slow disproportionation reaction and produces XeO_6^{4-} along with Xe(g) , $\text{H}_2\text{O(l)}$ and $\text{O}_2(\text{g})$ as a by-product.

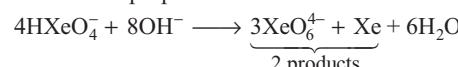
Oxidation half-cell in basic aqueous solution



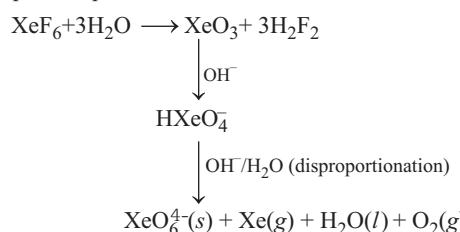
Reduction half-cell in basic aqueous solution



Balanced overall disproportionation reaction is

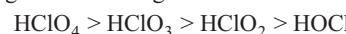


Complete sequence of reaction can be shown as

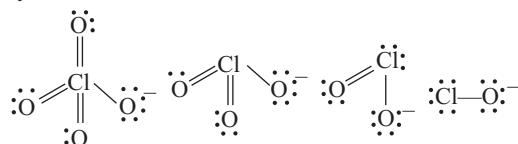


Thus, (c) is the correct answer.

13. Decreasing order of strength of oxoacids



Reason Consider the structures of conjugate bases of each oxyacids of chlorine.

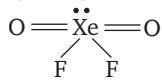


Negative charge is more delocalised on ClO_4^- due to resonance, hence, ClO_4^- is more stable (and less basic).

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Hence, we can say as the number of oxygen atom(s) around Cl-atom increases as oxidation number of Cl-atom increases and thus, the ability of loose the H^+ increases.

14. In XeO_2F_2 , the bonding arrangement around the central atom Xe is

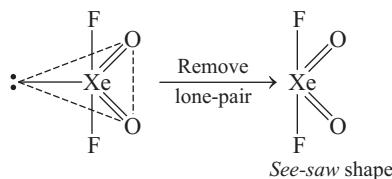


$$4\sigma \text{ bonds} + 1.01p = 5$$

Hybridisation of Xe = sp^3d

sp^3d -hybridisation corresponds to trigonal bipyramidal geometry.

Also, in trigonal bipyramidal geometry, lone pairs remain present on equatorial positions in order to give less electronic repulsion.

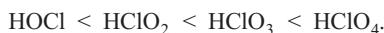


NOTE According to Bent's rule, the more electronegative atoms must be present on axial position. Hence, F are kept on axial positions.

15. Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$ gets oxidised by chlorine water as $\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} \longrightarrow 2\text{NaHSO}_4 + 8\text{HCl}$
 FeCl_3 oxidises $\text{Na}_2\text{S}_2\text{O}_3$ to $\text{Na}_2\text{S}_4\text{O}_6$.

16. I^- is oxidised by MnO_4^- in alkaline medium to form IO_3^-
 $2\text{KMnO}_4 + \text{KI} + \text{H}_2\text{O} \longrightarrow 2\text{KOH} + 2\text{MnO}_2 + \text{KIO}_3$

17. Amongst oxyacids of a given halogen, higher the oxidation number of halogen, stronger the acid. Hence,

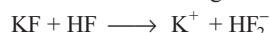


18. Pseudo halides must contain atleast one nitrogen atom.

19. Among oxyacids of halogens, if there are same number of oxygens bonded to central atom, higher the electronegativity of halogen, stronger the acid. Hence,

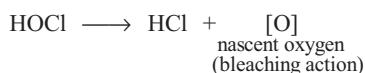


20. All others has at least one S-S linkage.



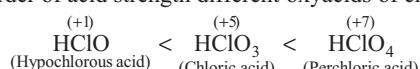
21. Among halogens, oxidising power decreases from top to bottom. Hence, the upper halogen oxidises lower halides from aqueous solution. Chlorine will oxidise bromide into bromine.

22. Moist chlorine gives nascent oxygen, act as oxidising agent :



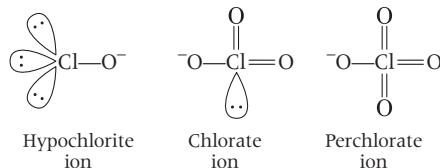
23. Fluorine, being the most electronegative, its size is very small. Therefore, it does not have a tendency to loose electrons. Hence, HF does not act as a reducing agent.

24. (a) Order of acid strength different oxyacids of chlorine are :

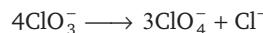


Weak acid have strong conjugate base thus hypochlorite ion has strongest conjugate base. Therefore, statement (a) is correct.

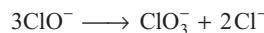
- (b) Hypochlorite ion is linear and perchlorate ion is tetrahedral and there is no effect of lone pair on hypochlorite ion. Thus statement (b) is correct.



- (c) In the disproportionation reaction, chlorate ion $\text{Cl}(+ 5)$ is oxidised to perchlorate, $\text{Cl}(+ 7)$ and reduced to chloride, $\text{Cl}(-1)$.



While in hypochlorite ion, chlorite ion $\text{Cl}(+ 1)$ is oxidised to chlorate, $\text{Cl}(+ 5)$ and reduced to chloride, $\text{Cl}(-1)$ ion.



Thus, statement (c) is incorrect.

- (d) The hypochlorite ion oxidises the sulphite ion to sulphate ion, because HOCl is the strongest oxidising Cl oxyacids,

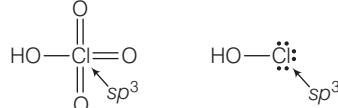


Thus, statement (d) is correct.

25. (a) ClO_4^- is more stable than ClO^- .

- (b) Incorrect : $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{HOCl}$

(c)

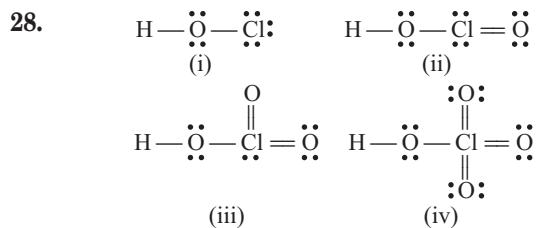


- (d) HClO_4 is stronger acid than H_2O .

26. Colour of halogen arises due to transition from HOMO to LUMO in the visible region. On moving down a group, the difference in energy between HOMO and LUMO decreases electronic transition occur more easily and colour intensity increases.

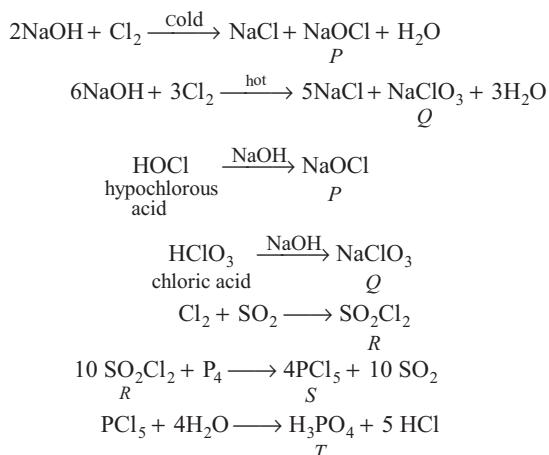
27.

Compounds	Hybridisation	Structures	Lone pair on central atom
BrF_5	sp^3d^2		1
ClF_3	sp^3d		2
XeF_4	sp^3d^2		2
SF_4	sp^3d		1



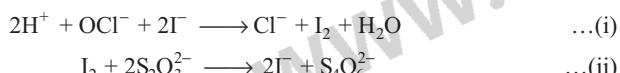
- (a) Number of $\text{Cl}^- = \text{O}$ bonds in (ii) and (iii) together is three. Hence, wrong.
 (b) Number of Lone Pair on Cl in (ii) and (iii) together is three. Hence, correct.
 (c) In (iv), Cl is sp^3 -hybridised. Hence, correct.
 (d) Amongst (i) to (iv), the strongest acid is (iv). Hence, wrong.

Passage 1 Q. Nos. (29-30)

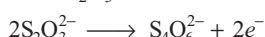


Passage 2 Q.Nos. (31-32)

31. The involved redox reactions are :



Also the n -factor of $\text{S}_2\text{O}_3^{2-}$ is one as



[one ' e ' is produced per unit of $\text{S}_2\text{O}_3^{2-}$]

\Rightarrow Molarity of $\text{Na}_2\text{S}_2\text{O}_3 = 0.25 \text{ N} \times 1 = 0.25 \text{ M}$

\Rightarrow m mol of $\text{Na}_2\text{S}_2\text{O}_3$ used up = $0.25 \times 48 = 12$

Now from stoichiometry of reaction (ii)

12 m mol of $\text{S}_2\text{O}_3^{2-}$ would have reduced 6 m mol of I_2 .

From stoichiometry of reaction (i)

m mol of OCl^- reduced = m mol in I_2 produced = 6

\Rightarrow Molarity of household bleach solution = $\frac{6}{25} = 0.24 \text{ M}$

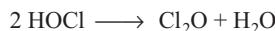
Shortcut Method

Milliequivalent of $\text{Na}_2\text{S}_2\text{O}_3$ = milliequivalent of OCl^-
 $= 0.25 \times 48 = 12$

Also n -factor of $\text{OCl}^- = 2[\text{Cl}^+ \longrightarrow \text{Cl}^-, \text{gain of } 2e^-]$

\Rightarrow m mol of $\text{OCl}^- = \frac{12}{2} = 6 \text{ m mol}$. Remaining part is solved in the same manner.

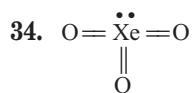
32. Bleaching powder is $\text{Ca}(\text{OCl})\text{Cl}$. Therefore, the oxoacid whose salt is present in bleaching powder is HOCl . Anhydride of HOCl is Cl_2O as



NOTE The oxidation number of element in anhydride and oxoacid remains the same.

Passage 3 Q.Nos. (33 to 35)

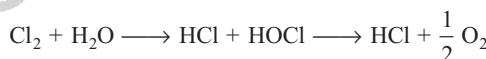
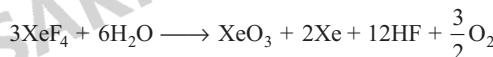
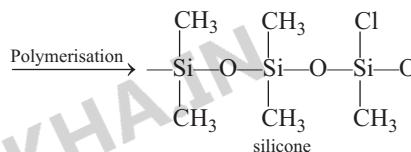
33. Ar, being inert, provide inert atmosphere in arc welding, and prevent from undesired oxidation.



Xe is sp^3 -hybridised with one lone pair. Hence, molecule of XeO_3 has pyramidal shape.

35. Both XeF_4 and XeF_6 are strong oxidising agent.

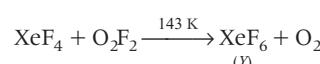
36. $(\text{CH}_3)_2\text{SiCl}_2 + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_2\text{Si}(\text{OH})_2 + 2\text{HCl}$



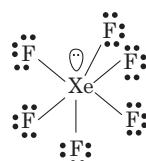
37. $\text{KI} + \text{I}_2 \longrightarrow \text{KI}_3$

38. Among HX , acidic strength increases from HF to HI.

39. XeF_4 reacts with O_2F_2 to form XeF_6 . O_2F_2 is fluorinating reagent.



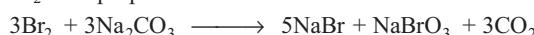
The structure of XeF_6 is



Y compound (XeF_6) has 3 lone pair in each fluorine and one lone pair in xenon.

Hence, total number of lone pairs electrons is 19.

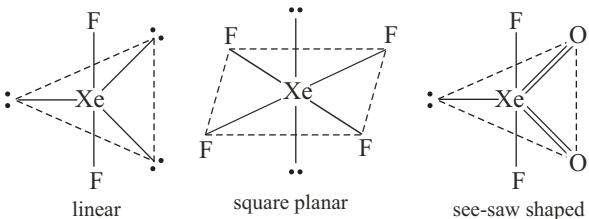
40. Br_2 is disproportionated in basic medium as



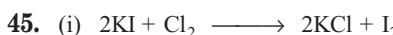
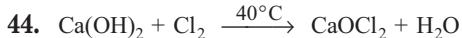
41. $2\text{XeF}_4 + 3\text{H}_2\text{O} \longrightarrow \text{Xe} + \text{XeO}_3 + \text{F}_2 + 6\text{HF}$

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42.

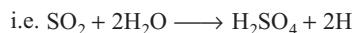


43. Halogen above in the group oxidises halide below to it from their aqueous solution, e.g.

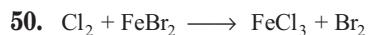
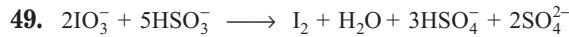
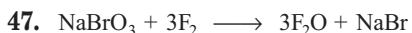


46. (i) Due to small size and high electron density of fluorine atom, there exist a significant repulsions between fluorine atoms in F_2 , they have greater tendency to get apart. Hence, bond energy of F_2 is less than that of Cl_2 . This is against to bond-length bond-energy relationship.,

- (ii) Sulphur dioxide is a more powerful reducing agent in alkaline medium because nascent hydrogen is produced in the presence of moisture



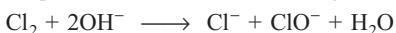
And alkaline solution neutralises the acid i.e. H_2SO_4 and shift the equilibrium in the forward direction producing more nascent hydrogen. But in acidic medium the equilibrium will suppressed resulting in a lesser amount of nascent hydrogen.



52. (i) Bond strength is inversely related to bond length. Hence, bond energy : $\text{HI} < \text{HBr} < \text{HCl} < \text{HF}$
(ii) $\text{HI}(-1) < \text{I}_2(0) < \text{ICl}(+1) < \text{HIO}_4(+7)$

53. F_2 itself, is the strongest oxidising agent. Therefore, chemical reagent cannot oxidise fluoride to fluorine.

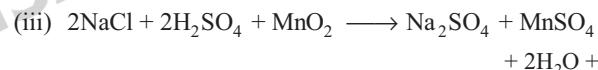
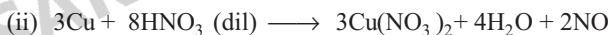
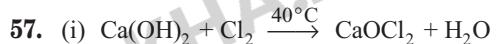
54. Complete and balance the following reactions



55. The bleaching action of bleaching powder is due to presence of available chlorine, but in contact of moisture, it releases chlorine decreasing the amount of available chlorine. Hence, bleaching property decreases gradually as bleaching powder is kept in open container for long time.

56. (i) HBr is a stronger reducing agent, reduces concentrated H_2SO_4 to SO_2 . Hence, HBr cannot be prepared by heating bromide salts with concentrated H_2SO_4 .

- (ii) Hypochlorous acid is acidic in nature, therefore it turns blue litmus paper into red. However, HOCl is also an oxidising acid (bleaching), it bleaches red colour to finally colourless.



17

Transition and Inner-Transition Elements

Objective Questions I (Only one correct option)

- 8.** The maximum number of possible oxidation states of actinoids are shown by (2019 Main, 9 April II)

 - berkelium, (Bk) and californium (Cf)
 - nobelium (No) and lawrencium (Lr)
 - actinium (Ac) and thorium (Th)
 - neptunium (Np) and plutonium (Pu)

9. The lanthanide ion that would show colour is (2019 Main, 8 April I)

 - Gd^{3+}
 - Sm^{3+}
 - La^{3+}
 - Lu^{3+}

10. The correct order of atomic radii is (2019 Main, 12 Jan II)

 - $\text{Ho} > \text{N} > \text{Eu} > \text{Ce}$
 - $\text{N} > \text{Ce} > \text{Eu} > \text{Ho}$
 - $\text{Eu} > \text{Ce} > \text{Ho} > \text{N}$
 - $\text{Ce} > \text{Eu} > \text{Ho} > \text{N}$

11. $\underline{A} \xrightarrow[{\text{Green}}]{4 \text{ KOH}, \text{O}_2} 2\underline{B} + 2\text{H}_2\text{O}$

$$3\underline{B} \xrightarrow[{\text{Purple}}]{4 \text{ HCl}} 2\underline{C} + \text{MnO}_2 + 2\text{H}_2\text{O}$$

$$2\underline{C} \xrightarrow{\text{H}_2\text{O}, \text{KI}} 2\underline{A} + 2\text{KOH} + \underline{D}$$

In the above sequence of reactions, \underline{A} and \underline{D} , respectively, are (2019 Main, 11 Jan II)

 - KI and KMnO_4
 - MnO_2 and KIO_3
 - KI and K_2MnO_4
 - KIO_3 and MnO_2

12. The element that usually does not show variable oxidation states is (2019 Main, 11 Jan I)

 - Sc
 - Cu
 - Ti
 - V

13. The 7th electron of an element X with an atomic number of 71 enters into the orbital (2019 Main, 10 Jan II)

 - $4f$
 - $6p$
 - $5d$
 - $6s$

14. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means (2019 Main, 10 Jan I)

 - increase in atomic radii and decrease in ionic radii
 - decrease in both atomic and ionic radii
 - increase in both atomic and ionic radii
 - decrease in atomic radii and increase in ionic radii

15. The transition element having least enthalpy of atomisation is (2019 Main, 9 April II)

 - Zn
 - V
 - Fe
 - Cu

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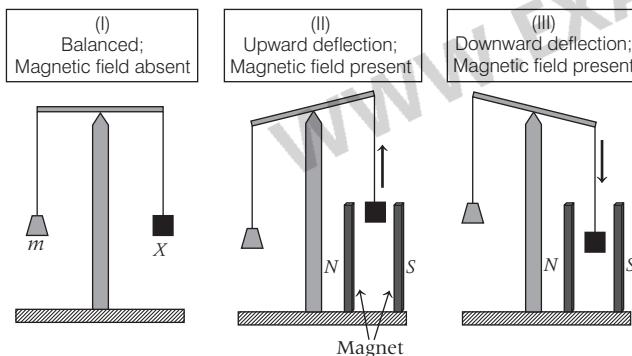
- 16.** In the following reactions, ZnO is respectively acting as a/an
(2017 Main)
- (i) $\text{ZnO} + \text{Na}_2\text{O} \longrightarrow \text{Na}_2\text{ZnO}_2$
 - (ii) $\text{ZnO} + \text{CO}_2 \longrightarrow \text{ZnCO}_3$
 - (a) base and acid (b) base and base
 - (c) acid and acid (d) acid and base
- 17.** Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4 . 'X' reacts with the acidified aqueous CaCl_2 solution to give a white precipitate which decolourises acidic solution of KMnO_4 . 'X' is
(2017 Main)
- (a) $\text{C}_6\text{H}_5\text{COONa}$ (b) HCOONa
 - (c) CH_3COONa (d) $\text{Na}_2\text{C}_2\text{O}_4$
- 18.** Which of the following combination will produce H_2 gas?
(2017 Adv.)
- (a) Fe metal and conc. HNO_3
 - (b) Cu metal and conc. HNO_3
 - (c) Au metal and NaCN (*aq*) in the presence of air
 - (d) Zn metal and NaOH (*aq*)
- 19.** Which of the following compounds is metallic and ferromagnetic?
(2016 Main)
- (a) CrO_2 (b) VO_2
 - (c) MnO_2 (d) TiO_2
- 20.** The reaction of zinc with dilute and concentrated nitric acid, respectively, produce
(2016 Main)
- (a) NO_2 and NO (b) NO and N_2O
 - (c) NO_2 and N_2O (d) N_2O and NO_2
- 21.** The geometries of the ammonia complexes of Ni^{2+} , Pt^{2+} and Zn^{2+} , respectively, are
(2016 Main)
- (a) octahedral, square planar and tetrahedral
 - (b) square planar, octahedral and tetrahedral
 - (c) tetrahedral, square planar and octahedral
 - (d) octahedral, tetrahedral and square planar
- 22.** Which of the following compounds is not yellow coloured?
(2015 Main)
- (a) $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ (b) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$
 - (c) $(\text{NH}_4)_3[\text{As}(\text{Mo}_3\text{O}_{10})_4]$ (d) BaCrO_4
- 23.** Which series of reactions correctly represents chemical relations related to iron and its compound?
(2014 Main)
- (a) $\text{Fe} \xrightarrow{\text{Dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{H}_2\text{SO}_4, \text{O}_2} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{Heat}} \text{Fe}$
 - (b) $\text{Fe} \xrightarrow{\text{O}_2, \text{Heat}} \text{FeO} \xrightarrow{\text{Dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}$
 - (c) $\text{Fe} \xrightarrow{\text{Cl}_2, \text{Heat}} \text{FeCl}_3 \xrightarrow{\text{Heat, air}} \text{FeCl}_2 \xrightarrow{\text{Zn}} \text{Fe}$
 - (d) $\text{Fe} \xrightarrow{\text{O}_2, \text{Heat}} \text{Fe}_3\text{O}_4 \xrightarrow{\text{CO, } 600^\circ\text{C}} \text{FeO} \xrightarrow{\text{CO, } 700^\circ\text{C}} \text{Fe}$
- 24.** Four successive members of the first row transition elements listed below with atomic numbers. Which one of them is expected to have the highest $E_{M^{3+}/M^{2+}}^{\circ}$ value?
(2013 Main)
- (a) Cr ($Z = 24$) (b) Mn ($Z = 25$)
 - (c) Fe ($Z = 26$) (d) Co ($Z = 27$)
- 25.** Consider the following reaction,
(2013 Main)
- $$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \longrightarrow x\text{Mn}^{2+} + 2y\text{CO}_2 + \frac{z}{2}\text{H}_2\text{O}$$
- The values of x , y and z in the reaction are, respectively
- (a) 5, 2 and 16 (b) 2, 5 and 8
 - (c) 2, 5 and 16 (d) 5, 2 and 8
- 26.** Which of the following arrangements does not represent the correct order of the property stated against it?
(2013 Main)
- (a) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: paramagnetic behaviour
 - (b) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: ionic size
 - (c) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: stability in aqueous solution
 - (d) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: number of oxidation states
- 27.** The colour of light absorbed by an aqueous solution of CuSO_4 is
(2012)
- (a) orange-red (b) blue-green (c) yellow (d) violet
- 28.** Which of the following will not be oxidised by O_3 ?
(2005)
- (a) KI (b) FeSO_4 (c) KMnO_4 (d) K_2MnO_4
- 29.** Which of the following pair is expected to exhibit same colour in solution?
(2005, 1M)
- (a) VOCl_2 ; FeCl_2 (b) CuCl_2 ; VOCl_2
 - (c) MnCl_2 ; FeCl_2 (d) FeCl_2 ; CuCl_2
- 30.** When I^- is oxidised by MnO_4^- in alkaline medium, I^- converts into
(2004)
- (a) IO_3^- (b) I_2 (c) IO_4^- (d) IO^-
- 31.** The pair of compounds having metals in their highest oxidation state is
(2004, 1M)
- (a) MnO_2 , FeCl_3 (b) $[\text{MnO}_4]^-$, CrO_2Cl_2
 - (c) $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_3]$ (d) $[\text{NiCl}_4]^{2-}$, $[\text{CoCl}_4]^-$
- 32.** $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating gives a gas which is also given by
(2004, 1M)
- (a) heating NH_4NO_2 (b) heating NH_4NO_3
 - (c) $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O}$ (d) $\text{Na}(\text{comp.}) + \text{H}_2\text{O}_2$
- 33.** When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is
(2003, 1M)
- (a) K_2MnO_4 , purple green (b) KMnO_4 , purple
 - (c) Mn_2O_3 , brown (d) Mn_3O_4 , black
- 34.** Amongst the following, identify the species with an atom in + 6 oxidation state
(2000, 1M)
- (a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2
- 35.** On heating ammonium dichromate, the gas evolved is
(1999, 2M)
- (a) oxygen (b) ammonia
 - (c) nitrous oxide (d) nitrogen
- 36.** In the dichromate dianion
(1999, 2M)
- (a) 4 Cr—O bonds are equivalent
 - (b) 6 Cr—O bonds are equivalent
 - (c) all Cr—O bonds are equivalent
 - (d) all Cr—O bonds are non-equivalent
- 37.** Which of the following compounds is expected to be coloured?
(1997, 1M)
- (a) Ag_2SO_4 (b) CuF_2 (c) MgF_2 (d) CuCl

- 38.** Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is (1997, 1M)
 (a) CrO_3 (b) Cr_2O_3 (c) Cr (d) CO
- 39.** The reaction which proceed in the forward direction is (1991, 1M)
 (a) $\text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$
 (b) $\text{NH}_3 + \text{H}_2\text{O} + \text{NaCl} \longrightarrow \text{NH}_4\text{Cl} + \text{NaOH}$
 (c) $\text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 \longrightarrow \text{SnCl}_2 + 2\text{HgCl}_2$
 (d) $2\text{CuI} + \text{I}_2 + 4\text{H}^+ \longrightarrow 2\text{Cu}^{2+} + 4\text{KI}$
- 40.** Zinc-copper couple that can be used as a reducing agent is obtained by (1984, 1M)
 (a) mixing of zinc dust and copper gauge
 (b) zinc coated with copper
 (c) copper coated with zinc
 (d) zinc and copper wires welded together
- 41.** How many unpaired electrons are present in Ni^{2+} ? (1981, 1M)
 (a) 0 (b) 2 (c) 4 (d) 8
- 42.** One of the constituent of German silver is (1980, 1M)
 (a) Ag (b) Cu (c) Mg (d) Al
- 43.** Which of the following dissolves in concentrated NaOH solution? (1980, 1M)
 (a) Fe (b) Zn (c) Cu (d) Ag

Objective Questions II

(One or more than one correct option)

- 44.** In an experiment, m grams of a compound X (gas/liquid/solid) taken in a container is loaded in a balance as shown in figure I below.

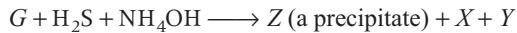


In the presence of a magnetic field, the pan with X is either deflected upwards (figure II), or deflected downwards (figure III), depending on the compound X . Identify the correct statement(s). (2020 Adv.)

- (a) If X is $\text{H}_2\text{O}(l)$, deflection of the pan is upwards.
 (b) If X is $\text{K}_4[\text{Fe}(\text{CN})_6](s)$, deflection of the pan is upwards.
 (c) If X is $\text{O}_2(g)$, deflection of the pan is downwards.
 (d) If X is $\text{C}_6\text{H}_6(l)$, deflection of the pan is downwards.
- 45.** Fusion of MnO_2 with KOH in presence of O_2 produces a salt W . Alkaline solution of W upon electrolytic oxidation yields another salt X . The manganese containing ions present in W and X , respectively, are Y and Z . Correct statement(s) is (are) (2019 Adv.)

- (a) Both Y and Z are coloured and have tetrahedral shape
 (b) Y is diamagnetic in nature while Z is paramagnetic
 (c) In both Y and Z , π -bonding occurs between p -orbitals of oxygen and d -orbitals of manganese
 (d) In aqueous acidic solution, Y undergoes disproportionation reaction to give Z and MnO_2

- 46.** Consider the following reactions (unbalanced).



Choose the correct option(s). (2019 Adv.)

- (a) The oxidation state of Zn in T is +1
 (b) R is a V-shaped molecule
 (c) Bond order of Q is 1 in its ground state
 (d) Z is dirty white in colour

- 47.** With reference to *aqua-regia*, choose the correct option(s). (2019 Adv.)

- (a) *Aqua-regia* is prepared by mixing conc. HCl and conc. HNO_3 in 3 : 1 (*v/v*) ratio
 (b) The yellow colour of *aqua-regia* is due to the presence of NOCl and Cl_2
 (c) Reaction of gold with *aqua-regia* produces an anion having Au in +3 oxidation state
 (d) Reaction of gold with *aqua regia* produces NO_2 in the absence of air

- 48.** The correct statement(s) about Cr^{2+} and Mn^{3+} is/are [atomic number of Cr = 24 and Mn = 25] (2015 Adv.)

- (a) Cr^{2+} is a reducing agent
 (b) Mn^{3+} is an oxidising agent
 (c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
 (d) when Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

- 49.** Fe^{3+} is reduced to Fe^{2+} by using (2015 Adv.)

- (a) H_2O_2 in presence of NaOH (b) Na_2O_2 in water
 (c) H_2O_2 in presence of H_2SO_4 (d) Na_2O_2 in presence of H_2SO_4

- 50.** Which of the following halides react(s) with $\text{AgNO}_3(aq)$ to give a precipitate that dissolves in $\text{Na}_2\text{S}_2\text{O}_3(aq)$? (2011)

- (a) HCl (b) HF (c) HBr (d) HI

- 51.** Reduction of the metal centre in aqueous permanganate ion involves (2011)

- (a) three electrons in neutral medium
 (b) five electrons in neutral medium
 (c) three electrons in alkaline medium
 (d) five electrons in acidic medium

- 52.** Which of the following statement (s) is/are correct? (1998)

- (a) The electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ (Atomic number of Cr = 24)
 (b) The magnetic quantum number may have a negative value
 (c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (Atomic number of Ag = 47)
 (d) The oxidation state of nitrogen in HN_3 is -3

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53. Which of the following statement(s) is/are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ? (1998, 2M)
- A deep red vapours is formed
 - Vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4
 - Chlorine gas is evolved
 - Chromyl chloride is formed
54. Which of the following alloys contains Cu and Zn? (1993, 1M)
- Bronze
 - Brass
 - Gun metal
 - Type metal
55. The aqueous solution of the following salts will be coloured in case of (1990, 1M)
- $Zn(NO_3)_2$
 - $LiNO_3$
 - $Co(NO_3)_2$
 - $CrCl_3$
 - potash alum
56. Potassium manganate (K_2MnO_4) is formed when (1988, 2M)
- chlorine is passed into aqueous $KMnO_4$ solution
 - manganese dioxide is fused with KOH in air
 - formaldehyde reacts with potassium permanganate in the presence of strong alkali
 - potassium permanganate reacts with conc. H_2SO_4

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
- (c) Statement I is true; Statement II is false.
- (d) Statement I is false; Statement II is true.
57. **Statement I** Zn^{2+} is diamagnetic.
Statement II The electrons are lost from $4s$ orbital to form Zn^{2+} . (1998, 2M)
58. **Statement I** To a solution of potassium chromate if a strong acid is added, it changes its colour from yellow to orange.
Statement II The colour change is due to the change in oxidation state of potassium chromate. (1988, 2M)

Fill in the Blanks

59. The compound $YBa_2Cu_3O_7$ which show super conductivity has copper in oxidation state assuming that the rare earth element Yttrium in its usual +3 oxidation state. (1994, 1M)
60. The outermost electronic configuration of Cr is (1994, 1M)
61. Fehling's solution *A* consists of an aqueous solution of copper sulphate while Fehling's solution *B* consists of an alkaline solution of (1990, 1M)
62. The salts and are isostructural. ($FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$) (1990, 1M)

63. Mn^{2+} can be oxidised to MnO_4^- by (SnO₂, PbO₂, BaO₂) (1981, 1M)

True/False

64. Dipositive zinc exhibit paramagnetism due to loss of two electrons from $3d$ -orbitals of neutral atom. (1987, 1M)
65. Copper metal reduces Fe^{2+} in an acidic medium. (1982, 1M)

Numerical Answer Type Questions

66. In the chemical reaction between stoichiometric quantities of $KMnO_4$ and KI in weakly basic solution, what is the number of moles of I_2 released for 4 moles of $KMnO_4$ consumed? (2020 Adv.)

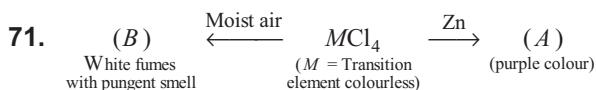
67. An acidified solution of potassium chromate was layered with an equal volume of amyl alcohol. When it was shaken after the addition of 1 mL of 3% H_2O_2 , a blue alcohol layer was obtained. The blue colour is due to the formation of a chromium (VI) compound 'X'. What is the number of oxygen atoms bonded to chromium through only single bond in a molecule of *X*? (2020 Adv.)

68. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitative oxidise thiosulphate anions to produce *X* moles of a sulphur containing product. The magnitude of *X* is (2016 Adv.)

69. In dilute aqueous H_2SO_4 the complex diaquadioxalatoferate (II) is oxidised by MnO_4^- . For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is (2015 Adv.)

70. Consider the following list of reagents, acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2 , Cl_2 , O_3 , $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is (2014 Adv.)

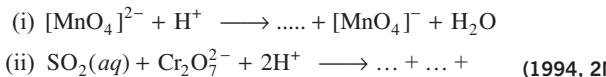
Subjective Questions



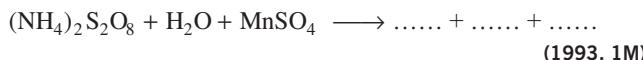
Identify the metal *M* and hence MCl_4 . Explain the difference in colours of MCl_4 and *A*. (2005)

72. Give reasons : CrO_3 is an acid anhydride. (1999, 2M)
73. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion of the compound. (1997)
74. Write balanced equations for the following
- Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.
 - Reaction of zinc with dilute nitric acid. (1997, 2M)

75. Complete and balance the following reactions



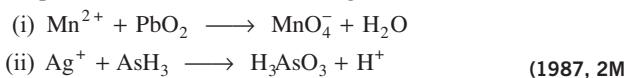
76. Complete and balance the following reaction.



77. Write the balanced chemical equations for the following reactions.

- (i) A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4 .
- (ii) Potassium permanganate is added to a hot solution of manganeseous sulphate. (1990, 2M)

78. Complete and balance the following reactions.



79. Give reason in one or two sentences

"Most transition metal compounds are coloured." (1986, 1M)

80. Show with balanced equations for the reactions when

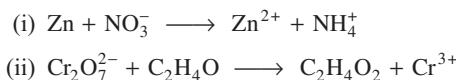
- (i) potassium permanganate interacts with manganese dioxide in the presence of potassium hydroxide.
- (ii) potassium ferricyanide is heated with concentrated sulphuric acid. (1985, 2M)

81. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.

"Potassium permanganate from manganese dioxide"

(1983, 1M)

82. Complete and balance the following reactions (1983, 2M)



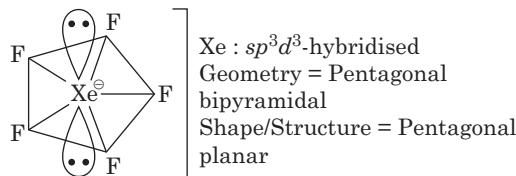
Answers

- | | | | |
|---------|---------|---------|---------|
| 1. (a) | 2. (b) | 3. (c) | 4. (d) |
| 5. (d) | 6. (b) | 7. (a) | 8. (d) |
| 9. (b) | 10. (c) | 11. (b) | 12. (a) |
| 13. (c) | 14. (b) | 15. (a) | 16. (d) |
| 17. (d) | 18. (d) | 19. (a) | 20. (d) |
| 21. (a) | 22. (a) | 23. (d) | 24. (d) |
| 25. (c) | 26. (a) | 27. (a) | 28. (c) |
| 29. (b) | 30. (a) | 31. (b) | 32. (a) |
| 33. (a) | 34. (d) | 35. (d) | 36. (b) |

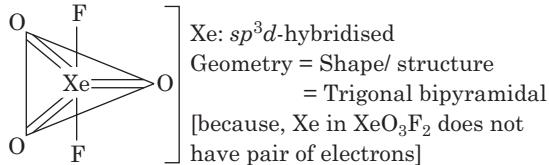
- | | | | |
|--------------------|---|----------------|------------------|
| 37. (b) | 38. (b) | 39. (a) | 40. (b) |
| 41. (b) | 42. (b) | 43. (b) | 44. (a,b,c) |
| 45. (a,c,d) | 46. (b,c,d) | 47. (a,b,c) | 48. (a, b, c) |
| 49. (a, b) | 50. (a, c, d) | 51. (a, c, d) | 52. (a, b, c, d) |
| 53. (a, b, d) | 54. (b, c) | 55. (c, d) | 56. (b, c) |
| 57. (b) | 58. (c) | 59. $x = +7/3$ | 60. $3d^54s^1$ |
| 61. Rochelle salt | 62. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ | | |
| 63. PbO_2 | 64. F | 65. F | 66. (6) |
| 67. (4) | 68. (6) | 69. (8) | 70. (7) |

Hints & Solutions

1. $[\text{XeF}_5]$



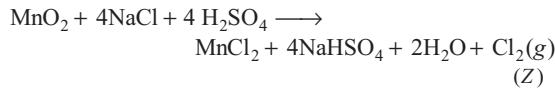
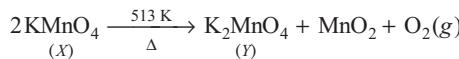
XeO_3F_2



2. Only statement 2 is incorrect, whereas 1 and 3 are correct.

KMnO_4 will not give satisfactory result when it is titrated by HCl , because same amount of KMnO_4 is consumed to oxidise HCl into Cl_2 .

3. Thermal decomposition of Mn compound (X), i.e. KMnO_4 at 513 K results in compound Y (i.e. K_2MnO_4), MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas Z (i.e. Cl_2). The reactions involved are as follows :



4. The pair that has similar atomic radii is Mo and W. It is due to lanthanoid contraction. The factor responsible for lanthanoid contraction is the imperfect shielding of one electron by another in the same set of orbitals. Shielding of $4f$ is very less due to its diffused shape. As a result, nuclear charge increases. Hence, Mo and W have similar atomic radii.

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5. The 3d-transition series is

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Outermost Electronic Configuration	$3d^0 4s^2$	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$

In 1st ionisation, one electron will be removed from $4s^2$ subshell/orbital.

With increase in atomic number (Z), i.e. with increase in number of protons in the nucleus, effective nuclear charge (Z') also increases from Sc to Zn.

$$IE \propto Z^*$$

So, IE order of the given elements will be,

$$Ti < Mn < Ni < Zn$$

6. Actinoids show a variety of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ energy levels.

In the actinoids family ($5f$ -block), uranium (U) neptunium (Np), plutonium (Pu) and americium (Am) have highest possible oxidation states of +6, +7, +7 and +6 respectively.

7. The spin only magnetic moment (μ) of each ion can be calculated as :

$$\mu = \sqrt{n(n+2)} BM$$

[$\because n$ = No. of unpaired electron(s)] $\Rightarrow \mu \propto n$, i.e. higher the number of unpaired electron, higher will be the value of μ .

Metal ion	Z	n (for metal ion)	M (BM)	Nature
Ti^{2+}	22	2 ($3d^2$)	$\sqrt{8}$	Paramagnetic
V^{2+}	23	3 ($3d^3$)	$\sqrt{15}$	Paramagnetic
Ti^{3+}	22	1 ($3d^1$)	$\sqrt{3}$	Paramagnetic
Sc^{3+}	21	0 ($3d^0$)	0	Diamagnetic

Thus, the correct order of spin only magnetic moments of given hydrated ions will be

$$Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$$

8. The maximum number of possible oxidation states of actinoids are shown by neptunium (Np) and plutonium (Pu). These actinoids exhibit oxidation states of +3, +4, +5 and +6.

9. The lanthanide ion that would show colour is Sm^{3+} . Colour of a compound depends on the number of electrons in $4f$ -orbitals.

Electronic configuration of given lanthanides are as follows:

$$Gd^{3+} = 4f^7$$

$$Sm^{3+} = 4f^5$$

$$La^{3+} = 4f^0$$

$$Lu^{3+} = 4f^{14}$$

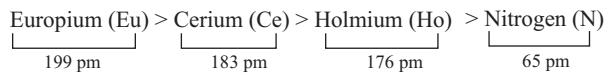
Gd^{3+} have half-filled $4f$ -orbitals.

La^{3+} have no electron in $4f$ -orbitals.

Lu^{3+} have fully-filled $4f$ -orbitals.

Only Sm^{3+} contain $4f^5$. The electrons can easily undergoes excitation. That result in a formation of colour.

10. The correct order of atomic radii is

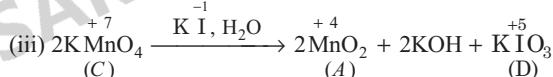
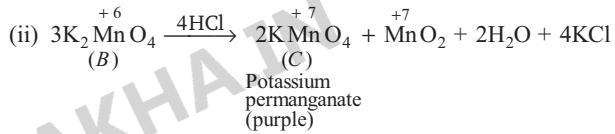
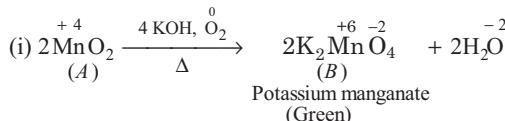


Note

- (i) N being the member of p -block and second period, have the smallest radii.
- (ii) Rest of all the 3 members are lanthanides with Eu having stable half-filled configuration thus with bigger size than rest two.
- (iii) Among Ce and Ho, Ce has larger size which can be explained on the basis of “**Lanthanoid contraction**”.

11. When $MnO_2(A)$ is fused with alkali in presence of air then potassium manganate (B) is formed. Potassium manganate (B) is of green colour which disproportionates in a neutral or acidic solution to produce potassium permanganate (C). Potassium permanganate (C) in presence of acidic medium oxidises iodide to iodate.

The reaction can be shown as:



Thus, A and D are MnO_2 and KIO_3 respectively.

12. The most stable oxidation states in the compounds of the given transition metals of $3d$ -series are,

$$\text{Sc : } +3; \text{ Ti : } +3, +4; \text{ V : } +2, +3, +4, +5; \text{ Cu : } +1, +2$$

The electronic configuration of Sc ($Z = 21$) is $[\text{Ar}] 3d^1, 4s^2$.

Due to the presence of only one $3d$ -electron (no pairing energy) and two $4s$ -electrons, they easily ionise to achieve most stable +3 oxidation state.

13. In the lanthanoid series, atomic number of fourteen $4f$ -block elements ranges from 58 (Ce) to 71 (Lu).

Ytterbium, $Yb(Z = 70)$ has electronic configuration : $[\text{Xe}] 4f^{14} 6s^2$. So, the 71th electron of lutetium, Lu ($Z = 71$) should enter into $5d$ orbital and its (here, Lu is ‘ X ’) electronic configuration will be : $[\text{Xe}] 4f^{14} 5d^1 6s^2$. It happens so, because f -block elements have general electronic configuration, $(n-2)f^{1-14}(n-1)d^{1-10}ns^2$. Therefore, option (c) is correct.

14. Lanthanoid contraction in the lanthanoid series takes place due to the presence of electron(s) in the $4f$ -orbitals. f -orbitals have poor shielding effect. As a result, the effective nuclear charge will be more experienced by the $5d$ and $6s$ -electrons and it will cause contraction or decrease in both atomic and ionic radii.

15. For transition metals,

$$\Delta H_{\text{Atomisation}}^\circ \propto \text{Strength of metallic bonding}$$

$$\propto \text{Number of unpaired electrons in the metal atom}$$

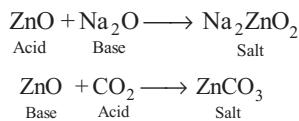
For the given 3d-transition metals,

V	Fe	Cu	Zn
$3d^34s^2$	$3d^64s^2$	$3d^{10}4s^1$	$3d^{10}4s^0$
$n = 3$	$n = 4$	$n = 0$	$n = 0$
[∴ n = no. of unpaired electrons]			

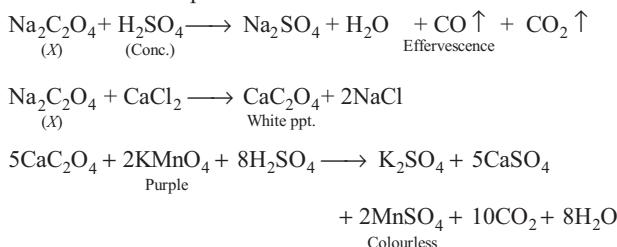
$$\Delta^{\circ}H_{\text{Atomisation}} \text{ (kJ mol}^{-1}\text{)} = 515 \quad 418 \quad 339 \quad 130$$

So, absence of unpaired d -electrons and larger size of Zn atoms, make the crystal lattice of Zn less closely packed.

16. Zinc oxide (ZnO) when react with Na₂O it act as acid while with CO₂ it act as base. Therefore, it is an amphoteric oxide.



17. The reaction takes place as follows

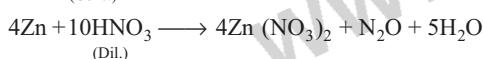


Hence, X is Na₂C₂O₄.

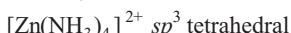
18. $\text{Zn}_{\text{Amphoteric}} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$

19. Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. CrO₂ is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

20. $\text{Zn} + 4\text{HNO}_3 \xrightarrow[\text{(Conc.)}]{\text{}} \text{Zn}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$



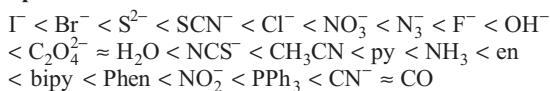
21. $[\text{Ni}(\text{NH}_3)_6]^{2+}$ sp³d² octahedral



22. Zn₂[Fe(CN)₆]₃, K₃[Co(NO₂)₆] and (NH₄)₃As [Mo₃O₁₀]₄ show colour due to d-d transition while BaCrO₄ is coloured due to charge transfer phenomenon.

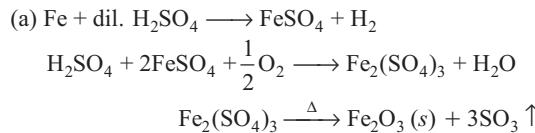
Further according to spectrochemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO₂, NH₄⁺, O²⁻ etc., ligands show yellow colour while CN⁻ forces the complex to impart white colour.

Spectrochemical series



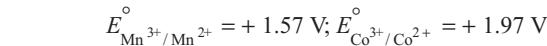
23. **PLAN** Analyse each reaction given in the question and choose the correct answer on the basis of oxidation state and stability of iron compounds. Use the concept of Ellingham diagram to solve this problem.

The correct reactions are as follows:



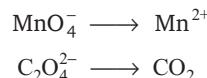
The given reaction is incorrect in question

24. SRP value normally increases from left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. e.g.

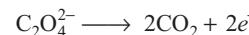
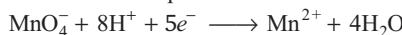


Thus, $E_{\text{M}^{3+}/\text{M}^{2+}}^{\circ}$ is highest for Co.

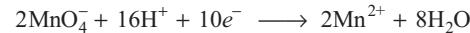
25. The half equations of the reaction are



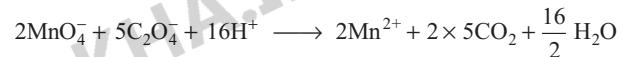
The balanced half equations are



On equating number of electrons, we get



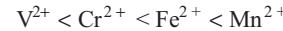
On adding both the equations, we get



Thus x , y and z are 2, 5 and 16 respectively.

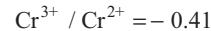
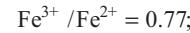
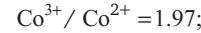
26. (a) V²⁺ = 3 unpaired electrons
Cr²⁺ = 4 unpaired electrons
Mn²⁺ = 5 unpaired electrons
Fe²⁺ = 4 unpaired electrons

Hence, the order of paramagnetic behaviour should be



- (b) Ionic size decreases from left to right in the same period.

- (c) (As per data from NCERT)



Sc³⁺ is highly stable (It does not show + 2).

- (d) The oxidation states increases as we go from group 3 to group 7 in the same period.

27. The aqueous solution of CuSO₄ consist of the complex [Cu(H₂O)₄]²⁺ ion which absorbed in orange-red region and impart deep blue colouration to solution.

28. KMnO₄ is itself a very strong oxidising agent, O₃ cannot oxidise it.

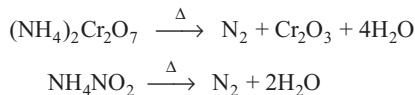
29. In CuCl₂, Cu²⁺ has d⁹ configuration, exhibit d-d transition and show colour. Similarly in VOCl₂, V⁴⁺ has d¹ configuration, can exhibit d-d transition and show colour.



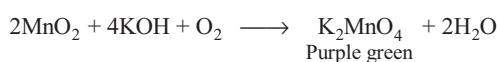
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31. In MnO_4^- , Mn^{7+} is in highest oxidation state possible for Mn. In CrO_2Cl_2 , Cr^{6+} is in highest oxidation state possible for Cr.

32. Ammonium dichromate on heating produces $\text{N}_2(g)$. NH_4NO_2 also gives N_2 on heating :



33. K_2MnO_4 (purple green) is formed which is the first step of preparation of KMnO_4 .



34. In CrO_2Cl_2 , Cr is in +6 oxidation state because Cl is in (-1) and, oxygen is in (-2) oxidation states.



36. The structure of dichromate ion is :

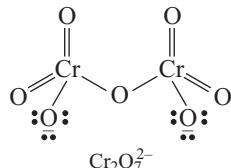


Exhibit resonance phenomena. Except the bridged Cr—O—Cr, all Cr—O bonds are equivalent.

37. $\text{Cu}^{2+}(3d^9)$ undergo $d-d$ transition, exhibit colour.

38. Ammonium dichromate $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]$ on heating decomposes producing green powder of Cr_2O_3 and $\text{N}_2(g)$ is evolved.

39. Fe_2O_3 is a basic oxide, neutralised by HCl spontaneously forming FeCl_3 and water.

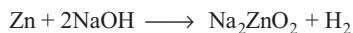
40. Zinc coated with copper is used as a reducing agent.

41. The valence shell electronic configuration of Ni^{2+} is :



42. German silver is an alloy of copper (56%), Zn (24%) and Ni(20%).

43. Zn being amphoteric, dissolves in both acid and base :



44. Paramagnetism is a form of magnetism whereby some materials are attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field. So, magnetic balance shows downward deflection. While diamagnetic substance shows repulsion in magnetic field and magnetic balance shows upward deflection.

(a) $X = \text{H}_2\text{O}$ (l)

(Water has no unpaired electrons and is thus diamagnetic). Hence, statement (a) is correct.

(b) $X = \text{K}_4[\text{Fe}(\text{CN})_6](s)$

(CN is a strong field ligand which forces the d -orbital electrons to pair up ($t_{2g}^6 e_g^0$) and making it diamagnetic).

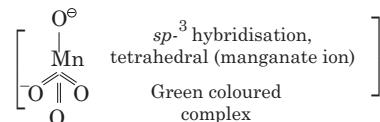
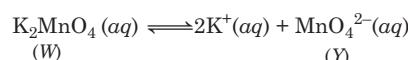
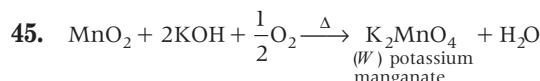
Hence, statement (b) is correct

(c) $X = \text{O}_2(g)$

[Here, $\text{O}_2(g)$ is paramagnetic due to two-unpaired electrons present in π^* (antibonding orbitals). Hence, statement (c) is correct.

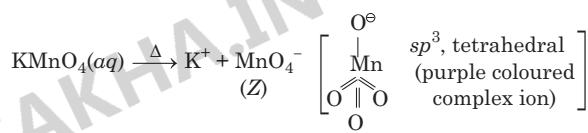
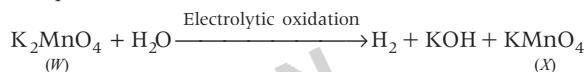
(d) $X = \text{C}_6\text{H}_6(l)$

(Here, C_6H_6 is diamagnetic due to presence of 0 unpaired electrons). Hence, statement (d) is incorrect.

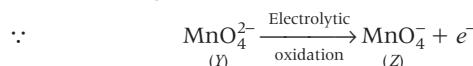


MnO_4^{2-} ion has one unpaired electrons, therefore it gives $d-d$ transition to form green colour. Y complex has paramagnetic nature due to presence of one unpaired electron.

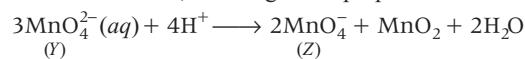
In aqueous solution,



MnO_4^- ions gives charge transfer spectrum in which a fraction of electronic charge is transferred between the molecular entities.



In acidic medium, Y undergoes disproportionation reaction.

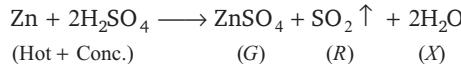


MnO_4^{2-} and MnO_4^- both ions form π -bonding between p -orbitals

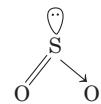
(Y) (Z) of oxygen and d -orbitals of manganese.

Thus, options (a, c, d) are correct.

46. When Zn react with hot conc. H_2SO_4 then SO_2 is released and ZnSO_4 is obtained.

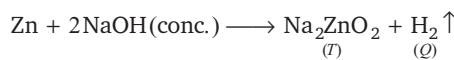


R(SO_2) molecule is V-Shaped



Thus, option (b) is correct.

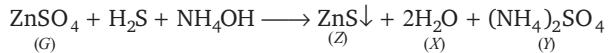
When Zn is react with conc. NaOH then H_2 gas is evolved and Na_2ZnO_2 is obtained.



In ground state, H—H (Q) (bond order = 1)
Thus, option (c) is correct.

The oxidation state of Zn in $T(\text{Na}_2\text{ZnO}_2)$ is +2

Thus, option (a) is incorrect.



ZnS (Z) compound is dirty white coloured.

Thus, option (d) is correct.

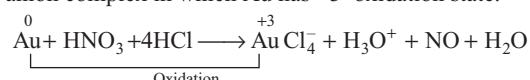
47. The explanation of given statements are as follows:

(a) *Aqua-regia* is prepared by mixing conc. HCl and conc. HNO_3 in 3:1 (v/v) ratio and is used in oxidation of gold and platinum. Hence, option (a) is correct.

(b) Yellow colour of *aqua-regia* is due to its decomposition into NOCl (orange yellow) and Cl_2 (greenish yellow).

Hence, option (b) is correct.

(c) When gold reacts with *aqua-regia* then it produces AuCl_4^- anion complex in which Au has +3 oxidation state.



Hence, option (c) is correct.

(d) Reaction of gold with *aqua-regia* produces NO gas in absence of air.

Hence, option (d) is incorrect.

48. In aqueous solution Cr^{2+} ($3d^4$) acts as a reducing agent, oxidising itself to Cr^{3+} ($3d^3$) that gives a completely half-filled t_{2g} level in octahedral ligand field of H_2O .

(b) Mn^{3+} ($3d^4$) is an oxidising agent as it is reduced to Mn^{2+} ($3d^5$), a completely half-filled stable configuration.

(c) Both Cr^{2+} and Mn^{3+} have d^4 configuration.

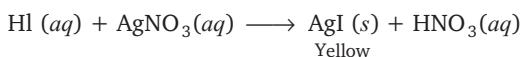
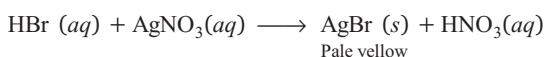
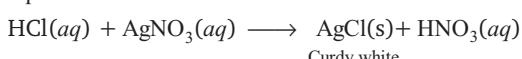
(d) $3d^4 \text{Cr}^{2+}(aq) \xrightarrow{\text{R.A.}} \text{Cr}^{3+}(aq) + e^-$

Hence (d) is wrong statement.

49. H_2O_2 is alkaline medium acts as reducing agent, reduces Fe^{3+} to Fe^{2+} . In acidic medium the same H_2O_2 oxidises Fe^{2+} to Fe^{3+} .

50. Solubilities of silver halides in water decreases from fluoride (AgF) to iodide (AgI). Silver fluoride is readily soluble in water, hence when AgNO_3 solution is added to HF solution (HF being weak acid, its solution maintains very low concentration of F^-) no precipitate of AgF is formed.

HCl, HBr and HI being all strong acids, forms precipitates of AgCl , AgBr and AgI when AgNO_3 solution is added to their aqueous solution.



The solubilities decrease from AgCl to AgI , AgCl dissolves in aqueous ammonia, AgBr dissolves only slightly in concentrated ammonia while AgI does not dissolve in ammonia solution.

$\text{Na}_2\text{S}_2\text{O}_3$ solution dissolves all three, AgCl , AgBr , AgI by forming complex $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ as $\text{S}_2\text{O}_3^{2-}$ is a stronger complexing agent than ammonia.

51. In neutral medium



In alkaline medium



In acidic medium



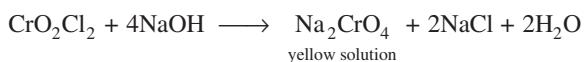
52. $\text{Cr} : [\text{Ar}]3d^5 4s^1$

Magnetic quantum number : $-l, \dots, 0, \dots, +l$.

$\text{Ag}(4d^{10} 5s^1)$ All paired electrons have opposite spin. The last one has unpaired spin.

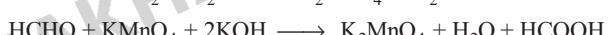


Chromyl chloride
(red vapour)



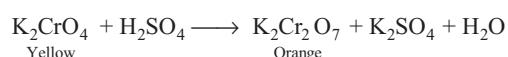
54. Brass = Cu and Zn Gun metal = Cu, Sn, Zn
Bronze = Cu and Sn Type metal = Pb, Sn, Sb

55. Co^{2+} ($3d^7$) and Cr^{3+} ($3d^3$) have allowed $d-d$ transition, therefore produces coloured aqueous solution.



57. Both Statement I and Statement II are independently true but Statement II is not the correct explanation of Statement I. Diamagnetism is due to lack of unpaired electron in Zn^{2+} ($3d^{10}$).

58. Statement I is true but Statement II is false :



In both K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, chromium is in +6 oxidation state.

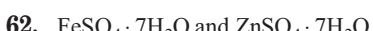
59. $Y = +3, 2\text{Ba} = 2 \times 2 = 4$

$$7 \cdot O = 7 \times (-2) = -14$$

$$3 + 4 + (-14) + 3x = 0 \Rightarrow x = + \frac{7}{3}$$

60. $3d^5 4s^1$

61. Rochelle salt.

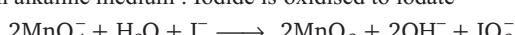


63. PbO_2 , a strong oxidising agent, oxidises Mn^{2+} to MnO_4^- .

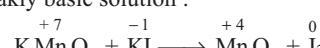
64. Zn^{2+} ($3d^{10}$) has no unpaired electron—diamagnetic.

65. Cu cannot reduce Fe^{2+}

66. In alkaline medium : Iodide is oxidised to iodate



But, in weakly basic solution :

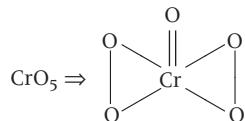
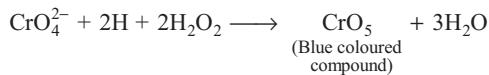


Eq. of KMnO_4 = Eq. of I_2

$$4 \times 3 = n \times 2 \Rightarrow n = 6$$

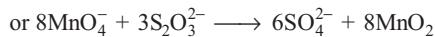
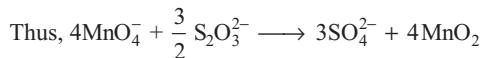
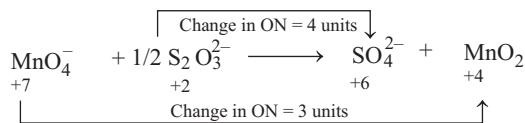
258 Transition and Inner-Transition Elements

67. When a solution of K_2CrO_4 is treated with amyl alcohol and acidified H_2O_2 , the layer of amyl alcohol turns blue because acidified H_2O_2 converts K_2CrO_4 to CrO_5 to give the blue colouration,



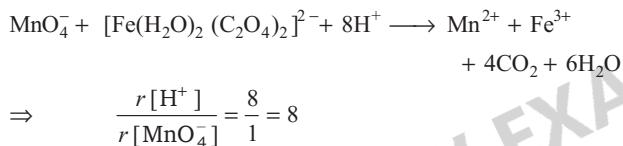
Number of oxygen atom bonded with chromium with single bond is (4).

68. In neutral or faintly alkaline solution, MnO_4^- is reduced to MnO_2 and $S_2O_3^{2-}$ is oxidised to SO_4^{2-} .



Thus, moles of SO_4^{2-} formed by 8 moles of MnO_4^- = 6

69. The balanced redox reaction is



70. Acidified $K_2Cr_2O_7$, $CuSO_4$, H_2O_2 , Cl_2 , O_3 , $FeCl_3$ and HNO_3 oxidise aq. iodide to iodine. Alkaline $KMnO_4$ oxidises aq. iodide to IO_3^- .

$Na_2S_2O_3$ is a strong reducing agent which on reaction with I_2 produces I^- .

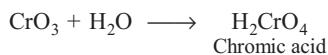


Therefore, no reaction takes place between $Na_2S_2O_3$ and iodide ion.

Hence, correct integer is (7).

71. $A = [Ti(H_2O)_6]^{3+}$ and $M = Ti$, $B = TiO_2$, $Ti(IV)$ has no electron in $3d$ -orbital, no $d-d$ transition is possible, therefore MC_4 is colourless. In A , there is one electron in $3d$ -orbital and its $d-d$ transition is responsible for colour.

72. CrO_3 is anhydride of chromic acid :



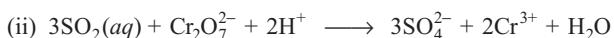
73. $\mu = \sqrt{n(n+2)}$ BM where 'n' is number of unpaired electrons.

$$1.73 = \sqrt{n(n+2)} \Rightarrow n = 1; V^{4+} = 3d^1$$

74. (i) $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$

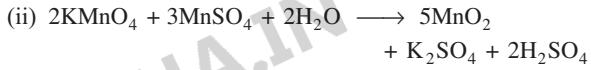


75. (i) $3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$

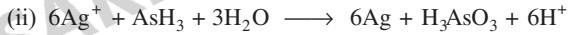


76. $(NH_4)_2S_2O_8 + 2H_2O + MnSO_4 \longrightarrow MnO_2 + 2H_2SO_4 + (NH_4)_2SO_4$

77. (i) $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 4NaHSO_4 + 3H_2O + 2KHSO_4$

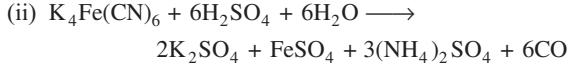


78. (i) $2Mn^{2+} + 5PbO_2 + 4H^+ \longrightarrow 2MnO_4^- + 2H_2O + 5Pb^{2+}$



79. Most transition metals have partially filled d -orbitals which absorb in visible region and undergo $d-d$ transition, which is responsible for colour.

80. (i) $2KMnO_4 + 4KOH + MnO_2 \longrightarrow 3K_2MnO_4 + 2H_2O$



81. Potassium permanganate can be prepared from MnO_2 under the following conditions :



82. (i) $4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$



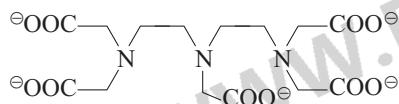
18

Coordination Compounds

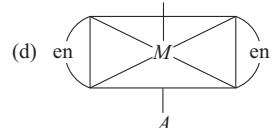
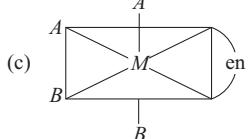
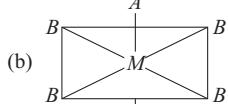
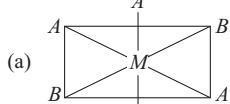
Topic 1 Nomenclature and Isomerism of Coordination Compounds

Objective Questions I (Only one correct option)

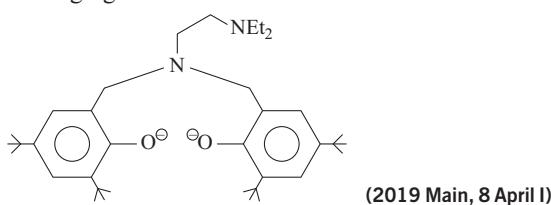
1. If AB_4 molecule is a polar molecule, a possible geometry of AB_4 is
(a) square pyramidal (b) square planar
(c) rectangular planar (d) tetrahedral
2. The coordination numbers of Co and Al in $[\text{CoCl}(\text{en})_2]\text{Cl}$ and $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$, respectively, are (en = ethane-1, 2-diamine)
(a) 5 and 3 (b) 3 and 3 (c) 6 and 6 (d) 5 and 6
3. The species that can have a *trans*-isomer is (en = ethane-1, 2-diamine, ox = oxalate)
(a) $[\text{Pt}(\text{en})\text{Cl}_2]$ (b) $[\text{Cr}(\text{en})_2(\text{ox})]^+$
(c) $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ (d) $[\text{Zn}(\text{en})\text{Cl}_2]$
4. The maximum possible denticities of a ligand given below towards a common transition and inner-transition metal ion, respectively, are
(a) 8 and 8 (b) 8 and 6 (c) 6 and 6 (d) 6 and 8



5. The one that will show optical activity is (en = ethane-1, 2-diamine)
(a)



6. The following ligand is



- (a) hexadentate (b) tetridentate
(c) bidentate (d) tridentate
7. The total number of isomers for a square planar complex $[\text{M}(\text{F})(\text{Cl})(\text{SCN})(\text{NO}_2)]$ is
(a) 12 (b) 16 (c) 4 (d) 8
8. The oxidation states of Cr, in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{C}_6\text{H}_6)_2]$, and $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O}_2)(\text{O}_2)(\text{NH}_3)]$ respectively are
(a) +3, +4 and +6 (b) +3, +2 and +4
(c) +3, 0 and +6 (d) +3, 0 and +4
9. Consider the following reaction and statements :
 $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+ + \text{Br}^- \longrightarrow [\text{Co}(\text{NH}_3)_3\text{Br}_3] + \text{NH}_3$
- I. Two isomers are produced if the reactant complex ion is a *cis*-isomer.
- II. Two isomers are produced if the reactant complex ion is a *trans*-isomer.
- III. Only one isomer is produced if the reactant complex ion is a *trans*-isomer.
- IV. Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are

(2018 Main)

- (a) (I) and (II) (b) (I) and (III)
(c) (III) and (IV) (d) (II) and (IV)

10. Which one of the following complexes shows optical isomerism?
(a) *cis* $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (b) *trans* $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
(c) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (d) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
11. The number of geometric isomers that can exist for square planar $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ is (py = pyridine).
(a) 2 (b) 3 (c) 4 (d) 6
12. Which of the following complex species is not expected to exhibit optical isomerism?
(a) $[\text{Co}(\text{en})_3]^{3+}$ (b) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
(c) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (d) $[\text{Co}(\text{en})(\text{NH}_3)\text{Cl}_2]^+$

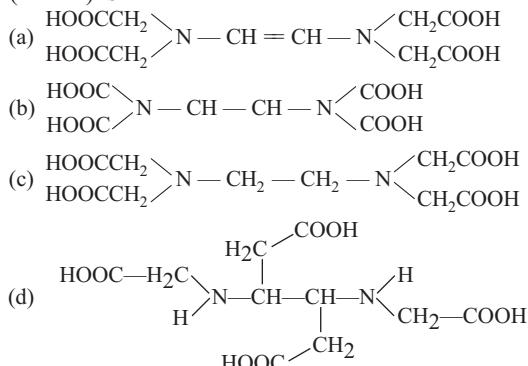
13. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is
(a) tetraquadiaminocobalt (III) chloride
(b) tetraquadiaminocobalt (III) chloride
(c) diaminetetraaquacobalt (III) chloride
(d) diamininetetraaquacobalt (III) chloride

260 Coordination Compounds

14. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O , respectively, are (2011)

- (a) octahedral, tetrahedral and square planar
- (b) tetrahedral, square planar and octahedral
- (c) square planar, tetrahedral and octahedral
- (d) octahedral, square planar and octahedral

15. The correct structure of ethylenediaminetetraacetic acid (EDTA) is (2010)



16. The ionisation isomer of $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}(\text{NO}_2)]\text{Cl}$ is (2010)

- (a) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$
- (b) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
- (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$
- (d) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$

17. The IUPAC name of $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$ is (2008, 3M)

- (a) Tetrachloronickel (II)-tetraamminenickel (II)
- (b) Tetraamminenickel (II)-tetrachloronickel (II)
- (c) Tetraamminenickel (II)-tetrachloronickelate (II)
- (d) Tetrachloronickel (II)-tetraamminenickelate (0)

18. Which kind of isomerism is shown by $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}_2$? (2005, 1M)

- (a) Geometrical and ionisation
- (b) Optical and ionisation
- (c) Geometrical and optical
- (d) Geometrical only

Objective Questions II

(One or more than one correct option)

19. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is/are (2013 Adv.)

- (a) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
- (b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$
- (c) $[\text{CoBr}_2\text{Cl}_2]^{2-}$ and $[\text{PtBr}_2\text{Cl}_2]^{2-}$
- (d) $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$

20. The compound(s) that exhibit(s) geometrical isomerism is/are (2009)

- (a) $[\text{Pt}(\text{en})\text{Cl}_2]$
- (b) $[\text{Pt}(\text{en})_2]\text{Cl}_2$
- (c) $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$
- (d) $[\text{Pt}(\text{NH}_3)_2]\text{Cl}_2$

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

- (c) Statement I is true; Statement II is false.
- (d) Statement I is false; Statement II is true.

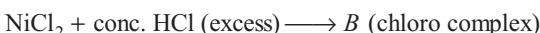
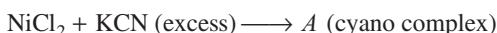
21. **Statement I** The geometrical isomers of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ are optically inactive.

- Statement II** Both geometrical isomers of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ possess axis of symmetry. (2008, 3M)

Passage Based Question

Passage

The coordination number of Ni^{2+} is 4.



22. The IUPAC name of *A* and *B* are (2006, 3 × 4M = 12M)

- (a) potassium tetracyanonicelate (II), potassium tetrachloronickelate (II)
- (b) tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II)
- (c) tetracyanonickel (II), tetrachloronickel (II)
- (d) potassium tetracyanonickel (II), potassium tetrachloronickel (II)

Fill in the Blank

23. The type of magnetism exhibited by $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion is ... (1994, 1M)

Integer Answer Type Questions

24. The possible number of geometrical isomers for the complex $[\text{CoL}_2\text{Cl}_2]^-$ ($L = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$) is (are) ... (2016 Adv.)

25. Among the complex ions, $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{—NH}_2)_2\text{Cl}_2]^+$, $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$, $[\text{Co}(\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ the number of complex ion(s) that show(s) *cis-trans* isomerism is (2015 Adv.)

26. The volume (in mL) of 0.1 M AgNO_3 required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$, as silver chloride is close to (2011)

27. Total number of geometrical isomers for the complex $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$ is (2010)

Subjective Questions

28. Write the formulae of the following complexes :

- (i) Pentamminechlorocobalt (III) ion
- (ii) Lithium tetrahydridoaluminate (III) (1997, 2M)

29. Write the IUPAC name for $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$. (1996, 1M)

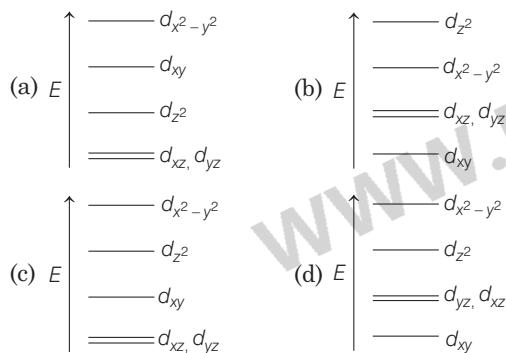
30. Write the IUPAC name of the following compounds :

- (i) $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
- (ii) $\text{K}_3[\text{Cr}(\text{CN})_6]$ (1995, 2M)

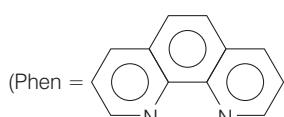
Topic 2 Bonding and Important Property of Coordination Compounds

Objective Questions I (Only one correct option)

1. Consider that a d^6 metal ion (M^{2+}) forms a complex with *aqua* ligands and the spin only magnetic moment of the complex is 4.90 BM. The geometry and the crystal field stabilisation energy of the complex is (2020 Main, 2 Sep I)
- tetrahedral and $-1.6\Delta_t + 1P$
 - octahedral and $-2.4\Delta_o + 2P$
 - octahedral and $-1.6\Delta_o$
 - tetrahedral and $-0.6\Delta_t$
2. The d -electron configuration of $[\text{Ru}(\text{en})_3]\text{Cl}_2$ and $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$, respectively are (2020 Main, 3 Sep II)
- $t_{2g}^6 e_g^0$ and $t_{2g}^6 e_g^0$
 - $t_{2g}^6 e_g^0$ and $t_{2g}^4 e_g^2$
 - $t_{2g}^4 e_g^2$ and $t_{2g}^6 e_g^0$
 - $t_{2g}^4 e_g^2$ and $t_{2g}^4 e_g^2$
3. The compound used in the treatment of lead poisoning is (2019 Main, 12 April II)
- D-penicillamine
 - desferrioxime-B
 - cis-platin
 - EDTA
4. Complete removal of both the axial ligands (along the z -axis) from an octahedral complex leads to which of the following splitting patterns? (relative orbital energies not on scale). (2019 Main, 12 April I)



5. The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is



- Ignore pairing energy (2019 Main, 12 April I)
- $[\text{Co}(\text{phen})_3]^{2+}$
 - $[\text{Ni}(\text{phen})_3]^{2+}$
 - $[\text{Zn}(\text{phen})_3]^{2+}$
 - $[\text{Fe}(\text{phen})_3]^{2+}$

6. The crystal field stabilisation energy (CFSE) of $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ and $\text{K}_2[\text{NiCl}_4]$, respectively, are (2019 Main, 10 April II)

- $-0.4\Delta_o$ and $-1.2\Delta_t$
- $-0.4\Delta_o$ and $-0.8\Delta_t$
- $-2.4\Delta_o$ and $-1.2\Delta_t$
- $-0.6\Delta_o$ and $-0.8\Delta_t$

7. The incorrect statement is (2019 Main, 10 April II)
- the gemstone, ruby, has Cr^{3+} ions occupying the octahedral sites of beryl
 - the color of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ is violet as it absorbs the yellow light
 - the spin only magnetic moments of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ are nearly similar
 - the spin only magnetic moment of $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is 2.83 BM
8. Three complexes, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ (I), $[\text{Co}(\text{NH}_3)_5 \text{H}_2\text{O}]^{3+}$ (II) and $[\text{Co}(\text{NH}_3)_6]^{3+}$ (III) absorb light in the visible region. The correct order of the wavelength of light absorbed by them is (2019 Main, 10 April I)
- II > I > III
 - I > II > III
 - III > I > II
 - III > II > I
9. The degenerate orbitals of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ are (2019 Main, 9 April I)
- d_{z^2} and d_{xz}
 - d_{xz} and d_{yz}
 - $d_{x^2-y^2}$ and d_{xy}
 - d_{yz} and d_{z^2}
10. The calculated spin only magnetic moments (BM) of the anionic and cationic species of $[\text{Fe}(\text{H}_2\text{O})_6]_2^-$ and $[\text{Fe}(\text{CN})_6]^{4-}$, respectively, are (2019 Main, 8 April II)
- 0 and 4.9
 - 2.84 and 5.92
 - 0 and 5.92
 - 4.9 and 0
11. The compound that inhibits the growth of tumors is (2019 Main, 8 April II)
- $\text{trans-}[\text{Pt}(\text{Cl})_2(\text{NH}_3)_2]$
 - $\text{cis-}[\text{Pd}(\text{Cl})_2(\text{NH}_3)_2]$
 - $\text{cis-}[\text{Pt}(\text{Cl})_2(\text{NH}_3)_2]$
 - $\text{trans-}[\text{Pd}(\text{Cl})_2(\text{NH}_3)_2]$
12. The correct order of the spin only magnetic moment of metal ions in the following low spin complexes, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ru}(\text{NH}_3)_6]^{3+}$, and $[\text{Cr}(\text{NH}_3)_6]^{2+}$, is (2019 Main, 8 April I)
- $\text{Cr}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+} > \text{V}^{2+}$
 - $\text{V}^{2+} > \text{Cr}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+}$
 - $\text{V}^{2+} > \text{Ru}^{3+} > \text{Cr}^{2+} > \text{Fe}^{2+}$
 - $\text{Cr}^{2+} > \text{V}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+}$
13. The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is (2019 Main, 8 April II)
- CN^-
 - ethylenediamine
 - NCS^-
 - CO
14. The pair of metal ions that can give a spin-only magnetic moment of 3.9 BM for the complex $[\text{M}(\text{H}_2\text{O})_6]\text{Cl}_2$, is (2019 Main, 12 Jan I)
- Co^{2+} and Fe^{2+}
 - Cr^{2+} and Mn^{2+}
 - V^{2+} and Co^{2+}
 - V^{2+} and Fe^{2+}
15. The metal d -orbitals that are directly facing the ligands in $\text{K}_3[\text{Co}(\text{CN})_6]$ are (2019 Main, 12 Jan I)
- d_{xz} , d_{yz} and d_{z^2}
 - $d_{x^2-y^2}$ and d_{z^2}
 - d_{xy} , d_{xz} and d_{yz}
 - d_{xz} and $d_{x^2-y^2}$

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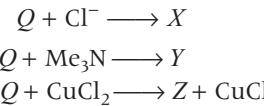
- 34.** Consider the following complex ions, P , Q and R .
 $P = [\text{FeF}_6]^{3-}$, $Q = [\text{V}(\text{H}_2\text{O})_6]^{2+}$ and $R = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 The correct order of the complex ions, according to their spin-only magnetic moment values (in BM) is (2013 Adv.)
- (a) $R < Q < P$ (b) $Q < R < P$
 (c) $R < P < Q$ (d) $Q < P < R$
- 35.** $\text{NiCl}_2 \{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic) the coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states respectively, are (2012)
- (a) tetrahedral and tetrahedral
 (b) square planar and square planar
 (c) tetrahedral and square planar
 (d) square planar and tetrahedral
- 36.** Among the following complexes ($K-P$), (2011)
- $\text{K}_3[\text{Fe}(\text{CN})_6]$ (K), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (L),
 $\text{Na}_3[\text{Co}(\text{ox})_3]$ (M), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (N),
 $\text{K}_2[\text{Pt}(\text{CN})_4](\text{O})$, $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (P)
 the diamagnetic complexes are
- (a) K, L, M, N (b) K, M, O, P
 (c) L, M, O, P (d) L, M, N, O
- 37.** The complex showing a spin only magnetic moment of 2.82 BM is (2010)
- (a) $\text{Ni}(\text{CO})_4$ (b) $[\text{NiCl}_4]^{2-}$
 (c) $\text{Ni}(\text{PPh}_3)_4$ (d) $[\text{Ni}(\text{CN})_4]^{2-}$
- 38.** The spin only magnetic moment value (in Bohr magneton units) of $\text{Cr}(\text{CO})_6$ is (2009)
- (a) 0 (b) 2.84 (c) 4.90 (d) 5.92
- 39.** Among the following, the coloured compound is (2008, 3M)
- (a) CuCl (b) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (c) CuF_2 (d) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$
- 40.** Both $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes respectively, are (2008, 3M)
- (a) sp^3, sp^3 (b) $sp^3, d\text{sp}^2$
 (c) $d\text{sp}^2, sp^3$ (d) $d\text{sp}^2, d\text{sp}^2$
- 41.** Among the following metal carbonyls, the C—O bond order is lowest in (2007, 3M)
- (a) $[\text{Mn}(\text{CO})_6]^+$ (b) $[\text{Fe}(\text{CO})_5]$
 (c) $[\text{Cr}(\text{CO})_6]$ (d) $[\text{V}(\text{CO})_6]^-$
- 42.** If the bond length of CO bond in carbon monoxide is 1.128 Å, then what is the value of CO bond length in $\text{Fe}(\text{CO})_5$? (2006)
- (a) 1.15 Å (b) 1.128 Å (c) 1.72 Å (d) 1.118 Å
- 43.** Spin only magnetic moment of the compound $\text{Hg}[\text{Co}(\text{SCN})_4]$ is (2004, 1M)
- (a) $\sqrt{3}$ (b) $\sqrt{15}$ (c) $\sqrt{24}$ (d) $\sqrt{8}$
- 44.** The compound having tetrahedral geometry is (2004, 1M)
- (a) $[\text{Ni}(\text{CN})_4]^{2-}$ (b) $[\text{Pd}(\text{CN})_4]^{2-}$
 (c) $[\text{PdCl}_4]^{2-}$ (d) $[\text{NiCl}_4]^{2-}$

- 45.** Mixture $X = 0.02$ mole of $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and 0.02 mole of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ was prepared in 2 L of solution.
 1 L of mixture $X +$ excess $\text{AgNO}_3 \rightarrow Y$
 1 L of mixture $X +$ excess $\text{BaCl}_2 \rightarrow Z$
 Number of moles of Y and Z are (2003)
- (a) 0.01, 0.01 (b) 0.02, 0.01 (c) 0.01, 0.02 (d) 0.02, 0.02
- 46.** The complex ion which has no ‘ d ’-electrons in the central metal atom is (2001, 1M)
- (a) $[\text{MnO}_4]^-$ (b) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (c) $[\text{Fe}(\text{CN})_6]^{3-}$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- 47.** The geometry of $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ are (1999, 2M)
- (a) both square planar
 (b) tetrahedral and square planar, respectively
 (c) both tetrahedral
 (d) square planar and tetrahedral, respectively
- 48.** Which of the following is formed when excess of KCN is added to aqueous solution of copper sulphate? (1996, 1M)
- (a) $\text{Cu}(\text{CN})_2$ (b) $\text{K}_2[\text{Cu}(\text{CN})_4]$
 (c) $\text{K}[\text{Cu}(\text{CN})_2]$ (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$
- 49.** Among the following ions, which one has the highest paramagnetism? (1993, 1M)
- (a) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (c) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (d) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- 50.** Amongst $\text{Ni}(\text{CO})_4$, $[\text{Ni}(\text{CN})_4]^{2-}$ and NiCl_4^{2-} (1991, 1M)
- (a) $\text{Ni}(\text{CO})_4$ and NiCl_4^{2-} are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic
 (b) $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $\text{Ni}(\text{CO})_4$ is paramagnetic
 (c) $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{NiCl}_4]^{2-}$ is paramagnetic
 (d) $\text{Ni}(\text{CO})_4$ is diamagnetic and $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic
- 51.** Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by (1988, 2M)
- (a) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (d) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

Objective Question II

(One or more than one correct option)

- 52.** Choose the correct statement(s) among the following: (2020 Adv.)
- (a) $[\text{FeCl}_4]^-$ has tetrahedral geometry.
 (b) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ has 2 geometrical isomers.
 (c) $[\text{FeCl}_4]^-$ has higher spin-only magnetic moment than $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$.
 (d) The cobalt ion in $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ has sp^3d^2 hybridisation.
- 53.** A tin chloride Q undergoes the following reactions (not balanced)



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X is a monoanion having pyramidal geometry. Both *Y* and *Z* are neutral compounds. (2019 Adv.)

Choose the correct option(s).

- (a) There is a coordinate bond in *Y*
- (b) The central atom in *Z* has one lone pair of electrons
- (c) The oxidation state of the central atom in *Z* is + 2
- (d) The central atom in *X* is sp^3 hybridised

54. The correct statement (s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers : Fe = 26, Ni = 28) (2018 Adv.)

- (a) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16
- (b) These are predominantly low spin in nature
- (c) Metal-carbon bond strengthens when the oxidation state of the metal is lowered
- (d) The carbonyl C—O bond weakens when the oxidation state of the metal is increased

55. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ (*en* = $H_2NCH_2CH_2NH_2$) is (are)

- (a) It has two geometrical isomers (2018 Adv.)
- (b) It will have three geometrical isomers, if bidentate ‘en’ is replaced by two cyanide ligands
- (c) It is paramagnetic
- (d) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$

56. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 \cdot 6H_2O(X)$ and NH_4Cl gives an octahedral complex *Y* in the presence of air. In aqueous solution, complex *Y* behaves as 1 : 3 electrolyte. The reaction of *X* with excess HCl at room temperature results in the formation of a blue coloured complex *Z*. The calculated spin only magnetic moment of *X* and *Z* is 3.87 B.M., whereas it is zero for complex *Y*.

Among the following options, which statement(s) is (are) correct? (2017 Adv.)

- (a) The hybridisation of the central metal ion in *Y* is d^2sp^3
- (b) Addition of silver nitrate to *Y* given only two equivalents of silver chloride
- (c) When *X* and *Y* are in equilibrium at 0°C, the colour of the solution is pink
- (d) *Z* is a tetrahedral complex

Numerical Answer Type Question

57. Total number of *cis* N—Mn—Cl bond angles (that is Mn—N and Mn—Cl bonds in *cis* positions) present in a molecule of *cis* $[Mn(en)_2Cl_2]$ complex is

(*en* = $H_2NCH_2CH_2NH_2$) (2019 Adv.)

Assertion and Reason

Read the following questions and answer as per the direction given below :

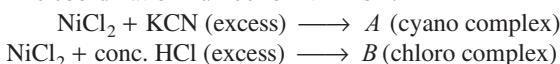
- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
- (c) Statement I is true; Statement II is false.
- (d) Statement I is false; Statement II is true.

58. Statement I $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.

Statement II The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. (2008, 3M)

Passage Based Questions

The coordination number of Ni^{2+} is 4.



59. Predict the magnetic nature of *A* and *B*.

- (a) Both are diamagnetic
- (b) *A* is diamagnetic and *B* is paramagnetic with one unpaired electron
- (c) *A* is diamagnetic and *B* is paramagnetic with two unpaired electrons
- (d) Both are paramagnetic

60. The hybridisation of *A* and *B* are

- | | |
|--------------------|------------------------|
| (a) dsp^2, sp^3 | (b) sp^3, sp^3 |
| (c) dsp^2, dsp^2 | (d) sp^3d^2, d^2sp^3 |

Match the Columns

61. Match each set of hybrid orbitals from List-I with complexes given in List-II.

List-I	List-II
<i>P.</i> dsp^2	1. $[FeF_6]^{4-}$
<i>Q.</i> sp^3	2. $[Ti(H_2O)_3Cl_3]$
<i>R.</i> sp^3d^2	3. $[Cr(NH_3)_6]^{3+}$
<i>S.</i> d^2sp^3	4. $[FeCl_4]^{2-}$
	5. $[Ni(CO)_4]$
	6. $[Ni(CN)_4]^{2-}$

The correct option is

(2018 Adv.)

- (a) *P* → 5; *Q* → 4, 6; *R* → 2, 3; *S* → 1
- (b) *P* → 5, 6; *Q* → 4; *R* → 3; *S* → 1, 2
- (c) *P* → 6; *Q* → 4, 5; *R* → 1; *S* → 2, 3
- (d) *P* → 4, 6; *Q* → 5, 6; *R* → 1, 2; *S* → 3

62. Match each coordination compound in Column I with an appropriate pair of characteristics from Column II and select the correct answer using the codes given below the Columns (*en* = $H_2NCH_2CH_2NH_2$; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78) (2014 Adv.)

Column I	Column II
(A) $[Cr(NH_3)_4Cl_2]Cl$	1. Paramagnetic and exhibits ionisation isomerism
(B) $[Ti(H_2O)_5Cl](NO_3)_2$	2. Diamagnetic and exhibits <i>cis-trans</i> isomerism
(C) $[Pt(en)(NH_3)Cl]NO_3$	3. Paramagnetic and exhibits <i>cis-trans</i> isomerism
(D) $[Co(NH_3)_4(NO_3)_2]NO_3$	4. Diamagnetic and exhibits ionisation isomerism

Codes

A	B	C	D	A	B	C	D
(a) 4	2	3	1	(b) 3	1	4	2
(c) 2	1	3	4	(d) 1	3	4	2

63. Match the complexes in Column I with their properties listed in Column II. (2007, 6M)

Column I	Column II
(A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$	p. Geometrical isomers
(B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	q. Paramagnetic
(C) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$	r. Diamagnetic
(D) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$	s. Metal ion with +2 oxidation state

Fill in the Blank

64. The IUPAC name of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is (1994, 1M)

True/False

65. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. (1989, 1M)
66. The electron density in the xy plane in $3d_{x^2-y^2}$ orbital is zero. (1986, 1M)

Integer Answer Type Questions

67. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [atomic number of Fe = 26] (2015 Adv.)
68. In the complex acetyl bromidodicarbonylbis (triethylphosphine) iron (II), the number of Fe—C bond (s) is (2015 Adv.)
69. EDTA⁴⁻ is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in $[\text{Co}(\text{EDTA})]^+$ complex ion is (2013 Adv.)

Subjective Questions

70. NiCl_2 in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH , giving a bright red colour.

- (a) Draw its structure and show H-bonding
 (b) Give oxidation state of Ni and its hybridisation
 (c) Predict whether it is paramagnetic or diamagnetic (2004, 4M)

71. Write the IUPAC name of the compound $\text{K}_2[\text{Cr}(\text{NO})(\text{CN})_4(\text{NH}_3)]$. Spin magnetic moment of the complex $\mu = 1.73 \text{ BM}$. Give the structure of anion. (2003, 4M)

72. Deduce the structures of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. (2002, 5M)

73. A metal complex having composition $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$ has been isolated in two forms *A* and *B*. The form *A* reacts with AgNO_3 to give a white precipitate readily soluble in dilute aqueous ammonia, whereas *B* gives a pale yellow precipitate soluble in concentrated ammonia.

Write the formula of *A* and *B* and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). (2001, 5M)

74. Draw the structures of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. (2000, 4M)

75. *A*, *B* and *C* are three complexes of chromium (III) with the empirical formula $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$. All the three complexes have water and chloride ion as ligands. Complex *A* does not react with concentrated H_2SO_4 , whereas complexes *B* and *C* lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4 . Identify *A*, *B* and *C*. (1999, 2M)

76. Identify the complexes which are expected to be coloured. Explain
 (i) $[\text{Ti}(\text{NO}_3)_4]$ (ii) $[\text{Cu}(\text{NCCH}_3)]^+\text{BF}_4^-$
 (iii) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (iv) $\text{K}_3[\text{VF}_6]$ (1994, 2M)

77. Give reasons in two or three sentences only for the following :

“The species $[\text{CuCl}_4]^{2-}$ exists, while $[\text{CuI}_4]^{2-}$ does not exist.” (1992, 1M)

Answers

Topic 1

- | | | | |
|---------|---------|---------------------|-----------|
| 1. (a) | 2. (d) | 3. (c) | 4. (d) |
| 5. (c) | 6. (b) | 7. (a) | 8. (c) |
| 9. (b) | 10. (a) | 11. (b) | 12. (c) |
| 13. (d) | 14. (b) | 15. (c) | 16. (b) |
| 17. (c) | 18. (a) | 19. (b,d) | 20. (c,d) |
| 21. (b) | 22. (a) | 23. (paramagnetism) | |
| 24. (5) | 25. (6) | 26. (6) | 27. (3) |

Topic 2

- | | | | |
|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (d) | 4. (a) |
| 5. (d) | 6. (b) | 7. (a) | 8. (b) |
| 9. (b) | 10. (a) | 11. (c) | 12. (b) |
| 13. (c) | 14. (c) | 15. (b) | 16. (a) |
| 17. (d) | 18. (b) | 19. (c) | 20. (d) |
| 21. (c) | 22. (c) | 23. (c) | 24. (c) |
| 25. (a) | 26. (c) | 27. (c) | 28. (d) |
| 29. (a) | 30. (b) | 31. (c) | 32. (b) |

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- | | | | | | | | |
|------------|------------|---------------|---------------|---|---------|---------|---------|
| 33. (b) | 34. (b) | 35. (c) | 36. (c) | 57. (6) | 58. (a) | 59. (c) | 60. (a) |
| 37. (b) | 38. (a) | 39. (c) | 40. (b) | 61. (c) | 62. (b) | | |
| 41. (b) | 42. (a) | 43. (b) | 44. (d) | 63. (A → p, q, s B → p, r, s C → q, s D → q, s) | | | |
| 45. (a) | 46. (a) | 47. (c) | 48. (d) | 64. (hexaammine cobalt (III) chloride) | | 65. (F) | |
| 49. (b) | 50. (c) | 51. (b) | 52. (a,c) | 66. (F) | 67. (4) | 68. (3) | 69. (8) |
| 53. (a, d) | 54. (b, c) | 55. (a, b, d) | 56. (a, b, d) | | | | |

Hints & Solutions

Topic 1 Nomenclature and Isomerism of Coordination Compounds

1. If AB_4 molecule is a polar molecule, a possible geometry of AB_4 is square pyramidal.

All possible structures of AB_4 molecule are as follows:

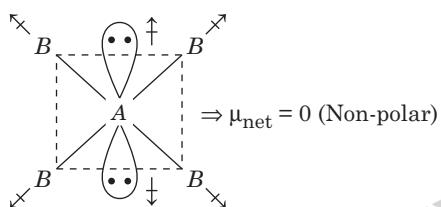
$$(i) AB_4 \Rightarrow L=0 \Rightarrow A \text{ is } sp^3 \text{ (tetrahedral) or}$$

$A \text{ is } dsp^2 \text{ (square planar)}$

\Rightarrow Dipole moment, $\mu = 0$ (Non-polar)

$$(ii) AB_4L_2 \Rightarrow L=2 \Rightarrow A \text{ is } sp^3d^2 \text{ (octahedral)}$$

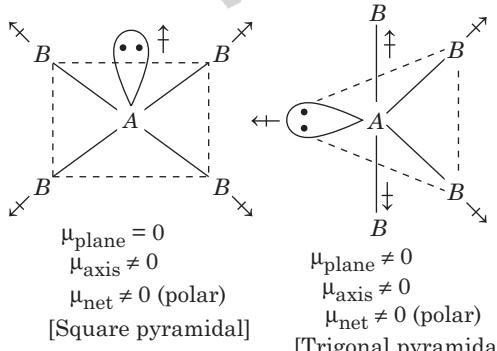
$\Rightarrow \mu = 0$ (Non-polar), because



(Assuming, B is more electronegative than A)

$$(iii) AB_4L \Rightarrow L=1 \Rightarrow A \text{ is } sp^3d \text{ (square pyramidal or trigonal bipyramidal)}$$

$\Rightarrow \mu \neq 0$ (polar), because



So, it can be seen that when AB_4 molecule is a polar molecule then possible geometry of AB_4 is square pyramidal.

2. **Key Idea** The total number of ligands to which the metal is directly attached is called coordination number.

The coordination numbers of Co and Al in $[Co(Cl)(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$ are 5 and 6 respectively.

In first complex, 'en' is a bidentate ligand and 'Cl' is a unidentate ligand.

$[Co(Cl)(en)_2]Cl$, coordination number = $1 + 2 \times 2 = 1 + 4 \Rightarrow 5$

So, the coordination number is 5.

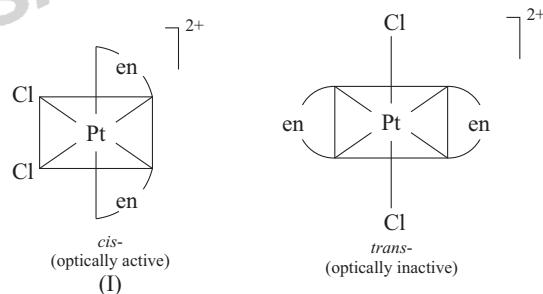
For $K_3[Al(C_2O_4)_3]$, ' $C_2O_4^{2-}$ ' is a bidentate ligand.

Coordination number = $3 \times 2 = 6$.

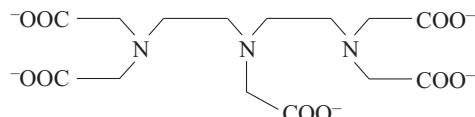
Hence, coordination number is 6.

3. **Key Idea** Square planar complexes of general formulae : $[M(a-a)b_2]$ and $[M(a-a)(b-b)]$ do not show geometrical isomerism. Whereas, an octahedral complex of general formula $[M(a-a)_2b_2]$ can show geometrical (*cis-trans*) isomerism.

$[Pt(en)_2(Cl_2)]^{2+}$ with formula $[M(a-a)_2b_2]$ will show geometrical isomerism as follows:

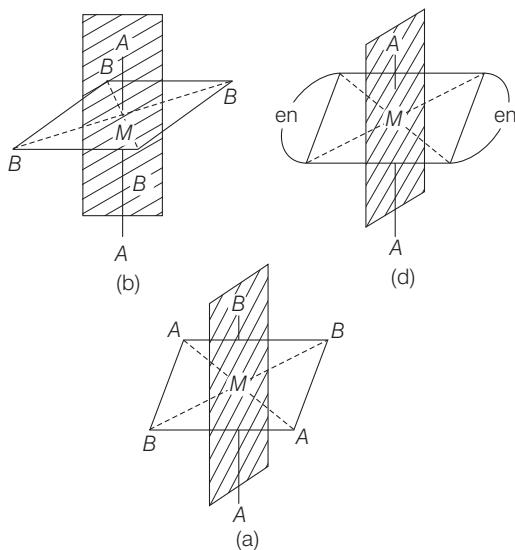


4. The maximum possible dentencies of given ligand towards a common transition and inner transition metal ion, are 6 and 8 respectively.



The given ligand act as hexadentate ligand in transition metal ion because the common oxidation state shown by them is +3. Whereas in case of inner transition metal ion, its denticity is 8 because their common oxidation state is +4.

5. Optical activity is the ability of a chiral molecule to rotate the plane of polarised light, measured by a polarimeter. A chiral molecule does not have any plane of symmetry. If a molecule possess any plane of symmetry, then it is an achiral molecule. Given options (a), (b) and (d) possess plane of symmetry.

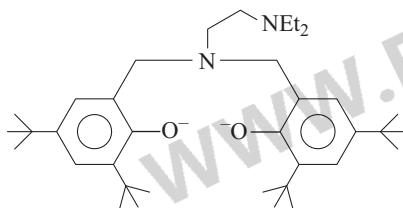


Only molecule (c) does not possess any plane of symmetry. Hence, it is a chiral molecule and shows optical activity.

- 6. Key Idea** Denticity of ligand is defined as donor sites or number of ligating groups.

The given ligand is tetradentate. It contains four donor atoms. It can bind through two nitrogen and two oxygen atom to the central metal ion.

Ligand bound to the central atom or ion through coordinate bond in the coordination entity. It act as a Lewis base. The attacking site of the given ligand is given in bold.



- 7.** A square planar complex of general formula, M_{abcd} gives three geometrical isomers only.

Let, $a = \text{F}^-$, $b = \text{Cl}^-$, $c = \text{SCN}^-$, $d = \text{NO}_2^-$

SCN^- and NO_2^- are ambidentate ligands and they also show linkage isomerism (structural). Considering both linkage and geometrical isomerism.

Total number of possible isomers given by the complex,

$$= 3 \times (2 + 2) = 12$$

- 8.** Let the oxidation state of Cr in all cases is ' x '

(i) Oxidation state of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 $x + (0 \times 6) + (-1 \times 3) = 0$

$$\text{or } x + 0 - 3 = 0 \text{ or } x = +3$$

(ii) Oxidation state of Cr in $[\text{Cr}(\text{C}_6\text{H}_6)_2]$

$$x + (2 \times 0) = 0 \text{ or } x = 0$$

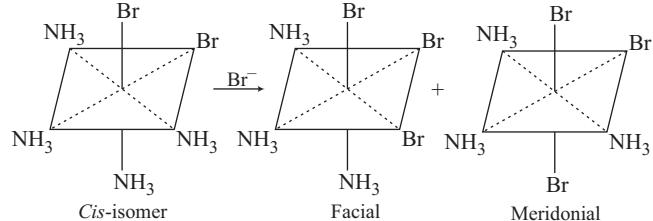
(iii) Oxidation state of Cr in

$$\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)] \\ 1 \times 2 + x + (-1 \times 2) + (-2 \times 2) + (-2) + 0 = 0$$

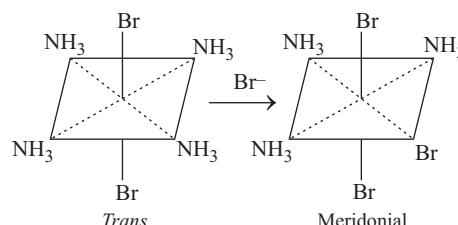
$$\text{or } 2 + x - 2 - 4 - 2 = 0 \text{ or } x - 6 = 0 \\ \text{hence } x = +6$$

Thus, +3, 0 and +6 is the answer.

- 9.** If the reactant is *cis* isomer than following reaction takes place.

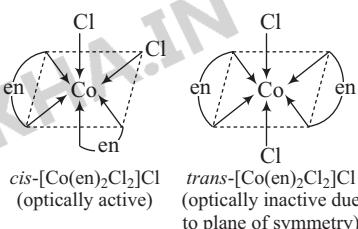


i.e. two isomers are produced. If the reactant is *trans* isomer than following reaction takes place.

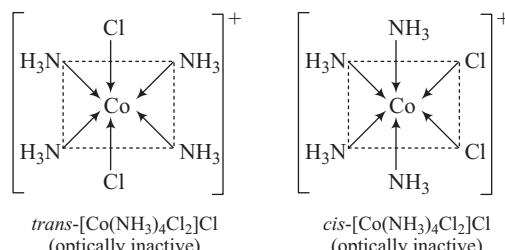


i.e. only 1 isomer is produced. Thus, statement (I) and (III) are correct resulting to option (b) as the correct answer.

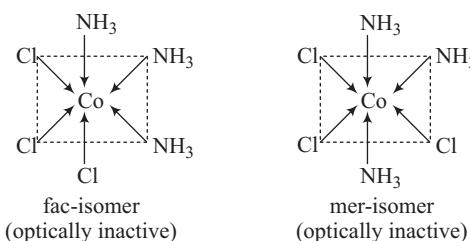
- 10.**



$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ can exist in both *cis* and *trans* forms that are given below:

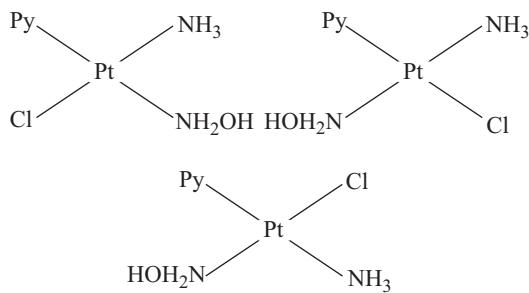


$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.



- 11.** $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ is square planar complex. The structures are formed by fixing a group and then arranging all the groups.

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Hence, this complex shows three geometrical isomers.

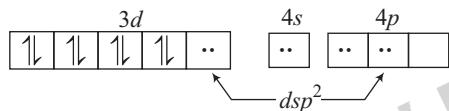
- 12.** Optical isomerism is exhibited by only those complexes which lacks elements of symmetry. $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

- 13.** First of all, the compound has complex positive part “ $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{3+}$ ” therefore, according to IUPAC conventions, positive part will be named first. Secondly, in writing name of complex, ligands are named first in alphabetical order, irrespective of its charge, hence “ammine” will be written prior to “aqua”. Therefore, name of the complex is $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$. Diamminetetraaqua cobalt (III) chloride.

NOTE In alphabetical order, original name of ligands are considered not the initials of prefixes. Also, special precaution should be taken in spelling name of NH_3 ligand as it is ammine.

- 14.** $\text{Ni}^{2+} + 4\text{CN}^- \rightarrow [\text{Ni}(\text{CN})_4]^{2-}$

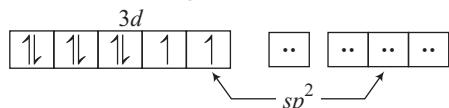
Here, Ni^{2+} has d^8 -configuration with CN^- as strong ligand.



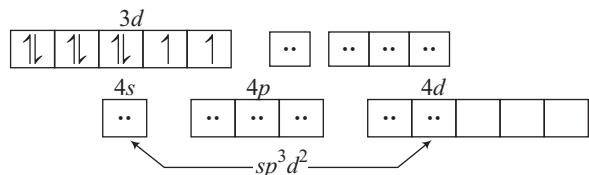
d^8 -configuration in strong ligand field gives dsp^2 -hybridisation, hence square planar geometry.



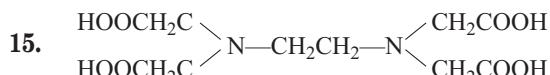
Here, Ni^{2+} has d^8 -configuration with Cl^- as weak ligand.



d^8 -configuration in weak ligand field gives sp^3 -hybridisation, hence tetrahedral geometry. Ni^{2+} with H_2O forms $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex and H_2O is a weak ligand.



Therefore, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has octahedral geometry.



- 16.** Ionisation isomers are the complexes that produce different ions in solution, i.e. they have ions interchanged inside and outside the coordination sphere.

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$ have different ions inside and outside the coordinate sphere and they are isomers.

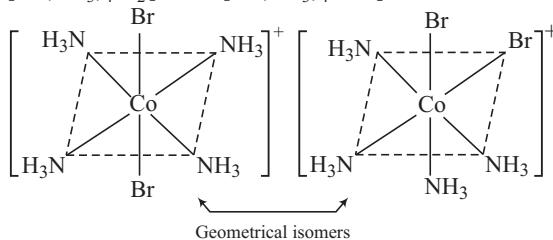
Therefore, they are ionisation isomers.

- 17.** $[\text{Ni}(\text{NH}_3)_4]^{2+}$ = tetraamminenickel (II)

$[\text{NiCl}_4]^{2-}$ = tetrachloronickelate (II)

Cationic part is named first, hence :
tetraamminenickel (II)-tetrachloronickelate(II)

- 18.** $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{BrCl}]\text{Br}$ are ionisation isomers.

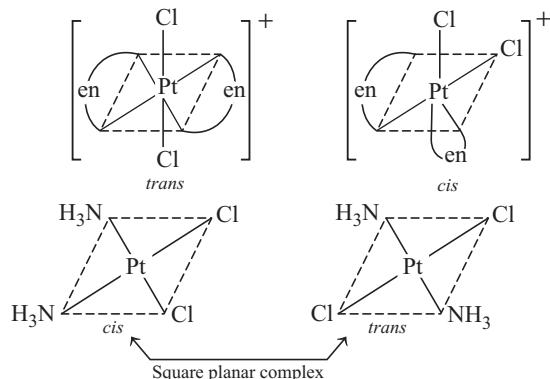


Geometrical isomers

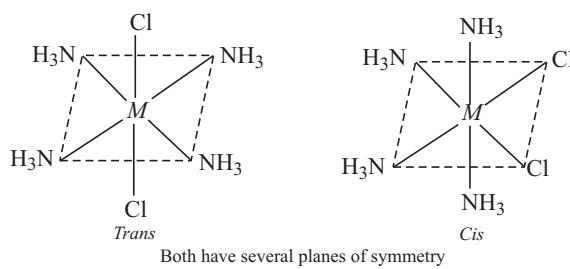
- 19. PLAN** Depending on the structure of the complex, different types of isomerism are shown.

Complex	Isomerism
A. $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	Neither of structural nor stereoisomerism
B. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	 <i>trans w.r.t. Cl</i>
	 <i>cis w.r.t. Cl</i>
$[\text{Pt}(\text{H}_2\text{O}) \cdot (\text{NH}_3)_2\text{Cl}]^+$	 <i>cis</i>
	 <i>trans</i>
C. $[\text{Co Br}_2\text{Cl}_2]^{2-}$ $[\text{PtBr}_2\text{Cl}_2]^{2-}$	<i>sp</i> ³ tetrahedral <i>dsp</i> ² square planar
D. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$	$[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)\text{Cl}]$ $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$ ionisation
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$ $[\text{Pt}(\text{NH}_3)_3\text{Br}]$ ionisation

20. Both $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ are capable of showing geometrical isomerism.



21. Both statements are true. However, axis of symmetry is not a criteria of optical isomerism. Optical inactivity of the two geometrical isomers of $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ is due to the presence of plane of symmetry.

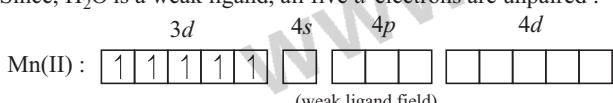


22. $A = \text{K}_2[\text{Ni}(\text{CN})_4]$; $B = \text{K}_2[\text{NiCl}_4]$

A : Potassium tetracyanonickelate (II)

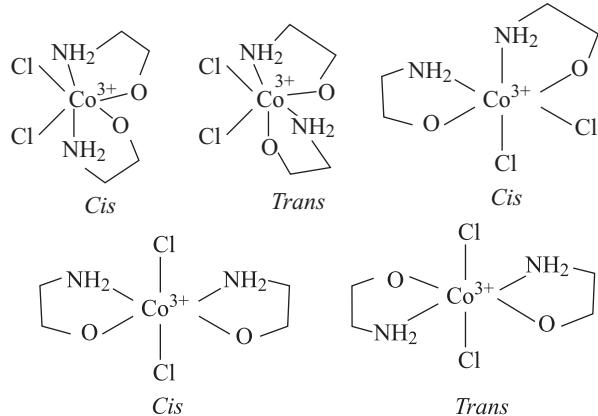
B : Potassium tetrachloronickelate (II)

23. Paramagnetism : In $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, Mn(II) has $3d^5$ configuration. Since, H_2O is a weak ligand, all five d -electrons are unpaired :

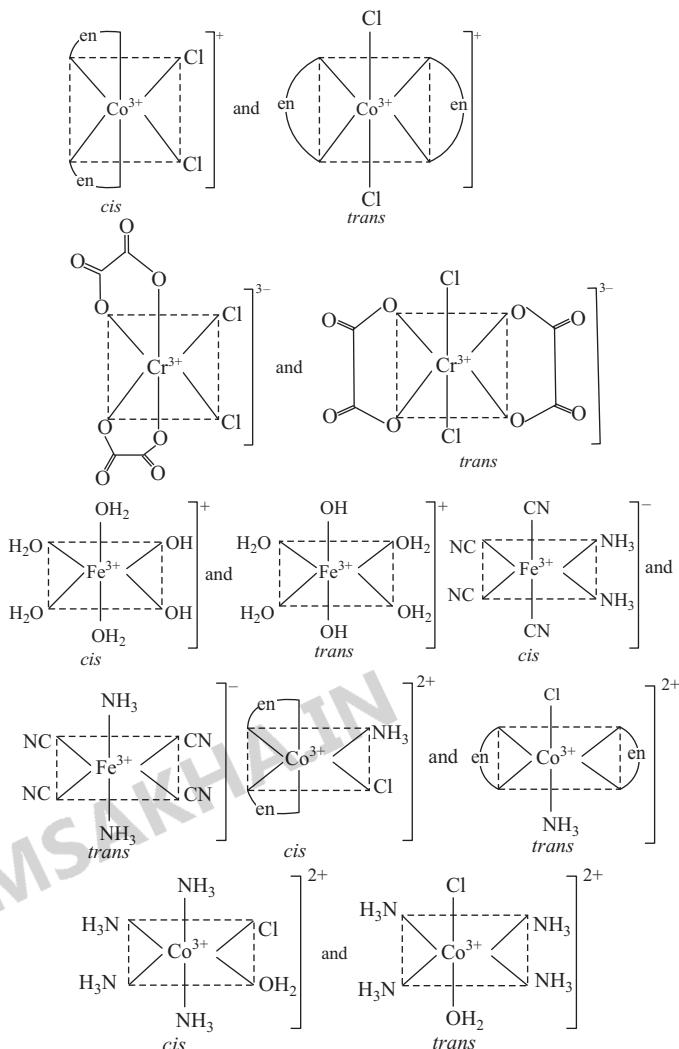


24. Ligand is $\begin{array}{c} \text{CH}_2 - \text{NH}_2 \\ | \\ \text{CH}_2\bar{\text{O}} \end{array}$

Geometrical isomers are

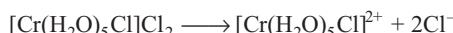


25. All six complex will show *cis-trans* isomerism



26. mmol of complex $= 30 \times 0.01 = 0.3$

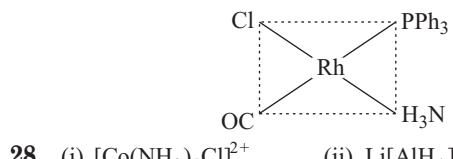
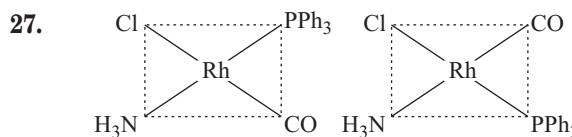
Also, 1 mole of complex $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ gives only two moles of chloride ion when dissolved in solution



\Rightarrow mmol of Cl^- ion produced from its 0.3 mmol $= 0.6$

Hence, 0.6 mmol of Ag^+ would be required for precipitation.

\Rightarrow 0.60 mmol of $\text{Ag}^+ = 0.1\text{M} \times V(\text{in mL}) \Rightarrow V = 6 \text{ mL}$



28. (i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (ii) $\text{Li}[\text{AlH}_4]$

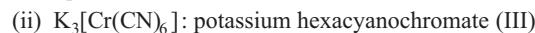
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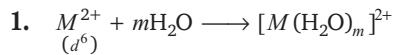
: pentaamminecarbonatochromium (III) chloride.



: pentaamminenitritocobalt (III) chloride.



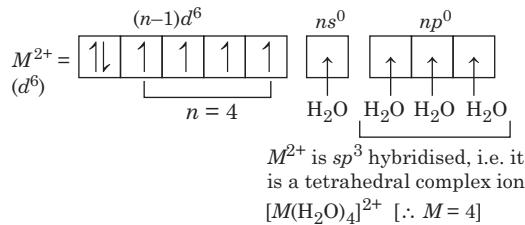
Topic 2 Bonding and Important Property of Coordination Compounds



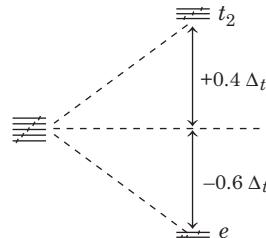
Here, H_2O is a weak field ligand and it should give a high spin paramagnetic ($\mu = 4.90 \text{ BM}$) complex ion

We know, $\mu = \sqrt{n(n+2)} \text{ BM} = 4.90 \text{ BM}$ ($n = 4$)

[$\therefore n$ = Number of unpaired electrons in the complex]



($n-1$)d-orbitals in tetrahedral field.



$\text{CFSE} = [(-0.6) \times 3 + (0.4) \times 3]\Delta_t = -0.6 \Delta_t$



So, the geometry and the crystal field stabilisation energy of the complex is tetrahedral and $-0.6 \Delta_t$, respectively.

2. The d-electron configuration $[\text{Ru}(\text{en})_3]\text{Cl}_2$ and $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ respectively are $t_{2g}^6 e_g^0$ and $t_{2g}^4 e_g^2$.

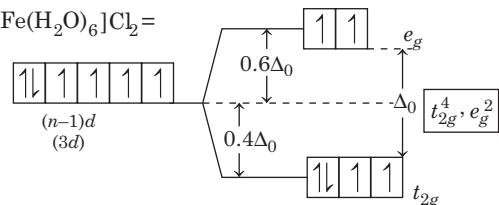
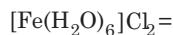
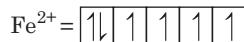


Ru = 4d series

en = bidentate ligand (strong field ligand)

C.N. = 6

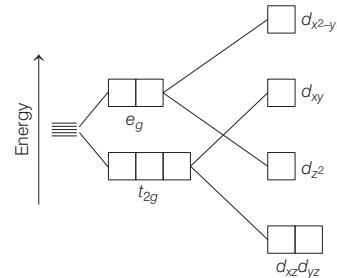
Oxidation number = +2



3. The compound used in the treatment of lead poisoning is EDTA. Medication occurs through chelation therapy. Calcium disodium ethylenediamine tetraacetic acid chelates divalent metal ion such as Pb^{2+} from plasma and interstitial body fluids.

The metal displaces Ca and is chelated, mobilised and usually excreted. Less than 5% CaNa₂EDTA is absorbed in the gastrointestinal tract and it possibly increases the absorption of Pb present in the tract. Therefore, it is not recommended for oral use. It is usually given intravenously.

4. Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to the following splitting pattern.

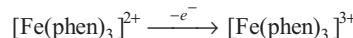


The single electron in the $d_{x^2-y^2}$ orbital is being repelled by four ligands, while the electron in the d_z^2 orbital is only being repelled by two ligands. Thus, the energy of the $d_{x^2-y^2}$ increases relative to that of d_z^2 . A more stable arrangement arises when both the e_g electrons pair up and occupy the lower energy d_z^2 orbital. This leaves the $d_{x^2-y^2}$ orbital empty.

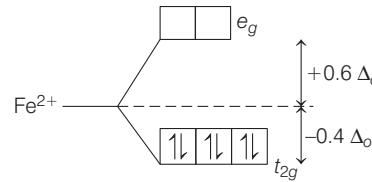
Thus, four ligands can now approach along +x, -x, +y and -y directions without any difficulty as $d_{x^2-y^2}$ orbital is empty. However, ligands approaching along +z and -z directions meet very strong repulsive forces from filled d_z^2 orbitals. Thus, only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.

5. **Key Idea** Crystal field splitting occurs due to the presence of ligands in a definite geometry. In octahedral complexes the energy of two, e_g orbitals will increase by $(0.6) \Delta_o$ and that of three t_{2g} will decrease by $(0.4) \Delta_o$.

The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is $[\text{Fe}(\text{phen})_3]^{2+}$.

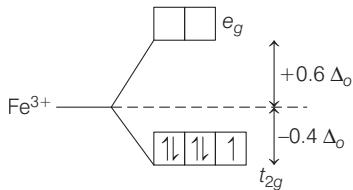


In $[\text{Fe}(\text{phen})_3]^{2+}$, electronic configuration of Fe^{2+} is $3d^6 4s^0$. Phenanthrene is a strong field symmetrical bidentate ligand. The splitting of orbital in Fe^{2+} is as follows:



$\text{CFSE} = 6 \times -0.4 \Delta_o = -2.4 \Delta_o$

The splitting of orbital and arrangement of electrons in Fe^{3+} is as follows :



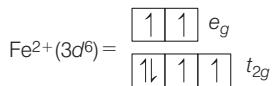
$$\text{CFSE} = 5 \times -0.4 \Delta_o = -2.0 \Delta_o$$

Fe^{2+} upon oxidation of its metal to +3 state lose its CFSE from $-2.4 \Delta_o$ to $-2.0 \Delta_o$.

6.

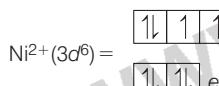
Key Idea Crystal field stabilisation energy (CFSE) for octahedral complexes $= (-0.4x + 0.6y)\Delta_o$
where, x = number of electrons occupying t_{2g} orbital.
 y = number of electrons occupying e_g orbital.
CFSE for tetrahedral complexes
 $= (-0.6x + 0.4y)\Delta_t$
where, x = number of electrons occupying e orbital.
 y = number of electrons occupying t orbital.

In $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$, H_2O is a weak field ligand, so it is a high spin (outer orbital) octahedral complex of Fe^{2+} .



$$\therefore \text{CFSE} = (-0.4x + 0.6y)\Delta_o \\ = [-0.4 \times 4 + 0.6 \times 2]\Delta_o = -0.4\Delta_o$$

In $\text{K}_2[\text{NiCl}_4]$, Cl^- is a weak field ligand, so it is a high spin tetrahedral complex of Ni^{2+} .



$$\therefore \text{CFSE} = (-0.6 \times 4 + 0.4 \times 4)\Delta_t = -0.8\Delta_t$$

7. The explanation of given statements are as follows :

(a) Ruby, a pink or blood-red coloured gemstone belongs to corundum (Al_2O_3 , alumina) system which has trigonal crystalline lattice containing the repeating unit of $\text{Al}_2\text{O}_3 - \text{Cr}^{3+}$. So, ruby does not belong to beryl lattice ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$).

Thus, statement (a) is incorrect.

(b) $[\text{Co}(\text{Cl})(\text{NH}_3)_5]^{2+}$ is a low spin octahedral complex of Co^{3+} . It absorbs low energy yellow light and high energy complementary violet light will be shown off. Thus, statement (b) is correct.

(c) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ are the high-spin octahedral complexes of Fe^{2+} ($3d^6, n = 4$) and Cr^{2+} ($3d^5, n = 5$) ions and weak field ligand, H_2O respectively. So, spin-only magnetic moment $= \sqrt{n(n+2)}$ of the complexes.

$$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}, \mu_1 = \sqrt{4(4+2)} \\ (n=4), \quad = \sqrt{24} = 4.89 \text{ BM}$$

$$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, \mu_2 = \sqrt{5(5+2)} \\ (n=5), \quad = \sqrt{35} = 5.92 \text{ BM}$$

So, $\mu_1 \approx \mu_2$. Thus, statement (c) is correct.

(d) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is also a high-spin octahedral complex of Ni^{2+} ($3d^8, n = 2$)
 $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$

Thus, statement (d) is correct.

8.

Key Idea The wavelength (λ) of light absorbed by the complexes is inversely proportional to its Δ_0 CFSE (magnitude). $\Delta_0(\text{CFSE}) \propto 1/\lambda$

The complexes can be written as:

- I. $[\text{CoCl}(\text{NH}_3)_5]^{2+} \equiv [\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$
- II. $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} \equiv [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$
- III. $[\text{Co}(\text{NH}_3)_5]^{3+} \equiv [\text{Co}(\text{NH}_3)_5(\text{NH}_3)]^{3+}$

So, the differentiating ligands in the octahedral complexes of Co (III) in I, II and III are Cl^- , H_2O and NH_3 respectively. In the spectrochemical series, the order of this power for crystal field splitting is $\text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3$.

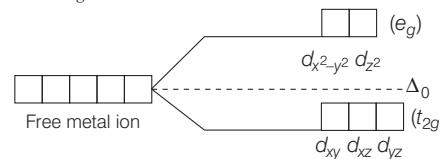
So, the crystal field splitting energy (magnitude) order will be

$$\Delta_0^{\text{CFSE}} (\text{I}) < \Delta_0^{\text{CFSE}} (\text{II}) < \Delta_0^{\text{CFSE}} (\text{III})$$

and the order of wavelength (λ) of light absorbed by the complexes will be

$$\lambda (\text{I}) > \lambda (\text{II}) > \lambda (\text{III}) \quad \left[\because \text{Energy } (\Delta_0^{\text{CFSE}}) \propto \frac{1}{\lambda} \right]$$

9. The degenerate orbitals of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ are d_{xz} and d_{yz} . Electronic configuration of Cr^{3+} is $3d^5 4s^1$. The five d -orbitals in an isolated gaseous atom or ion have same energy, i.e. they are degenerate. This degeneracy has been removed due to the ligand electron–metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.



10. $[\text{Fe}(\text{H}_2\text{O})_6]_2 \Rightarrow$ It will form 2 cationic species. i.e.

I. (i) As $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \Rightarrow$ High spin octahedral complex of Fe^{2+} .

$\text{Fe}^{2+} : 3d^6, x = 4$ (unpaired electrons)

$$\mu = \sqrt{4(4+2)} \text{ BM} = 4.9 \text{ BM}$$

or (ii) as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \Rightarrow$ High spin octahedral complex of Fe^{3+} .

$$\text{Fe}^{3+} : 3d^5, x = 5, \mu = \sqrt{5(5+2)} = 5.92 \text{ BM}$$

H_2O is a neutral weak field ligand

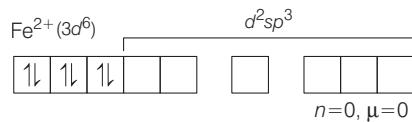
So, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ will be the cationic specie, $\mu = 4.9 \text{ BM}$.

$[\text{Fe}(\text{CN})_6]^{4-}$ will have two anionic complexes

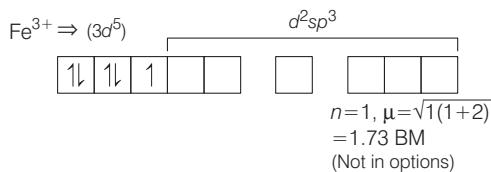
II. (i) $[\text{Fe}(\text{CN})_6]^{4-} \Rightarrow$ Low spin, octahedral complex of Fe^{2+} .

As CN^- is a strong ligand it will pair up the electrons.

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or, (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ \Rightarrow Low spin octahedral complex of Fe^{3+} .

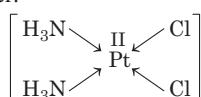


$[\text{CN}^-]$ is an anionic strong field ligand

So, the anionic species is $[\text{Fe}(\text{CN})_6]^{4-}, \mu = 0$

Thus, the calculated spin only magnetic moments (BM) of the anionic and cationic species of $[\text{Fe}(\text{H}_2\text{O})_6]_2$ and $[\text{Fe}(\text{CN})_6]$ respectively are 4.9 and 0.

11. cis - $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_2]$ is known as cis -platin. It is a σ -bonded organo-metallic compound and is used as an anti-tumor agent in the treatment of cancer.



12. **Key Idea** In presence of strong field ligands, $\Delta_0 > \rho$, for fourth electron it is more energetically favourable to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^0$ and form low spin complexes.

The correct order of the spin only magnetic moment of metal ions in the given low-spin complexes is $\text{V}^{2+} > \text{Cr}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+}$. All the given complexes possess strong field ligands (CN^- , NH_3). Hence, readily form low spin complexes.

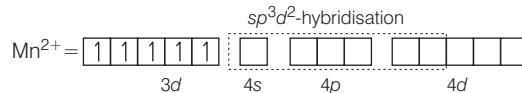
Complex Oxidation Configuration state	Orbital splitting	No. of unpaired electrons
$[\text{V}(\text{CN})_6]^{4-}$ V^{2+} $t_{2g}^3 e_g^0$		3
$[\text{Cr}(\text{NH}_3)_6]^{2+}$ Cr^{2+} $t_{2g}^4 e_g^0$		2
$[\text{Ru}(\text{NH}_3)_6]^{3+}$ Ru^{3+} $t_{2g}^5 e_g^0$		1
$[\text{Fe}(\text{CN})_6]^{4-}$ Fe^{2+} $t_{2g}^6 e_g^0$		0

13. The magnetic moment of the magnitude 5.9 BM suggest the presence of 5 unpaired electrons in $\text{Mn}(\text{II})$. This can be cross verified by putting the value (5) of unpaired electrons in the formula, $\mu = \sqrt{n(n+2)}$ BM

Thus, the valence electronic configuration of $\text{Mn}(\text{II})$ in the complex is



The octahedral homoleptic complex suggests sp^3d^2 -hybridisation in the complex, i.e.



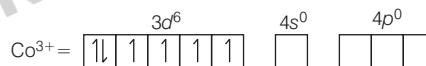
Thus, 5 unpaired electrons are present in the complex which suggest the presence of a weak ligand like NCS^- .

14. As H_2O is a weak field ligand. It readily forms high spin complexes. In $[\text{M}(\text{H}_2\text{O})_6]\text{Cl}_2$, M exist in +2 oxidation state. The arrangement of electrons in the given metal ions are as follows:

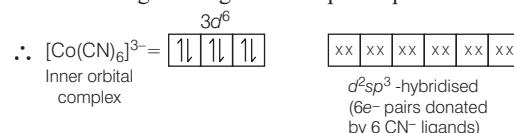
Metal Configuration	Number of unpaired electrons	Spin only Magnetic moment (in BM) = $\sqrt{n(n+2)}$
$\text{Co}^{2+} \quad (d^7) = t_{2g}^5 e_g^2$	3	3.9
$\text{Fe}^{2+} \quad (d^6) = t_{2g}^4 e_g^2$	4	4.9
$\text{Cr}^{2+} \quad (d^4) = t_{2g}^3 e_g^1$	4	4.9
$\text{Mn}^{2+} \quad (d^5) = t_{2g}^3 e_g^2$	5	5.9
$\text{V}^{2+} \quad (d^3) = t_{2g}^3 e_g^0$	3	3.9

Therefore, Co^{2+} and V^{2+} contains same value of magnetic moment (3.9 BM).

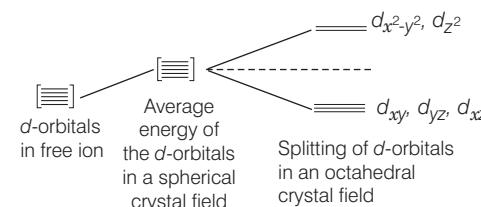
15. In $\text{K}_3[\text{Co}(\text{CN})_6]$, Co have +3 oxidation state and electronic configuration of Co^{3+} is $[\text{Ar}]_{18} 3d^6$.



As, CN^- is a strong field ligands so it pairs up the d^6 s



In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x , y and z under the influence of an octahedral field, the d -orbitals split as follow.

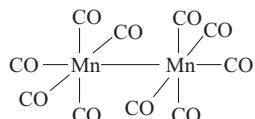


As the d -orbitals, i.e. $d_{x^2-y^2}$ and d_{z^2} are vacant. Hence, these both orbitals are directly facing the ligands in $\text{K}_3[\text{Co}(\text{CN})_6]$.

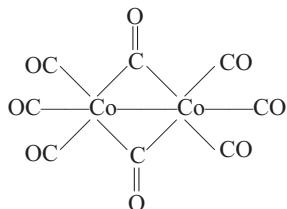
16. $\text{Mn}_2(\text{CO})_{10}$ is an organometallic compound due to the presence of Mn—C bond. The metal-carbon bond in organometallic compounds possess both σ and π character. The M—C σ bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The M—C π -bond is formed by the donation of pair of

electrons from a filled d-orbital of metal into vacant antibonding π^* orbital of CO. The M—L bonding creates a synergic effect which strengthens the bond between CO and the metal.

The structure of $Mn_2(CO)_{10}$ is shown below :



17. The structure of $Co_2(CO)_8$ (a polynuclear metal carbonyl) can be written as:



Total number of bridging CO ligands = 2
and the Co—Co bond = 1

18. Coordination number is defined as the total number of ligands to which the metal is directly attached.

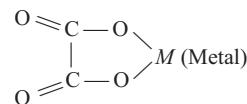
20. The difference in the number of unpaired electrons of different metal ions in their high spin and low spin octahedral complexes are given in the table below :

Metal ion	Number of e^- in high spin complex (n_1)	Number of e^- in low spin complex (n_2)	$n_2 - n_1$																														
Mn^{2+}	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$n_1=5$</td></tr> </table>	3d	4s	4p	1 1 1 1 1			4d						$n_1=5$			<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$n_2=1$</td></tr> </table>	3d	4s	4p	1 1 1 1			4d						$n_2=1$			$5 - 1 = 4$
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Fe^{2+}	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$n_1=4$</td></tr> </table>	3d	4s	4p	1 1 1 1 1			4d						$n_1=4$			<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$n_2=0$</td></tr> </table>	3d	4s	4p	1 1 1 1			4d						$n_2=0$			$4 - 0 = 4$
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Ni^{2+}	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$n_1=2$</td></tr> </table>	3d	4s	4p	1 1 1 1 1			4d						$n_1=2$																			
3d	4s	4p																															
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Ni^{2+} does not form low spin octahedral complexes.																																	
Co^{2+}	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$\therefore n_1=3$</td></tr> </table>	3d	4s	4p	1 1 1 1 1			4d						$\therefore n_1=3$			<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>3d</td><td>4s</td><td>4p</td></tr> <tr><td>1 1 1 1</td><td></td><td></td></tr> <tr><td colspan="3" style="text-align: center;">4d</td></tr> <tr><td colspan="3" style="height: 20px;"></td></tr> <tr><td colspan="3" style="text-align: center;">$\therefore n_1=1$</td></tr> </table>	3d	4s	4p	1 1 1 1			4d						$\therefore n_1=1$			$3 - 1 = 2$
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3d	4s	4p																															
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$\therefore n_1=1$																																	

21. According to the situation given in question, reactions are as follows:



Here, $C_2O_4^{2-}$ is a bidentate ligand,



and H_2O is a monodentate ligand, $H_2\ddot{O} \rightarrow M$

So, total number of sites offered by $C_2O_4^{2-}$ and H_2O ligands

$$\text{around Th(IV)} = \text{Coordination number of Th (IV)}$$

$$= 4 \times 2(\text{by } C_2O_4^{2-}) + 2 \times 1(\text{by } H_2O) = 10$$

19. (A) Co is present in vitamin B_{12} (iii) having molecular formula,

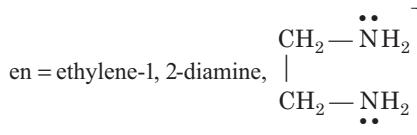


- (B) Zn is present in carbonic anhydrase (iv) in which three histidine units and the —OH group coordinate with one Zn (II) ion.

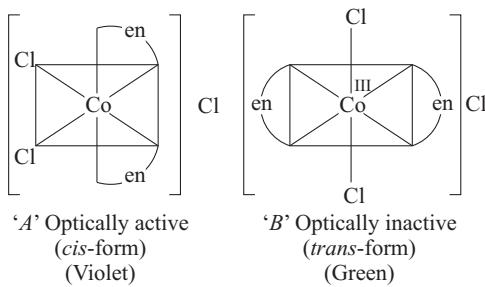
- (C) Rh is present in Wilkinson catalyst (i) having molecular formula $[(Ph_3P)_3RhCl]$.

- (D) Mg is present in chlorophyll (ii) having molecular formula $\overset{II}{C_{55}H_{70}O_6N_4Mg}$ (chlorophyll-b).

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22. Wilkinson's catalyst is a σ -bonded organometallic compound $[(\text{Ph}_3\text{P})_3\text{RhCl}]$. It is commercially used for hydrogenation of alkenes and vegetable oils (unsaturated).

IUPAC name Chloridotris (triphenylphosphine) rhodium (I).

23. In homoleptic complexes, the metal atom/ion is linked to only one type of ligand. Assuming, ligands are neutral, the octahedral complexes of M^{3+} can be,

$$[M(L_1)_6]^{3+}, [M(L_2)_6]^{3+} \text{ and } [M(L_3)_6]^{3+}$$

$$\begin{array}{ccc} \lambda_{\text{Absorption}} & \text{(I)} & \text{(II)} \\ \text{So,} & \lambda_{\text{III}}^{L_3} > \lambda_{\text{I}}^{L_1} > \lambda_{\text{II}}^{L_2} & \text{Green} & \text{Blue} & \text{Red (wavelength)} \end{array}$$

$$\therefore \Delta_{\text{absorption}}^{\circ} : \Delta_{\text{II}}^{L_2} > \Delta_{\text{I}}^{L_1} > \Delta_{\text{III}}^{L_3} \quad [\because \text{Energy } (\Delta, \text{CFSE}) \propto \frac{1}{\lambda}]$$

We know, ligand strength $\propto \Delta_{\text{absorption}}^{\circ}$

So, the increasing order of the ligand strength will be,
 $L_3 < L_1 < L_2$

24. All of the complex given are the octahedral complexes of Co (III) except $\text{K}_2[\text{CoCl}_4]$, which is a tetrahedral complex of Co (II) (sp^3 -hybridised).

$$\text{We know, } \Delta_t < \Delta_o \quad \left[\because \Delta_t = \frac{4}{9} \Delta_o \right]$$

So, the octahedral complexes (a, b, c) have higher Δ_o values than that of tetrahedral, $\text{K}_2[\text{CoCl}_4]$.

Now, for the complexes, a, b and c, the magnitude of $\Delta_o \propto$ ligand strength, which is based on their positions in the spectrochemical series.



Hence, $\text{K}_3[\text{Co}(\text{CN})_6]$ will have the highest Δ value.

25. The spin only magnetic moment (μ) (in BM) is given by

$$\mu(\text{in BM}) = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons

The highest value of n in transition metal complex is 5 in its d^5 -configuration.

$$\therefore \mu = \sqrt{5(5+2)} \text{BM} = 5.916 \text{BM}$$

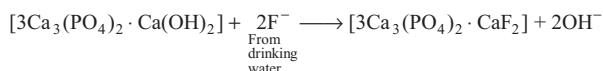
26. 'A' absorbs yellow light of less energy and emits violet light of high energy (complementary colour) because H_2O is a weak field ligand. But in case of 'B', due to presence of strong field ligand (NH_3), it absorbs high energy violet light and emits low energy complementary yellow colour.

$\Delta(\text{CFSE})$ is measured with help of wavelength of the colour absorbed by the given coordination compound, as

$$\Delta_O = h\nu = h \times \frac{c}{\lambda}$$

Both the complexes contain three unpaired electrons. Therefore, both are paramagnetic.

27. Fluoride ions help in making teeth enamel harder by converting $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2]$ i.e. Hydroxy apatite to $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$ i.e., Fluorapatite (Harder teeth enamel) via following reaction:



$$28. \text{Molarity } (M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$$

\therefore Number of moles of complex

$$= \frac{\text{Molarity} \times \text{volume (in mL)}}{1000} = \frac{0.1 \times 100}{1000} = 0.01 \text{ mole}$$

$$\text{Number of moles of ions precipitate} = \frac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02 \text{ moles}$$

\therefore Number of Cl^- present in ionisation sphere

$$= \frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}} = \frac{0.02}{0.01} = 2$$

$\therefore 2 \text{ Cl}^-$ are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is



Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (n)						
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	$\text{Cr}^{2+}; [\text{Ar}] 3d^4$	<table border="1"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td></td></tr></table> ; 4	1	1	1	1	1	
1	1	1	1	1				
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$\text{Fe}^{2+}; [\text{Ar}] 3d^6$	<table border="1"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> ; 4	1	1	1	1	1	1
1	1	1	1	1	1			
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$\text{Mn}^{2+}; [\text{Ar}] 3d^5$	<table border="1"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> ; 5	1	1	1	1	1	1
1	1	1	1	1	1			
$[\text{CoCl}_4]^{2-}$	$\text{Co}^{2+}; [\text{Ar}] 3d^7$	<table border="1"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> ; 3	1	1	1	1	1	1
1	1	1	1	1	1			

Compounds	Hybridisation	Unpaired electron(s)	Magnetic character
$\text{Ni}(\text{CO})_4$	sp^3	No	Diamagnetic
$[\text{NiCl}_4]^{2-}$	sp^3	two	Paramagnetic
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	sp^3d^2	No	Diamagnetic
$\text{Na}_3[\text{CoF}_6]$	sp^3d^2	three	Paramagnetic
Na_2O_2	—	No	Diamagnetic (O_2^{2-})
CsO_2	—	One	Paramagnetic O_2^- (superoxide ion is paramagnetic)



∴ In MnO_4^- , Mn has + 7 oxidation state having no electron in d-orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur $L \rightarrow M$ charge transfer, because ligand is able to donate the electron into the vacant d-orbital of metal.

Since, charge transfer is laporate as well as spin allowed, therefore, it shows colour.

Time saving Technique There is no need to check all the four options. Just find out the oxidation state of metal ion. If oxidation state is highest and ligand present there is of electron donating nature, gives LMCT, which shows more intense colour.

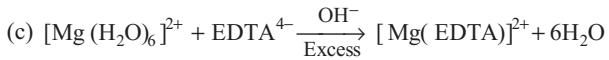
32. This problem is based on conceptual mixing of properties of lithium oxide and preparation, properties of coordination compounds. To answer this question, keep in mind that on adding acid, ammine complexes get destroyed.



This is wrong equation, since a stronger base K_2O cannot be generated by a weaker base Li_2O .

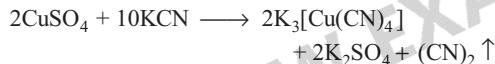


This is correct. All ammine complexes can be destroyed by adding H^\oplus . Hence, on adding acid to $[\text{CoCl}(\text{NH}_3)_5]$, it gets converted to $\text{Co}^{2+}(aq)$, NH_4^+ and Cl^- .



This is wrong, since the formula of complex must be $[\text{Mg}(\text{EDTA})]^{2+}$ as EDT.

- (d) The 4th reaction is incorrect. It can be correctly represented as



33. Arrange the complex formed by different ligands L_1 , L_2 , L_3 and L_4 , according to wavelength of their absorbed light, then use of the following relation to answer the question.

Ligand field strength \propto Energy of light absorbed

$$\propto \frac{1}{\text{Wavelength of light absorbed}}$$

λ	L_1	L_2	L_3	L_4
Absorbed light	Red	Green	Yellow	Blue

Wavelength of absorbed light decreases.

∴ Increasing order of energy of wavelengths absorbed reflect greater extent of crystal field splitting, hence, higher field strength of the ligand.

Energy blue (L_4) > green (L_2) > yellow (L_3) > red (L_1)

∴ $L_4 > L_2 > L_3 > L_1$ in field strength of ligands.

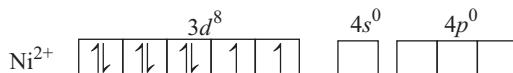
34. **PLAN** Spin only magnetic moment have the formula $\sqrt{n(n+2)}$ BM, where N is the number of unpaired electrons. In the presence of weak ligand (as H_2O , Cl^- , F^-) there is no pairing of electrons, and electrons donated by ligands are filled in outer vacant orbitals.

In the presence of strong ligand (as CN^- , CO , NH_3 , en) electrons are paired and electrons from ligands are filled in available inner orbitals

Complex	Atomic number of	O.N.	E.C.	Unpaired electrons	Magnetic moment
$P : [\text{FeF}_6]^{3-}$ weak ligand	26	+ 3	$[\text{Ar}]3d^5$	5	$\sqrt{35}$ BM
$Q : [\text{V}(\text{H}_2\text{O})_6]^{2+}$ weak ligand	23	+ 2	[Ar]	3	$\sqrt{15}$ BM
$R : [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	26	+ 2	$[\text{Ar}]3d^6$	4	$\sqrt{24}$ BM

Thus, order of spin-only magnetic moment = $Q < R < P$

35. In the given complex, $\text{NiCl}_2 \{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$ nickel is in + 2 oxidation state and the ground state electronic configuration of Ni^{2+} ions in free gaseous state is

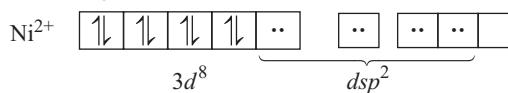


For the given four coordinated complex to be paramagnetic, it must possess unpaired electrons in the valence shell. To satisfy this condition, four lone pairs from the four ligands occupies the four sp^3 -hybrid orbitals as :



Therefore, geometry of paramagnetic complex must be **tetrahedral**. On the otherhand, for complex to be diamagnetic, there should not be any unpaired electrons in the valence shell.

This condition can be fulfilled by pairing electrons of $3d$ -orbitals against Hund's rule as



The above electronic arrangement gives dsp^2 -hybridisation and therefore, **square planar** geometry to the complex.

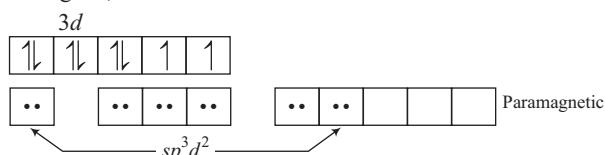
36. For a diamagnetic complex, there should not be any unpaired electron in the valence shell of central metal.

In $\text{K}_3[\text{Fe}(\text{CN})_6]$, Fe (III) has d^5 -configuration (odd electrons), hence it is paramagnetic.

In $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, Co (III) has d^6 -configuration in a strong ligand field, hence all the electrons are paired and the complex is diamagnetic.

In $\text{Na}_3[\text{Co}(\text{ox})_3]$, Co (III) has d^6 -configuration and oxalate being a chelating ligand, very strong ligand and all the six electrons remains paired in lower t_{2g} level, diamagnetic.

In $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$, Ni (II) has $3d^8$ -configuration and H_2O is a weak ligand, hence



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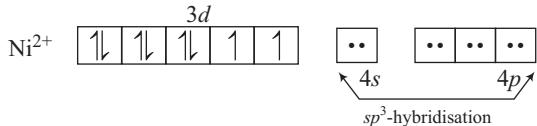
In $K_2[Pt(CN)_4]$, Pt(II) has d^8 -configuration and CN^- is a strong ligand, hence all the eight electrons are spin paired. Therefore, complex is diamagnetic.

In $[Zn(H_2O)_6](NO_3)_2$, Zn (II) has $3d^{10}$ configuration with all the ten electrons spin paired, hence diamagnetic.

37. Magnetic moment = 2.83 BM indicates that there are two unpaired electrons.

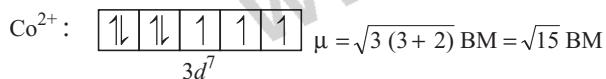
$$\mu = \sqrt{n(n+2)} \text{ BM} = \sqrt{8} \text{ BM} = 2.82 \text{ BM}$$

In $[NiCl_4]^{2-}$, Ni has d^8 configuration and Cl^- is a weak ligand :



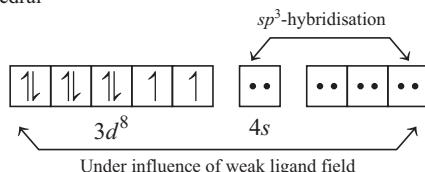
38. In $Cr(CO)_6$: $3d^6$, has no unpaired electrons, zero magnetic moment.
39. CuF_2 : Cu^{2+} has $3d^9$ -configuration, allowed $d-d$ transition, hence, coloured.
40. In $Ni(CO)_4$, Ni is sp^3 -hybridised while in $[Ni(CN)_4]^{2-}$, Ni^{2+} is dsp^2 -hybridised.
41. Greater the extent of $d\pi - p\pi$ back bonding, smaller will be the bond order of CO bond in metal carbonyls. In $Fe(CO)_5$, there is maximum number of valence shell electrons (d -electrons), greatest chances of $p\pi - d\pi$ back bonding, lowest bond order of CO bond.
42. In CO, bond order = 3. In metal carbonyls like $Fe(CO)_5$, due to $d\pi - p\pi$ back-bonding, bond order of CO decreases slightly therefore, bond length increases slightly.

43. In $Hg[Co(SCN)_4]$, Co^{2+} has $3d^7$ configuration. SCN^- produces weak ligand field, no pairing of electrons in d -orbitals occurs against Hund's rule, hence :



44. $[NiCl_4]^{2-}$: $Ni^{2+}(3d^8)$

Tetrahedral



In all other complexes, hybridisation at central metal is dsp^2 and complexes have square planar geometries.

45. In 1 L solution, there will be 0.01 mole of each $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$. Addition of excess of $AgNO_3$ will give 0.01 mole of $AgBr$. Addition of excess of $BaCl_2$ will give 0.01 mole of $BaSO_4$.

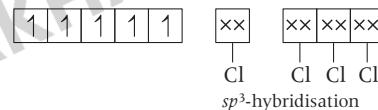
46. In MnO_4^- , Mn^{+7} has $3d^0$ configuration.

47. In $Ni(CO)_4$, Ni is in $3d^{10}$ state due to strong ligand field produced by CO. Hence, Ni is sp^3 -hybridised and complex is tetrahedral. In

$NiCl_2(PPh_3)_2$, Ni^{2+} has $3d^8$ -configuration. Due to weak ligand field, Ni is sp^3 -hybridised and complex is tetrahedral.

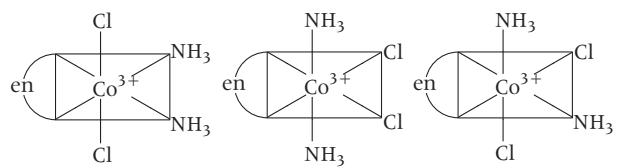
48. $Cu^{2+} + CN^- \longrightarrow CuCN \downarrow$
 $CuCN + 3CN^- \longrightarrow [Cu(CN)_4]^{3-}$
49. Fe in $[Fe(H_2O)_6]^{2+}$ has maximum (four) unpaired electrons, has highest paramagnetism.
50. In $Ni(CO)_4$, Ni has $3d^{10}$ -configuration, diamagnetic. In $Ni(CN)_4]^{2-}$, Ni has $3d^8$ -configuration but due to strong ligand field, all the d -electrons are spin paired giving dsp^2 -hybridisation, diamagnetic.
- In $[NiCl_4]^{2-}$, Ni has $3d^8$ -configuration and there are two unpaired electrons (weak chloride ligand do not pair up d -electrons), hence paramagnetic.
51. Salt with least number of unpaired electrons in d -orbital of central metal will show lowest degree of paramagnetism
 Mn^{2+} ($3d^5$, 5 unpaired electrons)
 Cu^{2+} ($3d^9$, 1 unpaired electron)
 Fe^{2+} ($3d^6$, 4 unpaired electrons)
 Ni^{2+} ($3d^8$, 2 unpaired electrons)
Hence, $CuSO_4 \cdot 5H_2O$ has lowest degree of paramagnetism.

52. (a) In $[FeCl_4]^-$, oxidation number of Fe atom = + 3
Electronic configuration of Fe in ground state = $3d^64s^2$
Electronic configuration of Fe^{3+} = $3d^54s^04p^0$



Thus, $[FeCl_4]^-$ has tetrahedral geometry.

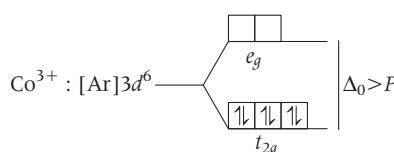
- (b) $[Co(en)(NH_3)_2Cl_2]^+$ have three geometrical isomers. Thus, statement (b) is incorrect.



- (c) Fe^{3+} in $[FeCl_4]^-$ is sp^3 -hybridised with 5 unpaired electrons. (higher spin-only magnetic moment = $\sqrt{n(n+2)}$ = 5.92 BM). While Co^{3+} in $[Co(en)(NH_3)_2Cl_2]^+$ is d^2sp^3 -hybridised with zero unpaired electrons (low spin-only magnetic moment = $\sqrt{n(n+2)}$ = 0 BM).

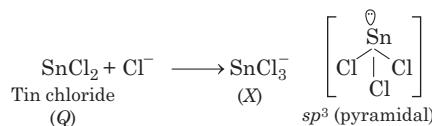
Thus, the statement (c) is correct.

- (d) $Co^{3+} [Co(en)(NH_3)_2Cl_2]^+$

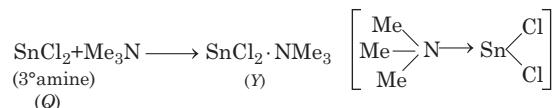


Co^{3+} in $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ is d^2sp^3 -hybridised and has octahedral geometry with 0 unpaired electron. Thus, statement (d) is incorrect.

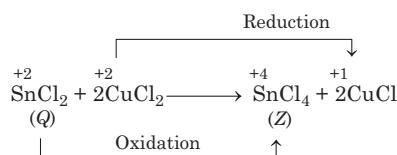
53.



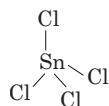
SnCl_3^- has $(3\sigma + 1p)$ and exist in pyramidal structure.



Y complex has coordinate bond in between nitrogen and Sn metal.



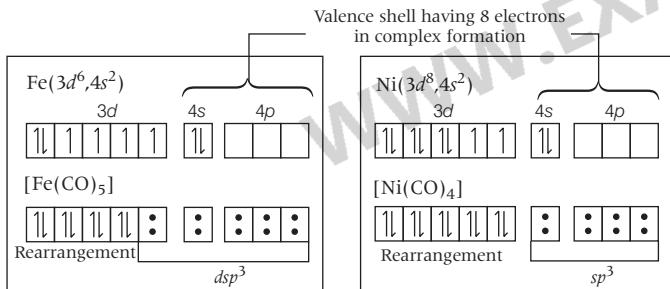
Z is oxidised product and oxidation state of Sn is +4 in Z compound. Structure of SnCl_4 (Z) is



Thus, options (a, d) are correct.

54. Statement wise explanation is

(i) **Statement (a)** The total number of valence shell electrons at metal centre in $\text{Fe}(\text{CO})_5$ or $\text{Ni}(\text{CO})_4$ is 8 instead of 16 as shown below



Hence, this statement is incorrect.

(ii) **Statement (b)** Carbonyl complexes are predominantly low spin complexes due to strong ligand fields. Hence, this statement is correct.

(iii) **Statement (c)** For central metal lowering of oxidation state results to increase in electron density on it. This in turn results to increase in extent of synergic bonding. Thus, we can say "metal carbonyl bond strengthens, when oxidation state of metal is lowered".

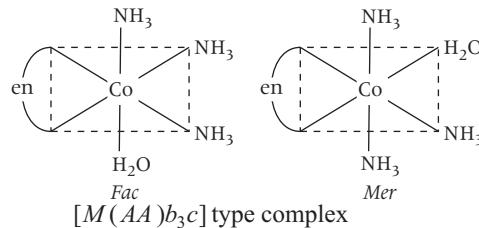
Hence, it is a correct statement.

(iv) **Statement (d)** Increase in positive charge on metal (i.e., increase in oxidation state) results to decrease in synergic bonding strength.

This in turn makes C—O bond stronger instead of weaker. Hence this statement is also incorrect.

55. Statement wise explanation is

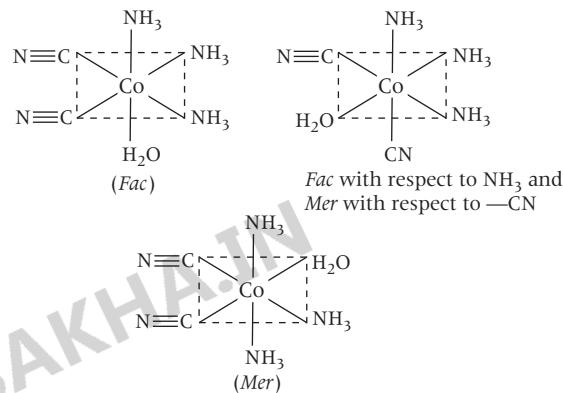
Statement (a) $[\text{Co}(\text{en})(\text{NH}_3)_3\text{H}_2\text{O}]^{3+}$ have following 2 geometrical isomers.



Hence, this is correct statement.

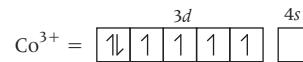
Statement (b) If bidentate ligand 'en' is replaced by two cyanide ligands then $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{CN})_2]^{3+}$ is formed.

It is $[Ma_3b_2c]$ type complex which has following 3 geometrical isomers.

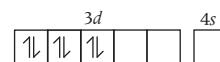


Hence, this statement is also correct.

Statement (c) Co metal has $[\text{Ar}]3d^7 4s^2$ configuration while in $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ it is in +3 oxidation state. Thus, Co^{3+} has $[\text{Ar}]3d^6$ configuration.



As en is a strong ligand, so pairing will occur



Due to the presence of all paired electrons it show diamagnetic behaviour rather than paramagnetic.

Hence, this statement is incorrect.

Statement (d) According to CFT, absorption of light by coordination complexes depends upon CFSE i.e., crystal field splitting energy (Δ_0) as

$$\Delta_0 \propto \frac{1}{\lambda}$$

Among the complexes given $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$ has more Δ_0 value as compared to complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$. Thus, $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ absorbs the light at longer wavelength for $d-d$ transition.

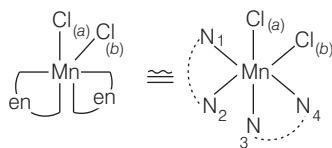
Hence, this statement is also correct.

Note : For any complex, the value of Δ_0 can be calculated via the difference or gap between e_g and t_{2g} values.

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56. $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2 \xrightarrow[\text{Pink (X)}]{\text{Excess NH}_4\text{OH/NH}_4\text{Cl}} \text{Co}(\text{NH}_3)_6\text{Cl}_3$
- $$\text{[Co}(\text{H}_2\text{O})_6\text{]}^{2+}_{\text{X}} + 4\text{Cl}^- \xrightarrow[\text{(Excess)}]{\text{O}_2(\text{Air})} \text{[CoCl}_4\text{]}^{2-}_{\text{blue Z}}$$
- (a) Since NH_3 is moderately strong ligand, hybridisation of cobalt in Y is d^2sp^3 .
- (b) Cobalt is sp^3 -hybridised in $[\text{CoCl}_4]^{2-}$.
- (c) $[\text{Co}(\text{NH}_3)_6\text{]}^{2-}\text{Cl}_3 + 3\text{AgNO}_3(aq) \longrightarrow 3\text{AgCl} \downarrow$
- (d) $[\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^-; \Delta H < 0$

57. The structure of $cis\text{-}[\text{Mn}(\text{en})_2\text{Cl}_2]$ complex is



Bond angles (Mn—N and Mn—Cl bond in *cis* positions)

Cl (a) — Mn — N₍₁₎

Cl (a) — Mn — N₍₂₎

Cl (a) — Mn — N₍₄₎

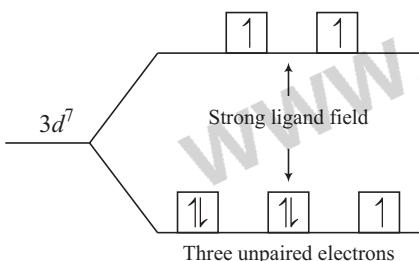
Cl (b) — Mn — N₁

Cl (b) — Mn — N₃

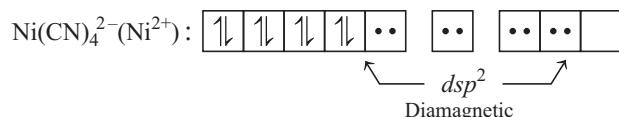
Cl (b) — Mn — N₄

Number of *cis* Cl—Mn—N = 6

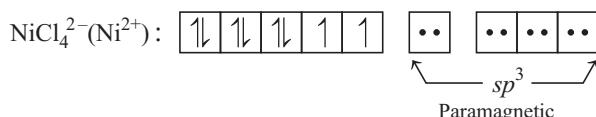
58. In the complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$, Fe is in +1 oxidation state because NO is in +1 state. Also NO is a strong ligand, complex has $3d^7$ -configuration at Fe(I) as :



59. A is diamagnetic, square planar complex because of strong ligand field of CN^- .

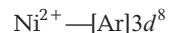


B is paramagnetic, tetrahedral complex because of weak ligand field of Cl^- .



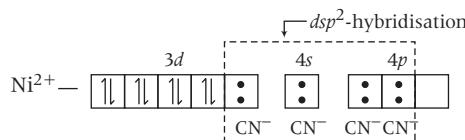
60. Described in 2, A has dsp^2 hybridisation while B has sp^3 -hybridisation of Ni.

61. For P i.e. dsp^2 , It is seen in $[\text{Ni}(\text{CN})_4]^{2-}$



as CN^- is a strong ligand so when it approaches towards central metal pairing of unpaired electrons takes place.

Thus, in $[\text{Ni}(\text{CN})_4]^{2-}$



Structure : Square planar

So correct match for P is 6.

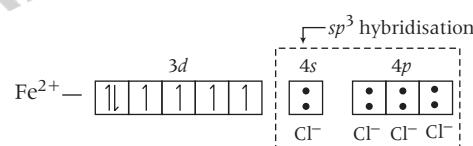
For Q i.e., sp^3

It is seen in $[\text{FeCl}_4]^{2-}$ and $\text{Ni}(\text{CO})_4$



As Cl^- is a weak ligand so when it approaches towards central metal pairing of unpaired electrons does not take place.

Thus, in $[\text{FeCl}_4]^{2-}$



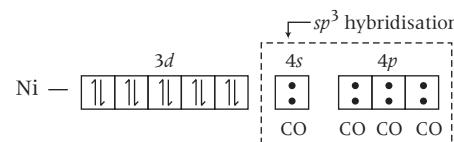
Structure-Tetrahedral

Likewise in $\text{Ni}(\text{CO})_4$



As CO is a strong ligand, hence when it approaches towards central metal atom pairing of unpaired electron of central atom takes place.

Thus, in $\text{Ni}(\text{CO})_4$



Structure Tetrahedral

So, for Q-4 and 5 are correct match.

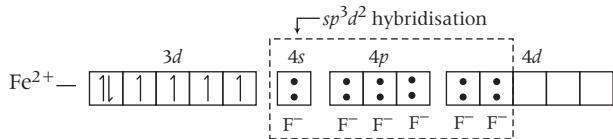
For R i.e., sp^3d^2

It is seen in $[\text{FeF}_6]^{4-}$





As F^- is a weak field ligand hence, when it approaches towards central metal atom, pairing of its electrons does not take place. Thus, in $[\text{FeF}_6]^{4-}$

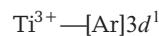


Structure : Octahedral

So, 1 is the correct match for R.

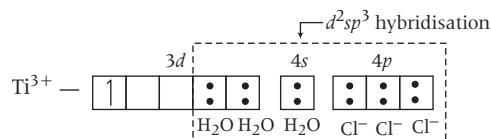
For S i.e., $d^2\text{sp}^3$

It is seen in $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}$



Here, both H_2O and Cl are weak ligands

So, in $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$



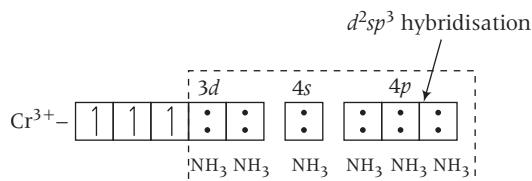
Structure Octahedral

Likewise in $[\text{Cr}(\text{NH}_3)_6]^{3+}$



Here, NH_3 is also a weak field ligand so due to its approach no pairing takes place in Cr.

Thus, In $[\text{Cr}(\text{NH}_3)_6]^{3+}$



So for, S-2 and 3 are the correct match.

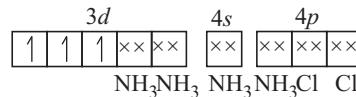
- 62. PLAN** This problem is based on concept of VBT and magnetic properties of coordination compound.

Draw VBT for each coordination compound.

If unpaired electron is present then coordination compound will be paramagnetic otherwise diamagnetic.

Coordination compounds of $[MA_4B_2]$ type show geometrical isomerism. Molecular orbital electronic configuration (MOEC) for various coordination compound can be drawn using VBT as

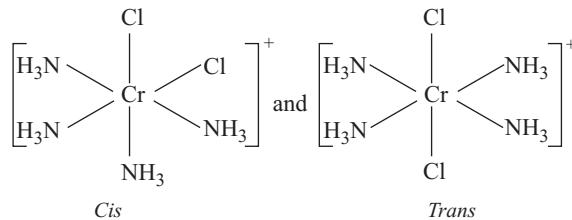
- A. MO EC for $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is



Number of unpaired electrons ($n = 3$)

Magnetic properties = paramagnetic

Geometrical isomers of $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ are



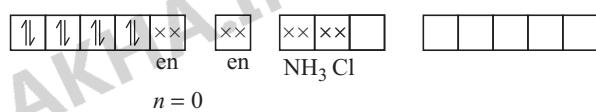
- B. $n = 1$

Magnetic properties = paramagnetic

Ionisation isomers of $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$ are

$[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$ and $[\text{Ti}(\text{H}_2\text{O})_5(\text{NO}_3)]\text{Cl}(\text{NO}_3)$

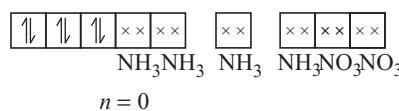
- C. MOEC of $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$ is



Magnetic property = diamagnetic

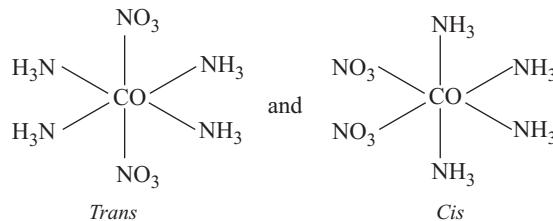
Ionisation isomers are $[\text{Pt}(\text{en})_2(\text{NH}_3)\text{Cl}]\text{NO}_3$ and $[\text{Pt}(\text{en})_2\text{NH}_3(\text{NO}_3)]\text{Cl}$

- D. MOEC of $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$



Magnetic property = Diamagnetic

Geometrical isomers are



Thus, magnetic property and isomerism in given coordination compound can be summarised as

(P) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \rightarrow$ Paramagnetic and exhibits *cis-trans* isomerism (3)

(Q) $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2 \rightarrow$ Paramagnetic and exhibits ionisation isomerism (1)

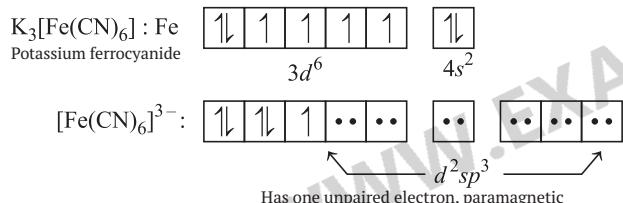
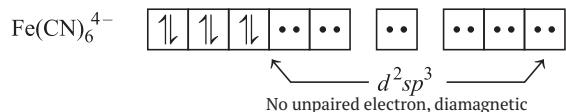
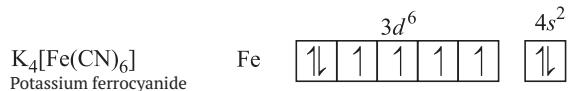
280 Coordination Compounds

- (R) $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3 \rightarrow$ Diamagnetic and exhibits ionisation isomerism (4)
- (S) $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3 \rightarrow$ Diamagnetic and exhibits *cis-trans* isomerism (2)
 $\therefore \text{P} \rightarrow 3, \text{Q} \rightarrow 1, \text{R} \rightarrow 4, \text{S} \rightarrow 2$
Hence, (b) is the correct choice.

63. (A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$: $\text{Co}^{2+}, 3d^7$
show geometrical isomerism, paramagnetic.
- (B) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$: Pt^{2+} has d^8 -configuration with all paired electrons. Show geometrical isomerism, diamagnetic.
- (C) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$: $\text{Co}^{2+}, 3d^7$
Cannot show geometrical isomerism, paramagnetic.
- (D) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$: $\text{Ni}^{2+}, 3d^8$, weak ligand, has two unpaired electrons. Paramagnetic but cannot show geometrical isomerism.

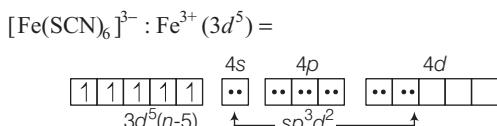
64. Complex part is cationic, named first : $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$: hexaammine cobalt (III) chloride.

65. False : Cyanide (CN^-) is a strong ligand, brings about pairing of $3d$ electrons.



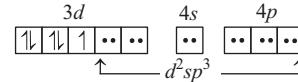
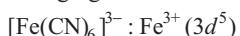
66. False : Lobes of $3d_{x^2-y^2}$ orbitals lies in XY plane on the X and Y coordinate axes, therefore electron density of $3d_{x^2-y^2}$ orbital in XY plane is non-zero.

67. When S is donor atom of SCN^- , it produces weak ligand field and forms high spin complex as



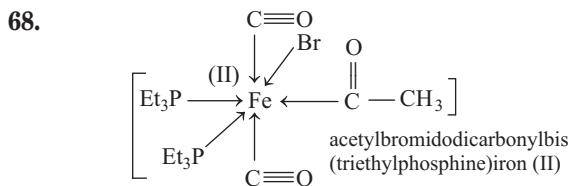
Spin only magnetic moment (μ_s) = $\sqrt{5(5+2)}$ BM = $\sqrt{35}$ BM

In case of CN^- ligand, carbon is the donor atom, it produces strong ligand field and forms low spin complex as

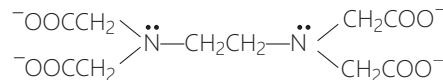


$$\text{Spin only magnetic moment } (\mu_s) = \sqrt{1(1+2)} \text{ BM} \\ = \sqrt{3} \text{ BM}$$

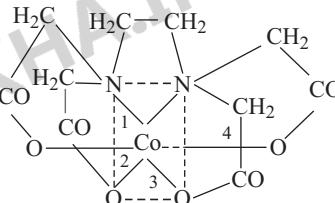
$$\text{Hence, difference in spin only magnetic moment} \\ = \sqrt{35} - \sqrt{3} \\ \approx 4 \text{ BM}$$



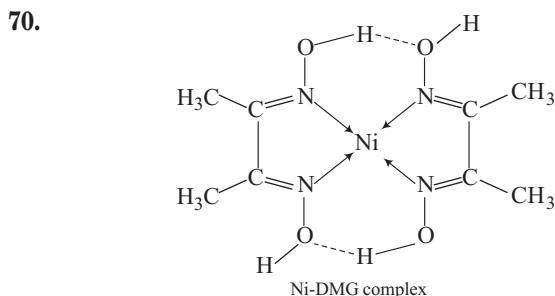
69. PLAN EDTA is a multidentate ligand as it can donate six pairs of electrons – two pair from the two nitrogen atoms and four pair from the four terminal oxygens of the $-\text{COO}^-$ groups.



The structure of a chelate of a divalent Co^{2+} with EDTA is shown as



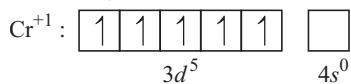
Each N has four N—Co—O bonds thus total eight N—Co—O bonds.



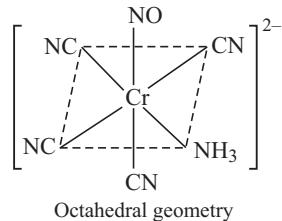
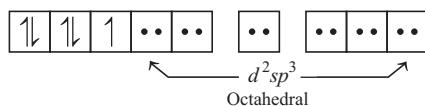
Oxidation state of Ni is +2 and hybridisation is dsp^2 .
 $\mu = 0$ (no unpaired electron) hence, diamagnetic.

71. The spin-only magnetic moment (μ) of the complex is 1.73 BM. It indicates that nucleus of complex, chromium ion has one unpaired electron. So, the ligand NO is unit positively charged.

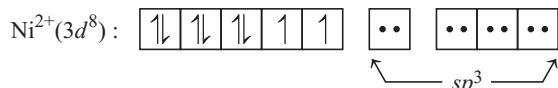
$K_2[Cr(NO)(CN)_4(NH_3)]$
potassium amminetetracyanonitrosoniumchromate (I)



Cr(I) "under influence of strong ligand field".

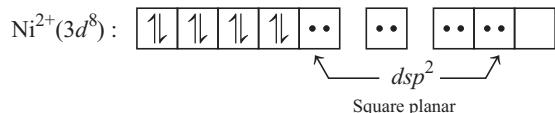


72. $[NiCl_4]^{2-} : Ni^{2+} (3d^8)$, weak ligand field.



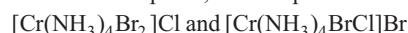
$$\mu = \sqrt{n(n+2)} BM = \sqrt{8} BM$$

$[Ni(CN)_4]^{2-} : Ni^{2+} (3d^8)$, strong ligand field.



$$\mu = 0 \text{ (no unpaired electron)}$$

73. In complexes A and B, one halide (Cl^- or Br^-) is outside coordination sphere, i.e. complexes are :

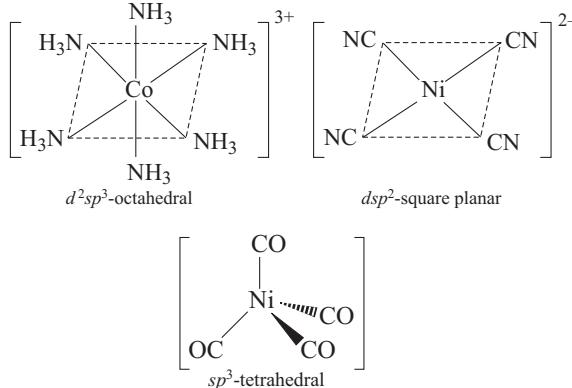


A gives white precipitate $AgCl$ with excess of $AgNO_3$ which dissolve in excess ammonia. Therefore, A must be $[Cr(NH_3)_4Br_2]Cl$.

B gives a pale yellow precipitate with excess of $AgNO_3$, which dissolve in concentrated ammonia solution. Therefore, precipitate is $AgBr$ and complex B is $[Cr(NH_3)_4ClBr]Br$.

In both A and B, hybridisation of chromium is d^2sp^3 and magnetic moment : $\mu = \sqrt{n(n+2)} BM = 0$
($3d^6$, strong ligand, no unpaired electron)

74.



75. A has no water molecules of crystallisation.

Hence, A is $[Cr(H_2O)_6]Cl_3$.

Both B and C loses weight with concentrated H_2SO_4 , therefore, both B and C have some water molecules of crystallisation.

Moreover, weight loss with C is just double of the same with B indicates that number of water molecules of crystallisation of C is double of the same for B. Therefore, B has one and C has two water molecules of crystallisation.

$$B = [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O, C = [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$$

76. (i) $[Ti(NO_3)_4]$: $Ti^{4+} (3d^0)$ No d-electron, no d-d transition possible, colourless.

(ii) $[Cu(NCCH_3)]BF_4 : Cu^+ (3d^{10})$ All d-orbitals are completely filled, no d-d transition possible, colourless.

(iii) $[Cr(NH_3)_6]Cl_3 : Cr^{3+} (3d^3)$ Complex has allowed d-d-transitions from t_{2g} to e_g level, hence coloured.

(iv) $K_3[VF_6] : V^{3+} (3d^2)$ Complex has allowed d-d-transitions from t_{2g} to e_g level, hence coloured.

77. I^- is a strong reducing agent, reduces Cu^{2+} to Cu^+ and precipitate out as stable CuI .

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Extraction of Metals

Objective Questions I (Only one correct option)

1. The processes of calcination and roasting in metallurgical industries, respectively, can lead to (2020 Main, 4 Sep II)
(a) global warming and acid rain
(b) global warming and photochemical smog
(c) photochemical smog and ozone layer depletion
(d) photochemical smog and global warming
2. An Ellingham diagram provides information about (2020 Main, 5 Sep I)
(a) the kinetics of the reduction process.
(b) the pressure dependence of the standard electrode potentials of reduction reactions involved in the extraction of metals.
(c) the temperature dependence of the standard Gibbs energies of formation of some metal oxides.
(d) the conditions of pH and potential under which a species is thermodynamically stable.
3. Calamine, malachite, magnetite and cryolite, respectively, are (2019 Adv.)
(a) ZnCO_3 , CuCO_3 , Fe_2O_3 , Na_3AlF_6
(b) ZnSO_4 , CuCO_3 , Fe_2O_3 , AlF_3
(c) ZnSO_4 , $\text{Cu}(\text{OH})_2$, Fe_3O_4 , Na_3AlF_6
(d) ZnCO_3 , $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, Fe_3O_4 , Na_3AlF_6
4. The correct statement is
(a) leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate. (2019 Main, 12 April II)
(b) the hall-heroult process is used for the production of aluminium and iron.
(c) pig iron is obtained from cast iron.
(d) the blistered appearance of copper during the metallurgical process is due to the evolution of CO_2 .
5. The idea of froth floatation method came from a person X and this method is related to the process Y of ores. X and Y , respectively, are (2019 Main, 12 April I)
(a) fisher woman and concentration
(b) washer woman and concentration
(c) fisher man and reduction
(d) washer man and reduction
6. The correct statement is (2019 Main, 10 April II)
(a) zone refining process is used for the refining of titanium.
(b) zincite is a carbonate ore.
(c) sodium cyanide cannot be used in the metallurgy of silver.
(d) aniline is a froth stabiliser.

7. Match the refining methods Column I with metals Column II.

Column I (Refining Methods)	Column II (Metals)
I. Liquation	(A) Zr
II. Zone refining	(B) Ni
III. Mond process	(C) Sn
IV. van Arkel method	(D) Ga

- (a) I- (C) ; II-(D); III-(B) ; IV-(A) (2019 Main, 10 April I)
(b) I- (B) ; II-(C); III-(D) ; IV-(A)
(c) I- (C) ; II-(A); III-(B) ; IV-(D)
(d) I- (B) ; II-(D); III-(A) ; IV-(C)

8. The one that is not a carbonate ore is (2019 Main, 9 April II)
(a) siderite (b) calamine (c) malachite (d) bauxite

9. Assertion For the extraction of iron, haematite ore is used.

Reason Haematite is a carbonate ore of iron.

(2019 Main, 9 April II)

- (a) Only the reason is correct.
(b) Both the assertion and reason are correct explanation for the assertion.
(c) Both the assertion and reason are correct and the reason is the correct explanation for the assertion.
(d) Only the assertion is correct.

10. The ore that contains the metal in the form of fluoride is (2019 Main, 9 April I)
(a) magnetite (b) sphalerite (c) malachite (d) cryolite

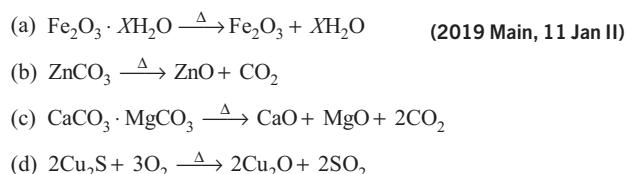
11. The Mond process is used for the (2019 Main, 8 April II)
(a) purification of Ni (b) extraction of Mo
(c) purification of Zr and Ti (d) extraction of Zn

12. With respect to an ore, Ellingham diagram helps to predict the feasibility of its (2019 Main, 8 April I)
(a) electrolysis (b) zone refining
(c) vapour phase refining (d) thermal reduction

13. The pair that does not require calcination is (2019 Main, 12 Jan II)
(a) ZnO and MgO (b) ZnO and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
(c) ZnCO_3 and CaO (d) Fe_2O_3 and $\text{CaCO}_3 \cdot \text{MgCO}_3$

14. In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of (2019 Main, 12 Jan I)
(a) platinum (b) carbon
(c) pure aluminium (d) copper

- 15.** The reaction that does not define calcination is



- 16.** Match the ores (Column A) with the metals (Column B).

Column A	Column B
Ores	Metals
A. Siderite	P. Zinc
B. Kaolinite	Q. Copper
C. Malachite	R. Iron
D. Calamine	S. Aluminium

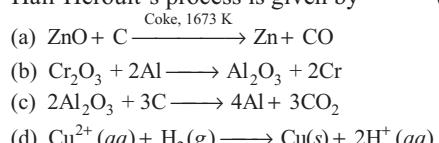
(2019 Main, 11 Jan I)

- (a) A - P; B - Q; C - R; D - S
 (b) A - R; B - S; C - P; D - Q
 (c) A - Q; B - R; C - S; D - P
 (d) A - R; B - S; C - Q; D - P

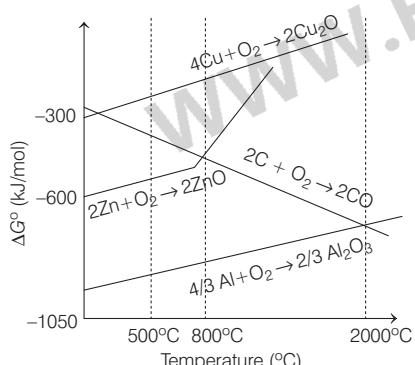
- 17.** The electrolytes usually used in the electroplating of gold and silver, respectively, are (2019 Main, 10 Jan II)

- (a) $[\text{Au}(\text{OH})_4]^-$ and $[\text{Ag}(\text{OH})_2]^-$ (b) $[\text{Au}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{CN})_2]^-$
 (c) $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$ (d) $[\text{Au}(\text{CN})_2]^-$ and $[\text{AgCl}_2]^-$

- 18.** Hall-Heroult's process is given by (2019 Main, 10 Jan I)



- 19.** The correct statement regarding the given Ellingham diagram is (2019 Main, 9 Jan II)



- (a) At 800°C, Cu can be used for the extraction of Zn from ZnO
 (b) At 1400°C, Al can be used for the extraction of Zn from ZnO
 (c) At 500°C, coke can be used for the extraction of Zn from ZnO
 (d) Coke cannot be used for the extraction of Cu from Cu₂O

- 20.** The ore that contains both iron and copper is (2019 Main, 9 Jan I)

- (a) malachite (b) azurite
 (c) dolomite (d) copper pyrites

- 21.** Which one of the following ores is best concentrated by froth floatation method? (2016 Main)

- (a) Siderite (b) Galena
 (c) Malachite (d) Magnetite

- 22.** From the following statements regarding H₂O₂ choose the incorrect statement. (2015 Main)

- (a) It can act only as an oxidising agent
 (b) It decomposed on exposure to light
 (c) It has to be stored in plastic or wax lined glass bottles in dark
 (d) It has to be kept away from dust

- 23.** In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false? (2015 Main)

- (a) CO and CO₂ are produced in this process
 (b) Al₂O₃ is mixed with CaF₂ which lowers the melting point of the mixture and brings conductivity
 (c) Al³⁺ is reduced at the cathode to form Al
 (d) Na₃AlF₆ serves as the electrolyte

- 24.** The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is (2014 Main)

- (a) Ag (b) Ca
 (c) Cu (d) Cr

- 25.** Sulphide ores are common for the metals (2013 Adv.)

- (a) Ag, Cu and Pb (b) Ag, Cu and Sn
 (c) Ag, Mg and Pb (d) Al, Cu and Pb

- 26.** In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are (2012)

- (a) O₂ and CO respectively
 (b) O₂ and Zn dust respectively
 (c) HNO₃ and Zn dust respectively
 (d) HNO₃ and CO respectively

- 27.** Oxidation states of the metal in the minerals haematite and magnetite, respectively, are (2011)

- (a) II, III in haematite and III in magnetite
 (b) II, III in haematite and II in magnetite
 (c) II in haematite and II, III in magnetite
 (d) III in haematite and II, III in magnetite

- 28.** Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of (2008, 3M)

- (a) nitrogen (b) oxygen
 (c) carbon dioxide (d) argon

- 29.** Extraction of zinc from zinc blende is achieved by

- (a) electrolytic reduction (b) roasting followed by reduction with carbon
 (c) roasting followed by reduction with another metal
 (d) roasting followed by self-reduction

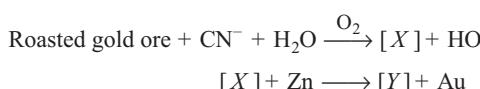
- 30.** Which ore contains both iron and copper? (2005, 1M)

- (a) Cuprite (b) Chalcocite
 (c) Chalcopyrite (d) Malachite

- 31.** The methods chiefly used for the extraction of lead and tin from their ores are respectively (2004, 1M)

- (a) self-reduction and carbon reduction
 (b) self-reduction and electrolytic reduction
 (c) carbon reduction and self-reduction
 (d) cyanide process and carbon reduction

- 32.** In the process of extraction of gold,



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- Identify the complexes $[X]$ and $[Y]$. (2003, 1M)
- $X = [\text{Au}(\text{CN})_2]^-$, $Y = [\text{Zn}(\text{CN})_4]^{2-}$
 - $X = [\text{Au}(\text{CN})_4]^{3-}$, $Y = [\text{Zn}(\text{CN})_4]^{2-}$
 - $X = [\text{Au}(\text{CN})_2]^-$, $Y = [\text{Zn}(\text{CN})_6]^{4-}$
 - $X = [\text{Au}(\text{CN})_4]^-$, $Y = [\text{Zn}(\text{CN})_4]^{2-}$
33. Anhydrous ferric chloride is prepared by (2002)
- heating hydrated ferric chloride at a high temperature in a stream of air
 - heating metallic iron in a stream of dry chlorine gas
 - reaction of ferric oxide with hydrochloric acid
 - reaction of metallic iron with hydrochloric acid
34. Which of the following process is used in extractive metallurgy of magnesium? (2002, 3M)
- Fused salt electrolysis
 - Self-reduction
 - Aqueous solution electrolysis
 - Thermite reduction
35. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is (2001, 1M)
- $\text{Cu}_2\text{O} + \text{FeS}$
 - FeSiO_3
 - CuFeS_2
 - $\text{Cu}_2\text{S} + \text{FeO}$
36. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out (2000, 1M)
- in the presence of NaCl
 - in the presence of fluorite
 - in the presence of cryolite which forms a melt with lower melting temperature
 - in the presence of cryolite which forms a melt with higher melting temperature
37. The chemical process in the production of steel from haematite ore involve (2000, 1M)
- reduction
 - oxidation
 - reduction followed by oxidation
 - oxidation followed by reduction
38. In the commercial electrochemical process for aluminium extraction, the electrolyte used is (1999, 2M)
- $\text{Al}(\text{OH})_3$ in NaOH solution
 - an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$
 - a molten mixture of Al_2O_3 and Na_3AlF_6
 - a molten mixture of $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$
39. The major role of fluorspar (CaF_2) which is added in small amount in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is (1993, 1M)
- as a catalyst
 - to make the fused mixture very conducting
 - to increase the temperature of the melt
 - to decrease the rate of oxidation of carbon at the anode
40. Hydrogen gas will not reduce (1985, 1M)
- heated cupric oxide
 - heated ferric oxide
 - heated stannic oxide
 - heated aluminium oxide
41. In the aluminothermic process, aluminium acts as (1983, 1M)
- an oxidising agent
 - a flux
 - a reducing agent
 - a solder
42. Type of bonds present in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are only (1983)
- electrovalent and covalent
 - electrovalent and coordinate covalent
 - electrovalent, covalent and coordinate covalent
 - covalent and coordinate covalent
43. In metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in (1982)
- slag
 - gangue
 - metallic calcium
 - calcium carbonate
44. Iron is rendered passive by treatment with concentrated (1982)
- H_2SO_4
 - H_3PO_4
 - HCl
 - HNO_3

Objective Questions II

(One or more than one correct option)

45. Which among the following statement(s) is(are) true for the extraction of aluminium from bauxite? (2020 Adv.)
- Hydrated Al_2O_3 precipitates, when CO_2 is bubbled through a solution of sodium aluminate.
 - Addition of Na_3AlF_6 lowers the melting point of alumina.
 - CO_2 is evolved at the anode during electrolysis.
 - The cathode is a steel vessel with a lining of carbon.
46. Extraction of copper from copper pyrite (CuFeS_2) involves (2016 Adv.)
- crushing followed by concentration of the ore by froth-floatation
 - removal of iron as slag
 - self reduction step to produce 'blister copper' following evolution of SO_2
 - refining of 'blister copper' by carbon reduction
47. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is/are (2015 Adv.)
- impure Cu strip is used as cathode
 - acidified aqueous CuSO_4 is used as electrolyte
 - pure Cu deposits at cathode
 - impurities settle as anode-mud
48. Upon heating with Cu_2S , the reagent(s) that give copper metal is/are (2014 Adv.)
- CuFeS_2
 - CuO
 - Cu_2O
 - CuSO_4
49. The carbon-based reduction method is not used for the extraction of (2013 Adv.)
- tin from SnO_2
 - iron from Fe_2O_3
 - aluminium from Al_2O_3
 - magnesium from MgCO_3 , CaCO_3
50. Extraction of metal from the ore cassiterite involves (2011)
- carbon reduction of an oxide ore
 - self-reduction of a sulphide ore
 - removal of copper impurity
 - removal of iron impurity
51. Addition of high proportions of manganese makes steel useful in making rails (1998)
- gives hardness to steel
 - helps the formation of oxides of iron
 - can remove oxygen and sulphur
 - can show highest oxidation state of + 7

52. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are
 (a) Ag (b) Mg (c) Cu (1990, 1M)
 (d) Al (e) Cr
53. In the electrolysis of alumina, cryolite is added to (1986, 1M)
 (a) lower the melting point of alumina
 (b) increase the electrical conductivity
 (c) minimise the anode effect
 (d) remove impurities from alumina

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
 (c) Statement I is correct; Statement II is incorrect.
 (d) Statement I is incorrect; Statement II is true.
54. **Statement I** $\text{Al}(\text{OH})_3$ is amphoteric in nature.
Statement II Al—O and O—H bonds can be broken with equal ease in $\text{Al}(\text{OH})_3$. (1998)

Passage Based Questions

Passage

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. (2010)

55. Partial roasting of chalcopyrite produces
 (a) Cu_2S and FeO (b) Cu_2O and FeO
 (c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3
56. Iron is removed from chalcopyrite as
 (a) FeO (b) FeS (c) Fe_2O_3 (d) FeSiO_3
57. In self-reduction, the reducing species is
 (a) S (b) O^{2-} (c) S^{2-} (d) SO_2

Numerical Answer Type Questions

58. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

$$\text{At } 298 \text{ K : } \Delta_f H^\circ[\text{SnO}_2(s)] = -581.0 \text{ kJ mol}^{-1},$$

$$\Delta_f H^\circ[(\text{CO}_2)(g)] = -394.0 \text{ kJ mol}^{-1}$$

$$S^\circ[\text{SnO}_2(s)] = 56.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ[\text{Sn}(s)] = 52.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ[\text{C}(s)] = 6.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ[\text{CO}_2(g)] = 210.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

Assume that, the enthalpies and the entropies are temperature independent. (2020 Adv.)

Match the Columns

59. Match the anionic species given in Column I that are present in the ore (s) given in Column II. (2015 Adv.)

Column I	Column II
A. Carbonate	p. Siderite
B. Sulphide	q. Malachite
C. Hydroxide	r. Bauxite
D. Oxide	s. Calamine
	t. Argentite

60. Match each of the reactions given in Column I with the corresponding product(s) given in Column II. (2009)

Column I	Column II
A. $\text{Cu} + \text{dil. HNO}_3$	p. NO
B. $\text{Cu} + \text{conc. HNO}_3$	q. NO_2
C. $\text{Zn} + \text{dil. HNO}_3$	r. N_2O
D. $\text{Zn} + \text{conc. HNO}_3$	s. $\text{Cu}(\text{NO}_3)_2$
	t. $\text{Zn}(\text{NO}_3)_2$

61. Match the conversions in Column I with the type(s) of reaction(s) given in Column II. (2008, 6M)

Column I	Column II
A. $\text{PbS} \longrightarrow \text{PbO}$	p. Roasting
B. $\text{CaCO}_3 \longrightarrow \text{CaO}$	q. Calcination
C. $\text{ZnS} \longrightarrow \text{Zn}$	r. Carbon reduction
D. $\text{Cu}_2\text{S} \longrightarrow \text{Cu}$	s. Self-reduction

62. Match the extraction processes listed in Column I with metals listed in Column II. (2006, 6M)

Column I	Column II
A. Self-reduction	p. Lead
B. Carbon reduction	q. Silver
C. Complex formation and displacement by metal	r. Copper
D. Decomposition of iodide	s. Boron

63. Each entry in Column X is in some way related to the entries in Columns Y and Z. Match the appropriate entries. (1988, 3M)

Column X	Column Y	Column Z
A. Invar	p. Co, Ni	m. Cutlery
B. Nichrome	q. Fe, Ni	n. Heating element
C. Stainless steel	r. Fe, Cr, Ni	o. Watch spring

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- 64.** Match the following choosing one item from Column X and the appropriate item from Column Y. (1983, 2M)

	Column X		Column Y
A.	Al	p.	Calamine
B.	Cu	q.	Cryolite
C.	Mg	r.	Malachite
D.	Zn	s.	Carnalite

- 65.** Match the following metals listed in Column I with extraction processes listed in Column II. (1979, 2M)

Column I	Column II
A. Silver	p. Fused salt electrolysis
B. Calcium	q. Carbon reduction
C. Zinc	r. Carbon monoxide reduction
D. Iron	s. Amalgamation
E. Copper	t. Self-reduction

Fill in the Blanks

66. Silver jewellery items tarnish slowly in the air due to their reaction with..... (1997)

67. In the extractive metallurgy of zinc, partial fusion of ZnO with coke is called and reduction of the ore to the molten metal is called (smelting, calcining, roasting, sintering). (1988, 1M)

68. Silver chloride is sparingly soluble in water because its lattice energy greater than energy. (1987)

69. Galvanisation of iron denote coating with (1983)

70. Cassiterite is an ore of (1980, 1M)

71. In the thermite process is used as a reducing agent. (1980, 1M)

72. In the basic Bessemer process for the manufacture of steel, the lining of the converter is made up of The slag formed consists of (1980, 1M)

73. AgCl dissolve in excess of KCN solution to give complex compound. (1980)

True/False

74. Cu^+ disproportionate to Cu^{2+} and elemental copper in solution. (1991)

75. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. (1984, 1M)

76. Dilute HCl oxidises metallic Fe to Fe^{2+} . (1983, 1M)

77. Silver fluoride is fairly soluble in water. (1982)

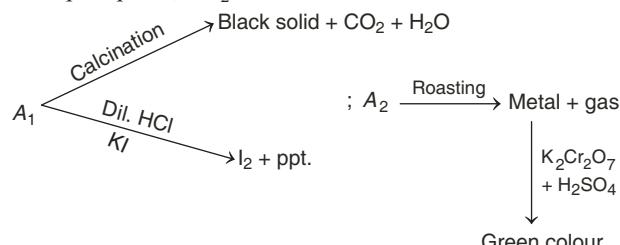
Subjective Questions

- 78.** Give the coordination number of Al in the crystalline state of AlCl_3 . (2009, 2M)

- 79.** Give the number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. (2009, 2M)

- 80.** Write balanced chemical equation for developing a black and white photographic film. Also give reason, why the solution of sodium thiosulphate on acidification turns milky white and give balance equation of this reaction. (2005, 2M)

- 81.** A_1 and A_2 are two ores of metal M . A_1 on calcination gives black precipitate, CO_2 , and water.



Identify A_1 and A_2 .

- 82.** Which of the two, anhydrous or hydrated AlCl_3 is more soluble in diethyl ether? Justify using the concepts of bonding in not more than 2 or 3 sentences. (2003)

- 83.** Write the balanced chemical reactions involved in the extraction of lead from galena. Mention oxidation state of lead in litharge. (2003, 2M)

- 84.** Write the balanced chemical equation for developing photographic films. (2000)

- 85.** Write the chemical reactions involved in the extraction of silver from argentite. (2000-2M)

- 86.** Work out the following using chemical equations.
In moist air, copper corrodes to produce a green layer on the surface. (1998)

87. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag, that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations. (1998, 4M)

- 88.** Give balance equation for the reaction of aluminium with aqueous sodium hydroxide. (1997)

- 89.** Write a balanced equation for the reaction of argentite with KCN and name the products in the solution. (1996)

- 90.** Give reasons for the following
“Although aluminium is above hydrogen in the

- electrochemical series, it is stable in air and water." (1994, 1M)

91. Complete the following reaction :
 $\text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \longrightarrow \dots + \dots$ (1994)

52. Give briefly the isolation of magnesium from sea water by the Dow's process.
Give equations for the steps involved (1993, 3M)

- 93.** Complete and balance the following reaction :
Copper reacts with HNO_3 to give NO and NO_2 in the molar ratio of 2:1



94. Write balanced equation for the extraction of "Copper from copper pyrites by self reduction." (1990, 2M)
95. Give balanced equations for the extraction of "Silver from silver glance by cyanide process." (1988, 1M)
96. Answer the following questions briefly
 (i) What is the actual reducing agent of haematite in blast furnace?
 (ii) Give the equation for the recovery of lead from galena by air reduction.
 (iii) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride?
 (iv) Zinc, not copper is used for the recovery of metallic silver from complex $[\text{Ag}(\text{CN})_2]^-$, explain.
 (v) Why is chalcocite roasted and not calcinated during recovery of copper? (1987, 5M)
97. Write balanced chemical equation for the following "Gold is dissolved in aqua regia." (1987)

98. Each of the following statement is true, only under some specific conditions. Write the condition for each subquestion in not more than 2 sentences.
 (i) Metals can be recovered from their ores by chemical methods
 (ii) High purity metals can be obtained by zone refining method. (1984, 2M)
99. Give reason for the following in one or two sentences : "Silver bromide is used in photography." (1983)
100. State the conditions under which the preparation of alumina from aluminium is carried out. Give the necessary equations which need not be balanced. (1983, 2M)
101. Write the chemical equations involved in the extraction of lead from galena by self reduction process. (1979, 2M)
102. Write balanced equation involved in the preparation of tin metal from cassiterite. (1979)

Answers

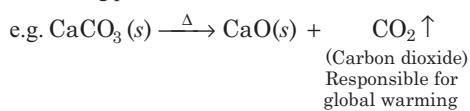
1. (a) 2. (c) 3. (d) 4. (a)
 5. (b) 6. (d) 7. (a) 8. (d)
 9. (d) 10. (d) 11. (a) 12. (d)
 13. (a) 14. (b) 15. (d) 16. (d)
 17. (c) 18. (c) 19. (b) 20. (d)
 21. (b) 22. (a) 23. (d) 24. (b)
 25. (a) 26. (b) 27. (d) 28. (b)
 29. (b) 30. (c) 31. (a) 32. (a)
 33. (b) 34. (a) 35. (b) 36. (c)
 37. (a) 38. (c) 39. (b) 40. (d)
 41. (c) 42. (c) 43. (a) 44. (d)
 45. (a,b,c,d) 46. (a,b,c) 47. (b,c,d) 48. (b,c,d)
 49. (c,d) 50. (a,d) 51. (a,c) 52. (b,d)
 53. (a,b) 54. (b) 55. (b) 56. (d)

57. (c) 58. (935)
 59. A → p, q, s; B → t; C → q; D → r
 60. A → p, s; B → q, s; C → r, t; D → q, t
 51. A → p; B → q; C → r, s; D → p, s
 62. A → p, r; B → p; C → q; D → s
 63. A → q, o; B → p, n; C → r, m
 64. A → q; B → r; C → s; D → p
 65. A → s; B → p; C → q; D → q, r; E → t
 66. (H₂S) 67. (Sintering, Smelting)
 68. (Hydration) 69. (Zn) 70. (Sn) 71. (Al)
 72. (Lime, calcium phosphate) 73. K [Ag(CN)₂]
 74. (T) 75. (T) 76. (T) 77. (T)
 78. (6) 79. (4) 83. (2)

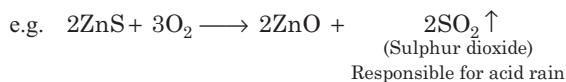
Hints & Solutions

1. Due to industrial process, CO₂ release from calcination and SO₂ release from roasting respectively which is responsible for global warming and acid rain.

Calcination It involves heating where the volatile matter escapes leaving behind the metal oxide. In this process, the ore is heated below its melting point in the absence of air or in the limited supply of air.



Roasting In this process the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal.



2. Ellingham diagram provides information about temperature dependence of the standard Gibbs energies of formation of some metal oxides.

It predicts the feasibility of thermal reduction of the ore. The criterion of feasibility is that at given temperature, Gibbs energy of the reaction must be negative.

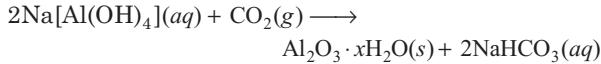
3. ZnCO₃-Calamine (zinc ore)
 CuCO₃·Cu(OH)₂-Malachite (copper ore)
 Fe₃O₄-Magnetite (iron ore)
 Na₃AlF₆-Cryolite (aluminium ore)
 Thus, option (d) is correct.

4. The correct statement is "leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate". Bauxite usually contains SiO₂, iron oxides and titanium oxide (TiO₂) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. Al₂O₃ is leached out as sodium aluminate (and SiO₂ too as sodium silicate) leaving the impurities behind.

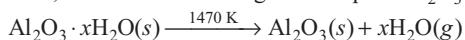


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The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. Here, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces precipitation.



The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 .



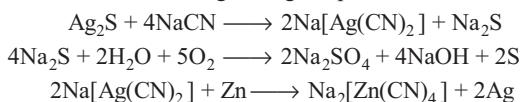
5. The idea of froth floatation method came from a person 'washer woman' (X) and this method is related to the process concentration (Y) of ores.

This method is based upon the preferential wetting properties with the frothing agent (collector) and water.

6. The explanation of given statements are as follows:

- (a) Zone refining process is used for the refining of B, Ga, In, Si and Ge.
Ti is refined by van Arkel method.
Thus, statement (a) is incorrect.
- (b) Zincite (ZnO) is an oxide ore of Zn.
Thus, statement (b) is incorrect.
- (c) NaCN is used in the hydrometallurgy of silver. It is known as Mc. Arthur Forrest process.

The reactions occurring during the process are as follows:



Thus, statement (c) is incorrect.

- (d) Aniline and cresol help in stabilising the froth in froth floatation process.

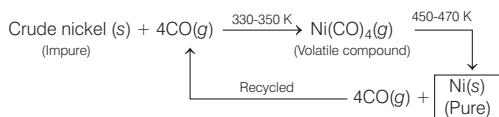
Thus, statement (d) is correct.

7. Refining of crude metals results pure metals and its impurities get separated out.

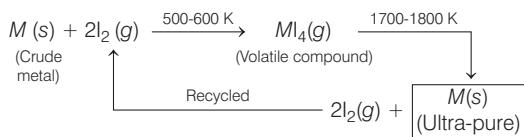
I. **Liquation** In this method low melting metals like Sn, Pb, Bi and Hg can be made to flow down through a sloping surface leaving behind the higher melting impurities on the hearth.

II. **Zone refining** The basic principle of the method is, impurities are more soluble in the molten metal than in the solid state of the metal. This method is useful to produce semiconductors and ultra-pure metals like B, Ga, In, Si and Ge.

III. Mond process



IV. van Arkel method



Here, $M = \text{Zr}, \text{Hf}, \text{Ti}$

Hence, the correct matching is

I → (C), II → (D), III → (B), IV → (A).

8. Bauxite is not a carbonate ore. Its chemical formula is Al_2O_3 or $\text{AlO}_x(\text{OH})_{3-2x}$, where $0 < x < 1$. Chemical formula of other ores given in options are as follows:

Siderite- FeCO_3

Calamine- ZnCO_3

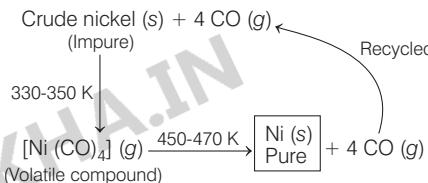
Malachite- $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

9. Only assertion is correct and reason is incorrect. Haematite is not a carbonate ore. It is an oxide ore, i.e. Fe_2O_3 . Cast iron is extracted chiefly from its oxide ore (haematite) by heating in the presence of coke and limestone in a blast furnace.

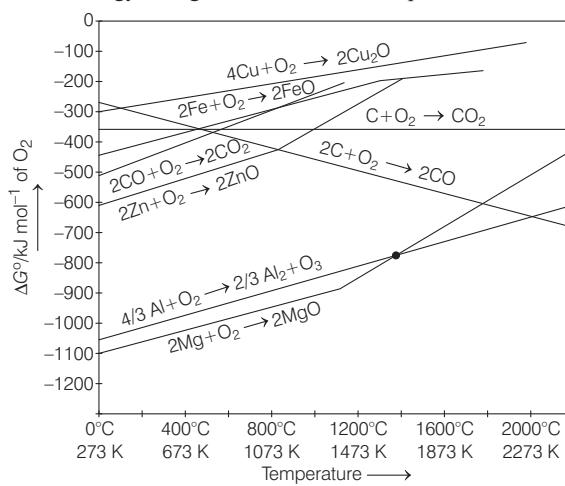
10. Cryolite ore (Na_3AlF_6 , sodium hexafluoroaluminate) contains fluorine while other given options such as malachite ($\text{Cu}_2(\text{CO})_3(\text{OH})_2$), sphalerite ($(\text{Zn}, \text{Fe})\text{S}$) and bauxite (Al_2O_3) does not contain fluorine.

11. Mond process is used in the purification of Ni. It is a vapour phase refining process.

It is based on the principle that Ni is heated in the presence of carbon monoxide to form nickel tetracarbonyl, which is a volatile complex. This complex is then decomposed by subjecting it to a higher temperature (450-470 K) to obtain pure nickel metal.

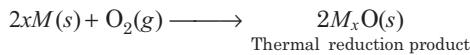


12. With respect to an ore, Ellingham diagram helps to predict the feasibility of its thermal reduction. It is a graph representation of Gibbs energy change versus absolute temperature.



Gibbs energy (ΔG°) versus T plots (schematic) for the formation of some oxides (Ellingham diagram)

Generally, the diagram consists of plots of ΔG° versus T for the formation of oxides of elements



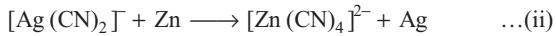
In this reaction, amount of gas decreases thus, randomness decreases. Hence, ΔS becomes negative. Therefore, the value of

- free energy increases with increase in temperature. There is a point in a curve below which ΔG is negative. So, M_xO is stable. Above this point, M_xO will decompose on its own.
13. The hydroxide, hydrated oxides and carbonate ores, after concentration, are subjected to calcination. In the process, the ore is heated below its melting point in the limited supply or absence of air. As the result, these are converted into their oxides. So, among the given options, the options having either carbonates (e.g. $ZnCO_3$ and $CaCO_3 \cdot MgCO_3$) or hydrated oxide (e.g. $Fe_2O_3 \cdot xH_2O$), require calcination while pair of option (a), i.e. ZnO and MgO does not require calcination.
14. In the Hall - Heroult's process, aluminium is formed at the cathode. The cathode is made out of carbon. In this method, Al_2O_3 is melted with cryolite, $Na_3[AlF_6]$ and electrolysed in a graphite lined steel tank, which serves as the cathode. The anode is also made of graphite. The cell runs continuously and at intervals molten aluminium is drained from the bottom of the cell and more bauxite is added. The electrolytic reactions are as follows:
- At cathode** $Al^{3+} + 3e^- \longrightarrow Al$
- At anode** $C(s) + O^{2-} (\text{melt}) \longrightarrow CO(g) + 2e^-$
 $C(s) + 2O^{2-} (\text{melt}) \longrightarrow CO_2(g) + 4e^-$
15. Calcination is one of the pyrometallurgical process, like roasting by which a concentrated ore gets converted into its oxide. In calcination, a hydrated carbonate or bicarbonate ore or a hydrated ore is heated at lower temperature (compared to roasting) in absence of air to give its oxide as in options (a), (b) and (c). Here, volatile non-metallic oxides like H_2O , CO_2 , are also produced. Roasting is valid mainly for sulphide ores like option (d), where SO_2 gets liberated. In this reaction, calcination cannot be used.
16. The correct match is: A \rightarrow R; B \rightarrow S; C \rightarrow Q; D \rightarrow P.
 (A) Siderite is an ore of iron with molecular formula $FeCO_3$ (R).
 (B) Kaolinite is an ore of aluminium with molecular formula $Al_2Si_2(OH)_5O_5$ (S).
 (C) Malachite is an ore of copper with molecular formula $CuCO_3 \cdot Cu(OH)_2$ (Q).
 (D) Calamine is an ore of zinc with molecular formula $ZnCO_3$ (P).
17. Electroplating is a process of coating one metal or metal object with a very thin layer of another metal typically applying a direct electric current. Electrolytes used in the electroplating of gold and silver are given in the table below:

Process	Article to be plated out acts as cathode	Pure metal block acts an anode by which electroplating will be done	Electrolyte (aqueous solution)
(a) Gold plating	Article	$Au(s)$	$Na[Au(CN)_2]^I$ (Sodium auro-cyanide)
(b) Silver plating	Article	$Ag(s)$	$Na[Ag(CN)_2]^I$ (Sodium argento cyanide)

18. Hall-Heroult's process is an electro-reduction process by which pure alumina (Al_2O_3) is reduced to crude Al. In this process, electrolysis of a fused mixture of Al_2O_3 , $Na_3[AlF_6]$ (cryolite) and CaF_2 (fluorspar) is carried out at carbon cathode and graphite anode. The overall reaction is represented as:
- $$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$
19. From the Ellingham diagram, we can say that any oxide with lower value of ΔG° is more stable than a oxide with higher value of ΔG° . We can also predict that the oxide placed higher in the diagram can be reduced by the element involved in the formation of its oxide placed lower at that temperature in the diagram. It is happening in case of ZnO for its reduction by Al at $1400^\circ C$.
20. The formulae of the given ores are as follows:
- | | |
|----------------|---------------------------|
| Malachite | : $CuCO_3 \cdot Cu(OH)_2$ |
| Copper pyrites | : $CuFeS_2$ |
| Dolomite | : $CaMg(CO_3)_2$ |
| Azurite | : $Cu_3(CO_3)(OH)_2$ |
21. Sulphide ores are concentrated by froth floatation method e.g. Galena (PbS)
22. H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is -1 . So, it can be oxidised to oxidation state 0 or reduced to oxidation state -2 . H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax linked glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.
23. (a) In Hall-Heroult process for extraction Al, carbon anode is oxidised to CO and CO_2 .
 (b) When Al_2O_3 is mixed with CaF_2 , it lowers the melting point of the mixture and brings conductivity.
 (c) Al^{3+} is reduced at cathode to form Al.
 (d) Here, Al_2O_3 is an electrolyte, undergoing the redox process. Na_3AlF_6 although is an electrolyte but serves as a solvent, not electrolyte.
24. Higher the position of element in the electrochemical series more difficult is the reduction of its cations. If $Ca^{2+}(aq)$ is electrolysed, water is reduced in preference to it. Hence, it cannot be reduced electrolytically from their aqueous solution.
- $$Ca^{2+}(aq) + H_2O \longrightarrow Ca^{2+} + OH^- + H_2 \uparrow$$
- 25.
- | Element | Ores | Name |
|---------|-----------------------|----------------|
| Ag | Ag_2S | Argentite |
| Cu | $CuFeS_2$ | Copper pyrites |
| Pb | PbS | Galena |
| Sn | SnO_2 | Cassiterite |
| Mg | $MgCO_3 \cdot CaCO_3$ | Dolomite |
| Al | $Al_2O_3 \cdot xH_2O$ | Bauxite |
26. The reactions involved in extraction of silver by cyanide process are
- $$Ag_2S + CN^- + O_2 \longrightarrow [Ag(CN)_2]^- + SO_2 \quad \dots(i)$$

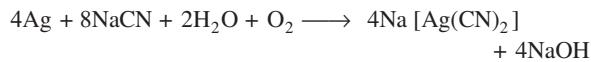
290 Extraction of Metals



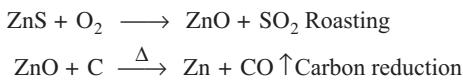
In reaction (i), sulphide is oxidised to SO_2 by oxygen. In the reaction (ii), silver ion (Ag^+) is reduced to Ag by Zn. Therefore, O_2 is oxidising agent and Zn is reducing agent.

27. Haematite is Fe_2O_3 , in which oxidation number of iron is III. Magnetite is Fe_3O_4 which is infact a mixed oxide ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), hence iron is present in both II and III oxidation state.

28. A water soluble complex with silver and dilute aqueous solution of NaCN is $\text{Na}[\text{Ag}(\text{CN})_2]$. In the cyanide process, the native silver is crushed and treated with aqueous NaCN solution and aerated.



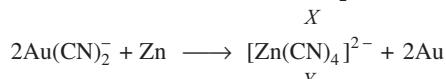
29. Zinc blende contain ZnS which is first roasted partially and then subjected to reduction with carbon



30. Chalcopyrite contain both iron and copper.

31. Lead is mainly extracted by self-reduction process while tin is extracted by carbon reduction method.

32. $\text{Au} + 2\text{CN}^- \longrightarrow [\text{Au}(\text{CN})_2]^-$



33. Heating iron in stream of dry chlorine gas gives FeCl_3 in anhydrous form. In all other cases (a and c) hydrated FeCl_3 is obtained while in (d), FeCl_2 is formed.

34. Mg is extracted by electrolysis of molten MgCl_2 .

35. Iron present in copper pyrite is removed by forming FeSiO_3 as slag.

36. Cryolite is added to alumina in order to lower the melting point.

37. Haematite ore contain Fe_2O_3 which is reduced by CO in the blast furnace as

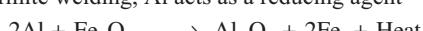


38. Al_2O_3 mixed with cryolite $\text{Na}_3[\text{AlF}_6]$ is fused and electrolysed in the extraction of Al.

39. Fluorspar (CaF_2) improve the electrical conductivity during electrolytic reduction of alumina.

40. Al itself is a very strong reducing agent.

41. In thermite welding, Al acts as a reducing agent



42. The actual representation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue vitriol) is $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and it has covalent, ionic and coordinate covalent bonds.

43. Ca^{2+} end up in CaSiO_3 (slag).

44. Iron is rendered passive by concentrated HNO_3 due to formation of a thick protective layer of Fe_3O_4 .

45. (a) $2\text{Na}[\text{Al}(\text{OH})_4](aq) + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + 2\text{Al}(\text{OH})_3 \downarrow$ or $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (ppt.)

Hence, the statement (a) is true.

(b) The electrolysis of alumina by Hall-Heroult's process is carried by using a fused mixture of alumina and cryolite ($\text{Na}_3[\text{AlF}_6]$) along with minor quantities of aluminium fluoride and fluorspar. The addition of cryolite and fluorspar increases the electrical conductivity of alumina and lowers the fusion temperature. Hence, the statement (b) is true.

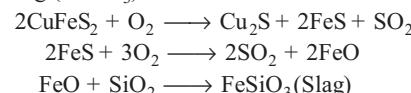
(c) At anode, alumina reacts with fluorine to liberate oxygen and evolved oxygen reacts with carbon to form carbon dioxide and hence, statement (c) is true.

(d) Steel cathode with carbon lining and graphite anode are used and hence, the statement (d) is true.

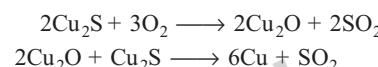
46. CuFeS_2 (copper pyrite) is converted into copper into following steps:

Step I Crushing (grinding) followed by concentration by froth-floatation process.

Step II Roasting of ore in the presence of SiO_2 which removes iron as slag (FeSiO_3).



Step III Self-reduction in Bessemer converter

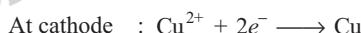
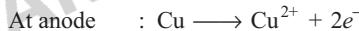


Copper obtained is blister copper (98% pure).

Step IV Refining of blister copper is done by electrolysis

Impure copper—Anode

Pure copper—Cathode

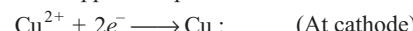


Carbon-reduction method is not used. Thus, (d) is incorrect.

47. (a) is wrong statement. Impure copper is set as anode where copper is oxidised to Cu^{2+} and goes into electrolytic solutions.

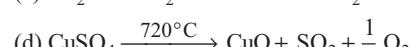
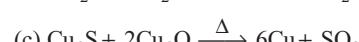
(b) CuSO_4 is used as an electrolyte in purification process.

(c) Pure copper is deposited at cathode as:

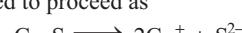


(d) Less active metals like Ag, Au etc settle down as anode mud.

48. (b) $4\text{CuO} \xrightarrow{1100^\circ\text{C}} 2\text{Cu}_2\text{O} + \text{O}_2$

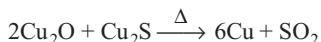
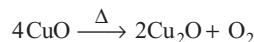
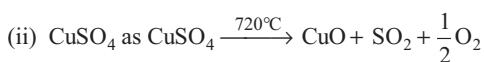
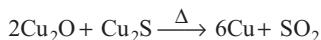
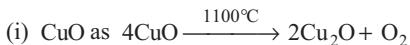


Reaction is believed to proceed as



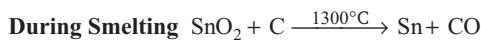
Here, copper sulphide is reduced to copper metal. Solidified copper has blistered appearance due to evolution of SO_2 and thus obtained copper is known as blister copper.

Other compounds which give Cu are



While CuFeS_2 will not give Cu on heating. The heating in the presence of O_2 gives Cu_2S and FeS with the evolution of SO_2 .

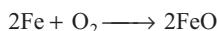
49. Al has greater affinity for oxygen, hence oxide is not reduced by carbon. MgO and CaO (formed in the calcination from carbonates) are stable species and not reduced by carbon.



50. The important ore of tin is cassiterite (SnO_2). Tin is extracted from cassiterite ore by carbon reduction method in a blast furnace.



The product often contain traces of iron which is removed by blowing air through the melt to oxidise to FeO which then floats to the surface.



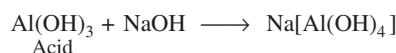
51. Addition of manganese to iron improve hardness of steel as well as remove oxygen and sulphur.

52. Magnesium and aluminium are both highly electropositive, more electropositive than water cannot be obtained by electrolysis of aqueous solution of their salts.

53. Alumina (Al_2O_3) has very high melting point and it is poor conductor of electricity. Both these factors posses difficulty in electrolysis of molten alumina.

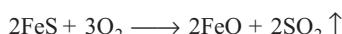
Cryolite, Na_3AlF_6 , when mixed with alumina, lowers melting point as well as improve electrical conductivity, hence helps in electrolysis of Al_2O_3 .

54. Al(OH)_3 is amphoteric

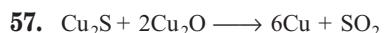


High charge and small size of Al^{3+} makes $\text{Al}-\text{O}$ and $\text{O}-\text{H}$ bonds equally ionisable.

55. $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2 \uparrow$



56. $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$ (Slag)



In Cu_2S , sulphur is S^{2-} and in SO_2 , sulphur is in +4 state. Hence, S^{2-} is acting as reducing agent.

58. Tin is obtained from cassiterite by reduction with coke and the balanced chemical reaction is



Standard enthalpy of reaction,

$$\Delta H_{R^n}^\circ = (\Delta H_f^\circ \text{ CO}_2(g)) - (\Delta H_f^\circ \text{ SnO}_2(s))$$

$$\Delta H_{R^n}^\circ = -394 - (-581) \Rightarrow 187 \text{ kJ}$$

Standard entropy of reaction, $\Delta S_{R^n}^\circ = \Delta S_{\text{Products}}^\circ - \Delta S_{\text{Reactants}}^\circ$

$$\Delta S_{R^n}^\circ = [S^\circ(\text{Sn}(s)) + S^\circ(\text{CO}_2(g))] -$$

$$[S^\circ(\text{SnO}_2(s)) + S^\circ(\text{C}(s))]$$

$$\Delta S_{R^n}^\circ = [52 + 210] - [56 + 6] \Rightarrow 200 \text{ JK}^{-1} \text{ mol}^{-1}$$

We know that, $\Delta H^\circ = T\Delta S^\circ$

$$\therefore T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{187 \times 1000}{200} \Rightarrow 935 \text{ K}$$

For the reaction to be spontaneous, the temperature should be greater than 935 K.

59. Siderite = FeCO_3 , Malachite = $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

Bauxite = $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}_2$ consisting some $\text{Al}(\text{OH})_3$

Calamine = ZnCO_3 , Argentite = Ag_2S

60. A. $3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
Dil.

- B. $\text{Cu} + 4\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
Conc.

- C. $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
Dil.

- D. $\text{Zn} + 4\text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
Conc.

- O₂

61. A. $\text{PbS} \xrightarrow{\Delta} \text{PbO} + \text{SO}_2$, roasting

- B. $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2 \uparrow$; calcination

- C. $\text{ZnS} \longrightarrow \text{Zn}$, can be done by carbon reduction
or self reduction

- D. $\text{Cu}_2\text{S} \longrightarrow \text{Cu}$, roasting followed by self reduction

	Extraction methods	Metals extracted
A.	Self reduction	r. Copper, (P) Lead
B.	Carbon reduction	p. Lead
C.	Complex formation and displacement by metal	q. Silver : $\text{Ag}_2\text{S} + \text{NaCN} \longrightarrow \text{Na}[\text{Ag}(\text{CN})_2]$ $\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + \text{Ag}$
D.	Decomposition of iodide	s. Boron : $\text{BI}_3 \xrightarrow{\Delta} \text{B} + \frac{3}{2}\text{I}_2$

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63.	Column X	Column Y	Column Z
	Invar	Fe, Ni	Watch spring
	Nichrome	Co, Ni	Heating element
	Stainless steel	Fe, Cr, Ni	Cutlery

64.	Column X (Metals)	Column Y (Ores)
A.	Al	q. Cryolite
B.	Cu	r. Malachite
C.	Mg	s. Carnalite
D.	Zn	p. Calamine

65. A. Silver is extracted by amalgamation process
 $\text{Ag} + \text{Hg} \longrightarrow \text{Ag}(\text{Hg}) \xrightarrow[\text{Amalgam}]{\text{Distillation}} \text{Ag}(s) + \text{Hg}(v) \uparrow$
- B. Calcium is extracted by electrolysis of fused CaCl_2 .
- C. Zinc is extracted by carbon reduction method
 $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
- D. Iron is extracted by both carbon reduction method and CO reduction methods
 $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
 $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$

E. Copper is extracted by self reduction methods
 $\text{Cu}_2\text{S} + \text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$
 $\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow \text{Cu} + \text{SO}_2$

66. H_2S Ag_2S (black) is formed on the surface.

67. $\text{ZnO} + \text{C} \xrightarrow[\text{sintering}]{\Delta} \text{Zn} + \text{CO}$ = Smelting

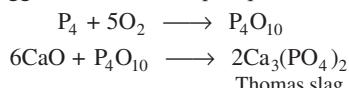
68. **Hydration energy** Energy required to break the crystal lattice during dissolving process comes from hydration. If lattice energy is very high and hydration energy is low, salt becomes sparingly soluble.

69. **Zn** Galvanisation involves coating of iron with zinc metal in order to prevent it from rusting.

70. **Sn** Cassiterite is an ore of tin.

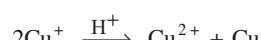
71. **Al** Aluminium reduces Fe_2O_3 to Fe.

72. **Lime, calcium phosphate** In basic Bessemer process, the Bessemer converter is lined with lime but in acid Bessemer process, it is lined with silica. In basic Bessemer process, phosphorus is slagged off as calcium phosphate :



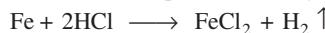
73. $\text{K}[\text{Ag}(\text{CN})_2]$: $\text{AgCl} + 2\text{KCN} \longrightarrow \text{K}[\text{Ag}(\text{CN})_2] + \text{KCl}$

74. **True:** Cu^+ is unstable



75. **True** Complex ($\text{Na}[\text{AgCl}_2]$) formation increases solubility of otherwise sparingly soluble AgCl .

76. **True** Iron is more electropositive than hydrogen

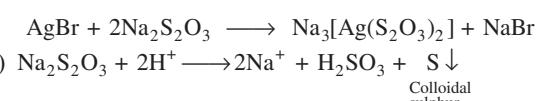


77. **True** : Solubility of silver halides decreases down in the group
Solubility : $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$

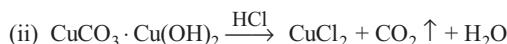
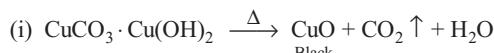
78. In crystalline state, AlCl_3 has rock-salt like structure with coordination number of Al = 6.

79. Four, the complex has formula $[\text{Cu}(\text{H}_2\text{O})_4] \text{SO}_4 \cdot \text{H}_2\text{O}$

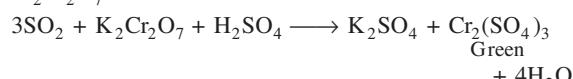
80. (a) $2\text{AgBr} + \text{C}_6\text{H}_4(\text{OH})_2 \longrightarrow 2\text{Ag} + 2\text{HBr} + \text{C}_6\text{H}_4\text{O}_2$
Hydroquinone
(developer)



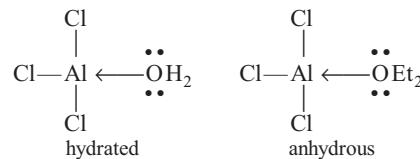
81. A_1 is basic copper carbonate ($\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$) while A_2 is Cu_2S . The confirmatory reactions are :



SO_2 is a reducing gas that gives green colour with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ as



82. Anhydrous AlCl_3 is more soluble in diethyl ether as the oxygen atom of ether donate its lone-pair of electrons to the vacant orbital of Al in electron deficient AlCl_3 . In case of hydrated AlCl_3 , Al is not electron deficient as oxygen of water molecule has already donated its lone-pair of electrons to compensate electron deficiency of Al.

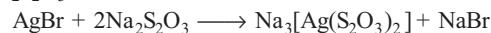


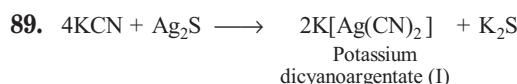
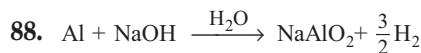
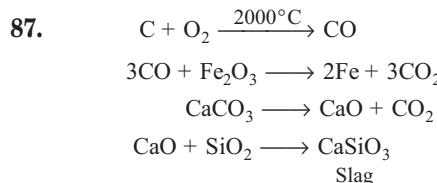
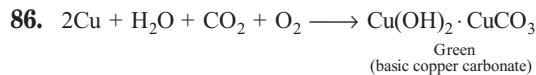
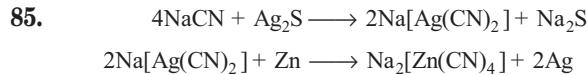
83. The reactions involved in the extraction of lead from galena (PbS) by self reduction are



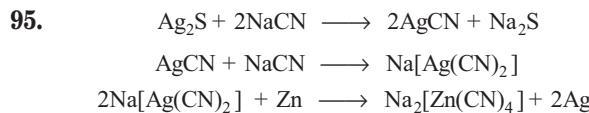
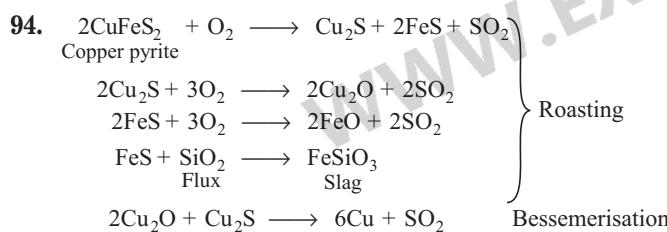
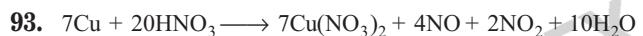
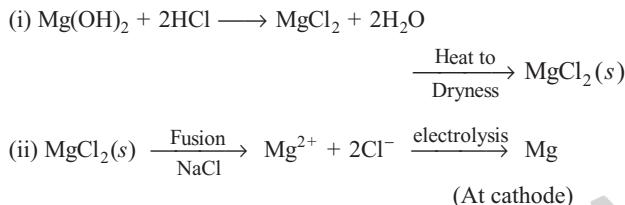
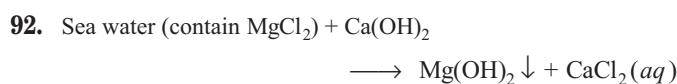
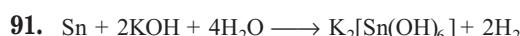
In litharge (PbO), the oxidation state of Pb is +2

84. The common photographic film is coated with AgBr and during developing of photographic film, the unreacted AgBr is removed by $\text{Na}_2\text{S}_2\text{O}_3$ as

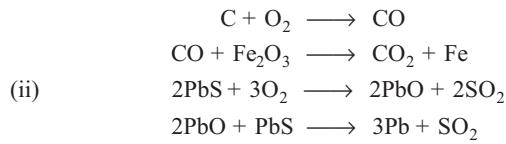




90. Due to formation of protective, inert layer of Al_2O_3 on surface.



96. (i) Carbon monoxide :

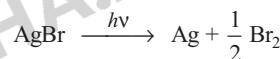


- (iii) To improve electrical conductivity of melt.
 (iv) A metal which is much more electropositive than Ag can only replace Ag^+ completely from $[\text{Ag}(\text{CN})_2]^-$ as
 $\text{Zn} + 2[\text{Ag}(\text{CN})_2]^- \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Ag}$
 (v) Chalcocite is a sulphide ore of copper, during roasting, SO_2 is liberated, which is not possible in calcination.

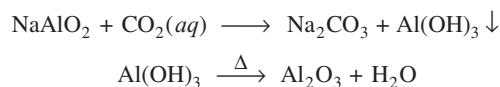
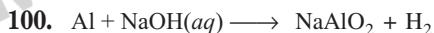


98. (i) If the metal is moderately electropositive, e.g. Fe, Sn, Pb or Cu, they can be obtained from their ore by chemical reduction methods.
 However, if the metal is highly electropositive, e.g. Al, Mg etc., no reducing agent exist for reduction of their ions (Al^{3+} , Mg^{2+}) and they are obtained by electrolytic reduction of their molten salt.
 (ii) Metals like Ge is required in high purity, can be readily melted and can easily crystallise out from the melt form.

99. AgBr is sensitive to visible light.



A photographic plate coated with AgBr , when exposed to light, gets blackened due to the above reaction.



101. In the first step, galena is heated in presence of O_2 (limited quantity) in a reverberatory furnace, where PbS is partially oxidised to PbO :



In the second step, more PbS is added and heated in absence of O_2 , where the following self reduction takes place



102. $\text{SnO}_2 + 2\text{C} \longrightarrow \text{Sn} + 2\text{CO}(g)$, Carbon reduction method.

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Qualitative Analysis

Objective Questions I (Only one correct option)

1. A colourless aqueous solution contains nitrates of two metals, X and Y . When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue P and a solution Q . The residue P was soluble in aqueous NH₃ and also in excess sodium thiosulphate. The hot solution Q gave a yellow precipitate with KI. The metals X and Y , respectively, are (2020 Adv.)
- (a) Ag and Pb (b) Ag and Cd
 (c) Cd and Pb (d) Cd and Zn

2. Reaction of an inorganic sulphite X with dilute H₂SO₄ generates compound Y . Reaction of Y with NaOH gives X . Further, the reaction of X with Y and water affords compound Z . Y and Z respectively, are (2020 Main, 6 Sep II)

- (a) SO₂ and Na₂SO₃ (b) SO₃ and NaHSO₃
 (c) SO₂ and NaHSO₃ (d) S and Na₂SO₃

3. Among (A) - (D), the complexes that can display geometrical isomerism are (2020 Main, 8 Jan II)

- (A) [Pt(NH₃)₃Cl]⁺ (B) [Pt(NH₃)Cl₅]⁻
 (C) [Pt(NH₃)₂Cl(NO₂)] (D) [Pt(NH₃)₄ClBr]²⁺
 (a) (D) and (A) (b) (C) and (D)
 (c) (A) and (B) (d) (B) and (C)

4. An organic compound X showing the following solubility profile is (2019 Main, 8 April I)

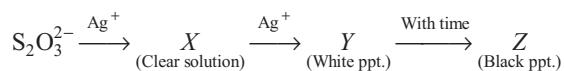
X →	Water	→ Insoluble
	5% HCl	→ Insoluble
	10% NaOH	→ Soluble
	10% NaHCO ₃	→ Insoluble

- (a) *o*-toluidine (b) oleic acid
 (c) *m*-cresol (d) benzamide

5. When metal ' M ' is treated with NaOH, a white gelatinous precipitate ' X ' is obtained, which is soluble in excess of NaOH. Compound ' X ' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal ' M ' is (2018 Main)

- (a) Zn (b) Ca (c) Al (d) Fe

6. In the following reaction sequence in aqueous solution, the species X , Y and Z , respectively, are (2016 Adv.)



- (a) [Ag(S₂O₃)₂]³⁻, Ag₂S₂O₃, Ag₂S
 (b) [Ag(S₂O₃)₃]⁵⁻, Ag₂SO₃, Ag₂S
 (c) [Ag(SO₃)₂]³⁻, Ag₂S₂O₃, Ag
 (d) [Ag(SO₃)₃]³⁻, Ag₂SO₄, Ag

7. In Carius method of estimation of halogens 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (atomic mass Ag = 108, Br = 80) (2015 Main)

- (a) 24 (b) 36 (c) 48 (d) 60

8. Upon treatment with ammoniacal H₂S, the metal ion that precipitates as a sulphide is (2013 Adv.)

- (a) Fe (III) (b) Al (III)
 (c) Mg (II) (d) Zn(II)

9. Passing H₂S gas into a mixture of Mn²⁺, Ni²⁺, Cu²⁺ and Hg²⁺ ions in an acidified aqueous solution precipitates

- (a) CuS and HgS (b) MnS and CuS (2011)
 (c) MnS and NiS (d) NiS and HgS

10. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is (2007, 3M)

- (a) Pb²⁺ (b) Hg²⁺
 (c) Cu²⁺ (d) Co²⁺

11. MgSO₄ on reaction with NH₄OH and Na₂HPO₄ forms a white crystalline precipitate. What is its formula? (2006)

- (a) Mg(NH₄)PO₄ (b) Mg₃(PO₄)₂
 (c) MgCl₂ · MgSO₄ (d) MgSO₄

12. CuSO₄ decolourises on addition of KCN, the product is

- (a) [Cu(CN)₄]²⁻ (2006, 3M)
 (b) Cu²⁺ get reduced to form [Cu(CN)₄]³⁻
 (c) Cu(CN)₂
 (d) CuCN

- 13.** A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH_4Cl / NH_4OH , the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH_4OH / NH_4Cl . (2006, 3M)
- (a) $Zn(OH)_2$ (b) $Al(OH)_3$
 (c) $Mg(OH)_2$ (d) $Ca(OH)_2$
- 14.** A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is (2005, 1M)
- (a) Hg^{2+} (b) Bi^{3+} (c) Sn^{2+} (d) Pb^{2+}
- 15.** $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by (2004, 1M)
- (a) Heating NH_4NO_2 (b) Heating NH_4NO_3
 (c) $Mg_3N_2 + H_2O$ (d) $Na(\text{comp.}) + H_2O_2$
- 16.** A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is (2004, 1M)
- (a) SO_4^{2-} (b) HCO_3^- (c) CO_3^{2-} (d) NO_3^-
- 17.** $[X] + H_2SO_4 \rightarrow [Y]$ a colourless gas with irritating smell
 $[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution
 $[X]$ and $[Y]$ are (2003, 1M)
- (a) SO_3^{2-}, SO_2 (b) Cl^-, HCl
 (c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2
- 18.** A gas X is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas Y . Identify X and Y . (2002, 3M)
- (a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$
 (c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$
- 19.** An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a (2000, 1M)
- (a) Hg_2^{2+} salt (b) Cr^{2+} salt (c) Ag^+ salt (d) Pb^{2+} salt
- 20.** In nitroprusside ion the iron and NO exist as Fe (II) and NO^+ rather than Fe (III) and NO. These forms can be differentiated by (1998, 2M)
- (a) estimating the concentration of iron
 (b) measuring the concentration of CN
 (c) measuring the solid state magnetic moment
 (d) thermally decomposing the compound
- 21.** An aqueous solution $FeSO_4 \cdot Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are (1996, 1M)
- (a) a colourless filtrate and a green residue
 (b) a yellow filtrate and a green residue
 (c) a yellow filtrate and a brown residue
 (d) a green filtrate and brown residue
- 22.** The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)^+] SO_4$. The oxidation state of iron is (1987, 1M)
- (a) 1 (b) 2 (c) 3 (d) 0
- 23.** Which one amongst the following pairs of ions cannot be separated by H_2S in dilute HCl? (1986, 1M)
- (a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+}
 (c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+}
- 24.** The compound insoluble in acetic acid is (1986, 1M)
- (a) calcium oxide (b) calcium carbonate
 (c) calcium oxalate (d) calcium hydroxide
- 25.** The ion that cannot be precipitated by both HCl and H_2S is (1982, 1M)
- (a) Pb^{2-} (b) Cu^+
 (c) Ag^+ (d) Sn^{2+}
- 26.** For the equilibrium, $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG° at 298 K is approximately (2019 Main 11 Jan II)
- (a) -80 kJ mol^{-1} (b) 100 kJ mol^{-1}
 (c) 80 kJ mol^{-1} (d) -100 kJ mol^{-1}

Objective Questions II

(One or more than one correct option)

- 27.** The correct option(s) to distinguish nitrate salts to Mn^{2+} and Cu^{2+} taken separately is (are) (2018 Adv.)
- (a) Mn^{2+} shows the characteristic green colour in the flame test
 (b) Only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium
 (c) Only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium
 (d) Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions)
- 28.** The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous solution is (are) (2016 Adv.)
- (a) $CuCl_2$ (b) $BaCl_2$
 (c) $Pb(OOCCH_3)_2$ (d) $Na_2[Fe(CN)_5NO]$
- 29.** The pair(s) of ions where both the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is (are) (2015 Adv.)
- (a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+}
 (c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}
- 30.** For the given aqueous reaction which of the statement(s) is (are) true? Excess $KI + K_3[Fe(CN)_6] \xrightarrow{\text{Dilute } H_2SO_4}$
- Brownish-yellow solution
 $\downarrow ZnSO_4$
 (White precipitate + Brownish-yellow filtrate)
 $\downarrow Na_2S_2O_3$
 Colourless solution (2012)

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- (a) The first reaction is a redox reaction
 (b) White precipitate is $Zn_3[Fe(CN)_6]_2$
 (c) Addition of filtrate to starch solution gives blue colour
 (d) White precipitate is soluble in NaOH solution
31. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are) (2008, 4M)
 (a) NH_4NO_3 (b) NH_4NO_2 (c) NH_4Cl (d) $(NH_4)_2SO_4$
32. Which of the following statement(s) is(are) correct when a mixture of $NaCl$ and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ? (1998, 2M)
 (a) A deep red vapour is evolved
 (b) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
 (c) Chlorine gas is evolved
 (d) Chromyl chloride is formed
33. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions ? (1998, 2M)
 (a) Fe^{3+} gives brown colour with potassium ferricyanide
 (b) Fe^{2+} gives blue precipitate with potassium ferricyanide
 (c) Fe^{3+} gives red colour with potassium thiocyanate
 (d) Fe^{2+} gives brown colour with ammonium thiocyanate
34. The reagents, NH_4Cl and aqueous NH_3 will precipitate (1991, 1M)
 (a) Ca^{2+} (b) Al^{3+} (c) Bi^{3+} (d) Mg^{2+}
 (e) Zn^{2+}

Assertion and Reason

Read the following questions and answer as per the direction given below :

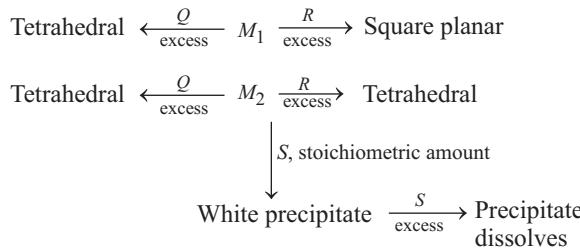
- (a) Statement I is correct Statement II is correct Statement II is a correct; explanation of Statement I
 (b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I.
 (c) Statement I is correct; Statement II is incorrect.
 (d) Statement I is incorrect; Statement II is correct.
35. **Statement I** Sulphate is estimated as $BaSO_4$, not as $MgSO_4$.
Statement II Ionic radius of Mg^{2+} is smaller than that of Ba^{2+} . (1998, 2M)
36. **Statement I** A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing H_2S .
Statement II Solubility product of CdS is more than that of NiS . (1989, 2M)

Passage Based Questions

Passage 1

An aqueous solution of metal ion M_1 reacts separately with reagents Q and R in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion

M_2 always forms tetrahedral complexes with these reagents. Aqueous solution of M_2 on reaction with reagent S gives white precipitate which dissolves in excess of S . The reactions are summarised in the scheme given below



37. M_1 , Q and R , respectively are

- (a) Zn^{2+} , KCN and HCl (b) Ni^{2+} , HCl and KCN
 (c) Cd^{2+} , KCN and HCl (d) Co^{2+} , HCl and KCN

38. Reagent S is

- (a) $K_4[Fe(CN)_6]$ (b) Na_2HPO_4
 (c) K_2CrO_4 (d) KOH

Passage 2

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and filtrate (Q). The precipitate (P) was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H_2O_2 in an aqueous NaOH medium.

39. The precipitate P contains (2013 Adv.)
 (a) Pb^{2+} (b) Hg_2^{2+} (c) Ag^+ (d) Hg^{2+}

40. The coloured solution S contains

- (a) $Fe_2(SO_4)_3$ (b) $CuSO_4$ (c) $ZnSO_4$ (d) Na_2CrO_4

Passage 3

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N , the solution turns light blue. Addition of aqueous $NaCl$ to the blue solution gives a white precipitate O . Addition of aqueous NH_3 dissolves O and gives an intense blue solution. (2011)

41. The metal rod M is

- (a) Fe (b) Cu (c) Ni (d) Co

42. The compound N is

- (a) $AgNO_3$ (b) $Zn(NO_3)_2$
 (c) $Al(NO_3)_3$ (d) $Pb(NO_3)_2$

43. The final solution contains

- (a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$
 (b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$
 (c) $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$
 (d) $[Ag(NH_3)_2]^+$ and $[Ni(NH_3)_6]^{2+}$

Passage 4

p-amino-N, N-dimethylaniline is added to a strongly acidic solution of X . The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation

of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate (II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate (III) leads to a brown colouration due to the formation of Z .

Fill in the Blanks

- 47.** The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is...
(1993, 1M)

48. If metal ions of group III are precipitated by NH_4Cl and NH_4OH without prior oxidation by conc. HNO_3 is not completely precipitated.
(1984, 1M)

True/False

- 49.** From the solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide. **(1987, 1M)**

50. Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia. **(1985, 1/2M)**

Integer Answer Type Question

- 51.** Among PbS, CuS, HgS, MnS, Ag₂S, NiS, CoS, Bi₂S₃ and SnS₂ the total number of black coloured sulphides is
(2014 Adv.)

Subjective Questions

- 52.** $B \xleftarrow{\text{moist air}} MCl_4 \xrightarrow{\text{Zn}} A$

B (White fumes having smell)	MCl_4 $M = (\text{Transition element colourless})$	A (Purple colour)
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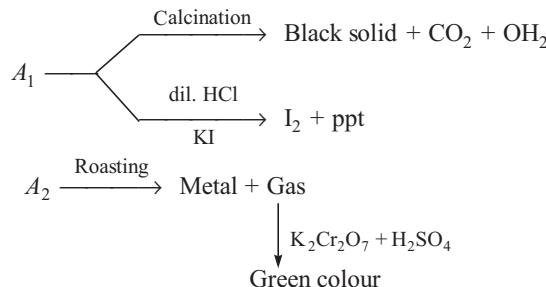
Identify the metal M and hence MCl_4 . Explain the difference in colours of MCl_4 and A . (2005, 4M)

53. $\text{Fe}^{3+} \xrightarrow{\text{SCN}^- \text{ (excess)}} \text{Blood red (A)}$

Identify A and B .

- (i) Write IUPAC name of A and B .
(ii) Find out spin only magnetic moment of B . (2005)

- 54.** A_1 and A_2 are two ores of metal M . A_1 on calcination gives black precipitate, CO_2 and water.



Identify A_1 and A_2 .

- 55.** A salt mixture consists of a yellow solid (*A*) and a colourless solid (*B*). The aqueous solution of the mixture

 - (i) On passing H_2S , we get a black precipitate of (*C*), which dissolves only in aqua-regia. On extraction and reaction with SnCl_2 a greyish white precipitate is obtained.
 - (ii) On treatment with ammonium hydroxide a reddish brown precipitate (*D*) is obtained.

The sodium extract of the solution gives the following tests:

- (i) On reaction with AgNO_3 it gives a yellow precipitate which is insoluble in NH_3 .
 - (ii) On shaking with FeCl_3 and CCl_4 a violet colouration in CCl_4 layer is obtained.

Mixture on performing flame test gives lilac colour. Identify the compounds (A), (B), (C) and (D). (2003)

- 56.** When a white crystalline compound X is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4 , a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution B is obtained. Neutralising the solution of B with acetic acid and on subsequent addition of lead acetate a yellow precipitate C is obtained.

When X is heated with NaOH solution, colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate D is formed. Identify A, B, C, D and X . Write the equations of reactions involved. (2002)

57. A white substance A reacts with dilute H_2SO_4 to produce a colourless gas B and a colourless solution C . The reaction between B and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate D . The substance D burns in air to produce a gas E which reacts with B to yield D and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or $NaOH$ to C produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify A , B , C , D and E . Write the equations of the reactions involved. (2001, 10M)

- 58.** Write the chemical reactions associated with the ‘borax bead test’ of cobalt (II) oxide. (2000, 3M)

- 59.** An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate A , which is insoluble in warm aqueous solution.

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- of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate *B*. Identify the transition metal ion. Write the chemical reactions involved in the formation of *A* and *B*. (2000, 4M)
60. Write the chemical reactions associated with the ‘brown ring test’. (2000, 1M)
61. An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl . Explain with equations. (1999, 3M)
62. During the qualitative analysis of a mixture containing Cu^{2+} and Zn^{2+} ions, H_2S gas is passed through an acidified solution containing these ions in order to test Cu^{2+} alone. Explain briefly. (1998, 2M)
63. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. (1997)
64. A soluble compound of a poisonous element *M*, when heated with $\text{Zn}/\text{H}_2\text{SO}_4$ gives a colourless and extremely poisonous gaseous compound *N*, which on passing through a heated tube gives a silvery mirror of element *M*. Identify *M* and *N*. (1997)
65. A colourless inorganic salt (*A*) decomposes completely at about 250°C to give only two products (*B*) and (*C*), leaving no residue. The oxide (*C*) is a liquid at room temperature and neutral to moist litmus paper, while the gas (*B*) is a neutral oxide. White phosphorus burns in excess of (*B*) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. (1996, 3M)
66. Gradual addition of KI solution of $\text{Bi}(\text{NO}_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. (1996, 2M)
67. A scarlet compound *A* is treated with conc. HNO_3 to give a chocolate brown precipitate *B*. The precipitate is filtered and the filtrate is neutralised with NaOH . Addition of KI to the resulting solution gives a yellow ppt *C*. The brown ppt *B* on warming with conc. HNO_3 in the presence of $\text{Mn}(\text{NO}_3)_2$ produces a pink coloured solution due to the formation of *D*. Identify *A*, *B*, *C* and *D*. Write the reaction sequence. (1995, 4M)
68. An orange solid *A* on heating gave a green residue *B*, a colourless gas *C* and water vapour. The dry gas *C* on passing over heated Mg gave a white solid *D*. *D* on reaction with water gave a gas *E* which formed dense white fumes with HCl . Identify *A* to *E* and give the reaction involved. (1993, 3M)
69. The acidic aqueous solution of ferrous ion forms a brown complex in the presence of NO_3^- , by the following two steps :

$$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO}_3^- + \text{H}^+ \longrightarrow \dots + [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$$

$$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \dots \longrightarrow \dots + \text{H}_2\text{O}$$
- Complete and balance the equation. (1993, 2M)
70. A light bluish green crystalline compound responds to the following tests
(i) Its aqueous solution gives a brown precipitate or colouration with $\text{K}_2[\text{HgI}_4]$.
(ii) Its aqueous solution gives a blue colour with $\text{K}_3[\text{Fe}(\text{CN})_6]$.
(iii) Its solution in hydrochloric acid gives a white precipitate with BaCl_2 .
- Identify the ions present and suggest the formula of the compound. (1992, 4M)
71. In the following reaction, identify the compounds/reaction conditions represented by the alphabets *A* and *B*.

$$\text{PbS} \xrightarrow[\text{air}]{\text{Heat in}} \text{A} + \text{PbS} \xrightarrow{\text{B}} \text{Pb} + \text{SO}_2$$
 (1991, 1M)
72. Give reason in one or two sentences for the following
“The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from other.” (1991, 2M)
73. The gas liberated, on heating a mixture of two salts with NaOH , gives a reddish brown precipitate with an alkaline solution of $\text{K}_2[\text{HgI}_4]$. The aqueous solution of the mixture on treatment with BaCl_2 gives a white precipitate which is sparingly soluble in conc. HCl.
- On heating the mixture with $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 , red vapours *A* are produced. The aqueous solution of the mixture gives a deep blue colouration *B* with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of *A* and *B*. (1991, 4M)
74. Write the balanced chemical equations for the following
(i) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium.
(ii) Cobalt (II) solution reacts with KNO_2 in acetic acid medium. (1989, 2M)
75. Give reasons for, “The colour of mercurous chloride, Hg_2Cl_2 , changes from white to black when treated with ammonia.” (1988, 1M)
76. A mixture of two salts was treated as follows :
(i) The mixture was heated with manganese dioxide and concentrated sulphuric acid, when yellowish green gas was liberated.
(ii) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.

- (iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.
- (iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate.
- Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii) and (iii). **(1987, 5M)**
- 77.** Write balanced equation for the following “potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid.” **(1987, 1M)**
- 78.** Mention the products formed in the following:
- Zinc oxide is treated with excess of sodium hydroxide solution.
 - Iodine is added to a solution of stannous chloride.
 - Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. **(1986, 3M)**
- 79.** What happen when
- hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.
 - aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess.
 - tin is treated with concentrated nitric acid.
 - $CrCl_3$ solution is treated with sodium hydroxide and then with hydrogen peroxide.
 - Pb_3O_4 is treated with nitric acid. **(1985, 5M)**
- 80.** Write down the balanced equations for the reactions, when, ‘a mixture of potassium chlorate, oxalic acid and sulphuric acid is heated.’ **(1985, 1M)**
- 81.** When 16.8 g of white solid, X were heated, 4.4 g of acid gas A , that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y , dissolved in water to give an alkaline solution, which with excess barium chloride solution gave a white precipitate Z . The precipitate effervesces with acid giving of carbon dioxide. Identify A , B and Y and write down the equation for the thermal decomposition of X . **(1984, 4M)**
- 82.** Compound A is a light green crystalline solid. It gives the following tests
- It dissolves in dilute sulphuric acid. No gas is produced.
 - A drop of $KMnO_4$ is added to the above solution. The pink colour disappears.
 - Compound A is heated strongly. Gases B and C , with pungent smell, come out. A brown residue D is left behind.
 - The gas mixture (B and C) is passed into a dichromate solution. The solution turns green.
 - The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate.
 - Residue D from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance.
- Name the compound A , B , C , D and E . **(1980, 4M)**
- 83.** Explain the following in not more than two sentences. A solution of $FeCl_3$ in water gives a brown precipitate on standing. **(1980, 1M)**
- 84.** The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in the presence of hydrochloric acid but not in nitric acid. Explain. **(1979, 2M)**
- 85.** A white amorphous powder A on heating yields a colourless, non-combustible gas B and a solid C . The later compound assumes a yellow colour on heating and changes to white on cooling. C dissolves in dilute hydrochloric acid and the resulting solution gives a white precipitate with $K_4Fe(CN)_6$ solution. A dissolves in dil. HCl with the evolution of gas, which is identical in all respect with B .
- The gas B turns lime water milky, but the milkiness disappears with the continuous passage of gas. The solution of A as obtained above, gives a white ppt E on addition of NaOH solution, which dissolves on further addition of base. Identify the compounds A , B , C , D and E . **(1979, 4M)**

Answers

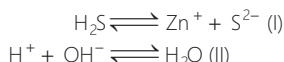
- | | | | |
|------------|---------------|---------------------|-------------------|
| 1. (a) | 2. (c) | 3. (b) | 4. (c) |
| 5. (c) | 6. (a) | 7. (a) | 8. (d) |
| 9. (a) | 10. (b) | 11. (a) | 12. (b) |
| 13. (a) | 14. (b) | 15. (a) | 16. (b) |
| 17. (a) | 18. (c) | 19. (d) | 20. (c) |
| 21. (c) | 22. (a) | 23. (a) | 24. (c) |
| 25. (c) | 26. (c) | 27. (b,d) | 28. (a) |
| 29. (c, d) | 30. (a, c, d) | 31. (a, b) | 32. (a, b, c, d) |
| 33. (b, c) | 34. (b, c) | 35. (b) | 36. (c) |
| 37. (b) | 38. (d) | 39. (d) | 40. (d) |
| 41. (b) | 42. (a) | 43. (c) | 44. (d) |
| 45. (c) | 46. (b) | 47. (CrO_2Cl_2) | 48. (Fe^{3+}) |
| 49. (True) | 50. (True) | 51. (6 or 7) | 53. (5.92 BM) |

7. Given, Weight of organic compound = 250 mg
 Weight of AgBr = 141 mg
 ∴ According to formula of % of bromine by Carius method

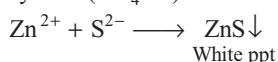
$$\% \text{ of Br} = \frac{\text{Atomic weight of Br}}{\text{Molecular weight of AgBr}} \times \frac{\text{Weight of AgBr}}{\text{Weight of organic bromide}} \times 100$$

$$\therefore \% \text{ of Br} = \frac{80}{188} \times \frac{141}{250} \times 100 = \frac{1128000}{47000} = 24\%$$

8. **PLAN** K_{sp} (ZnS) is very high and Zn^{2+} is precipitated as ZnS by high concentration of S^{2-} formed when H_2S is passed in ammoniacal solution.

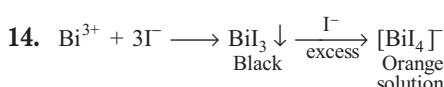
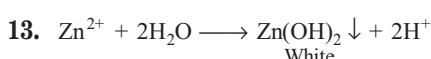
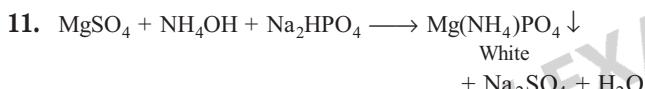
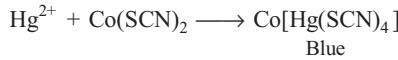
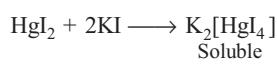
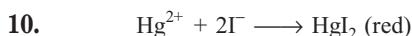


Reaction (I) is favoured in forward side if H^+ is removed immediately by OH^- (NH_4OH).



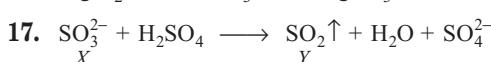
Fe^{3+} and Al^{3+} are precipitated as hydroxide.

9. In acidic medium, H_2S is very feebly ionised giving very small concentration of sulphide ion for precipitation. Therefore, the most insoluble salts CuS and HgS are precipitated only.

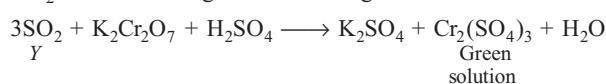


15. Both $(NH_4)_2Cr_2O_7$ and NH_4NO_2 on heating gives nitrogen gas.

16. A sodium salt of an unknown anion when treated with $MgCl$ gives white precipitate ($MgCO_3$) only on boiling. Hence, the action must be HCO_3^- ion.



SO_2 is a colourless gas with irritating odour.



18. $Cl_2 + H_2O \longrightarrow HCl + HOCl$
 X
 $HCl + AgNO_3 \longrightarrow AgCl \downarrow$ (white) + HNO_3
 $2HCl + Mg \longrightarrow MgCl_2 + H_2(g) \uparrow$
19. $PbCl_2$ is soluble in hot water and PbS (black) is formed on passing $H_2S(g)$ through acidic solution.
20. Fe(II) and Fe(III) will have different values of magnetic moment due to different number of unpaired electrons in their d -orbitals.
21. Yellow filtrate contains CrO_5 and brown residue contain Fe_2O_3 .
22. The total positive valency is +2 (because the only anion is SO_4^{2-}). Therefore, oxidation state of Fe must be +1.
23. Both Bi^{3+} and Sn^{4+} belongs to same analytical group II.
24. CaC_2O_4 is insoluble in acetic acid. This distinguishes Ca^{2+} from Ba^{2+} ion.
25. Ag^+ is precipitated by HCl only while all others are precipitated by passing H_2S in the presence of HCl .
26. We know that,
 $\Delta G^\circ = -2.303 RT \log K$
 Also, given equilibrium is
 $2H_2O \rightleftharpoons H_3O^+ + \bar{O}H$
 $[H^+] [OH^-] = 10^{-14}$ or $K = 10^{-14}$
 $\therefore \Delta G^\circ = -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log 10^{-14}$
 $= 79881.8 \text{ J mol}^{-1} = 79.8 \text{ kJ} \approx 80 \text{ kJ mol}^{-1}$
27. Statement wise explanation is
Statement (a) Mn^{2+} produces yellow-green colour in flame test while Cu^{2+} produces bluish-green colour in flame test. Thus, due to the presence of green colour in both the cases, flame test is not the suitable method to distinguish between nitrate salts of Cu^{2+} and Mn^{2+} . Hence this statement is wrong.
Statement (b) Cu^{2+} belong to group II of cationic or basic radicals. It gives black ppt. of CuS if H_2S is passed through it in the presence of acid (e.g. HCl). Mn^{2+} does not show this property hence this can be considered as a suitable method to distinguish between Mn^{2+} and Cu^{2+} .
 Hence, this statement is correct.
Statement (c) In faintly basic medium when H_2S is passed both Cu^{2+} and Mn^{2+} forms precipitates. Thus, it is not suitable method to distinguish between them.
 Hence, this statement is incorrect
Statement (d) The standard reduction potential of Cu^{2+}/Cu is +0.34 V while that of Mn^{2+}/Mn is -1.18V. This can be used to distinguish between Cu^{2+} and Mn^{2+} . In general less electropositive metals have higher SRP.
 Hence, this statement is correct.
28. (a) $S^{2-} + CuCl_2 \longrightarrow CuS \downarrow$ (black ppt.)
 $SO_4^{2-} + CuCl_2 \longrightarrow$ Soluble, Thus
 $CuCl_2$ selectively precipitates S^{2-} .

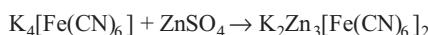
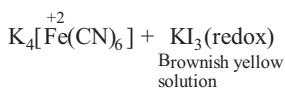
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- (b) $S^{2-} + BaCl_2 \longrightarrow BaS \downarrow$ (soluble)
 $SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 \downarrow$ (white ppt.)
 precipitates SO_4^{2-} and not S^{2-} .
- (c) $S^{2-} + Pb^{2+} \longrightarrow PbS \downarrow$ (black ppt.)
 $SO_4^{2-} + Pb^{2+} \longrightarrow PbSO_4 \downarrow$ (white ppt.)
 S^{2-} and SO_4^{2-} , both are precipitated.
- (d) $S^{2-} + Na_2[Fe(CN)]_5NO \longrightarrow Na_4[Fe(CN)]_5NOS$
 Sodium nitroprusside
 (Purple colour)
 But no colour with SO_4^{2-} .

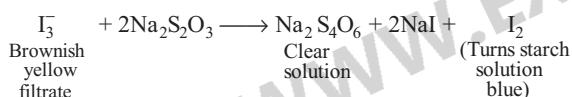
29. Only radicals of I and II group of qualitative analysis get precipitated with H_2S in the presence of dilute HCl.

- (c) $Cu^{2+} + H_2S \xrightarrow{H^+} CuS \downarrow$
 Black
 $Pb^{2+} + H_2S \xrightarrow{H^+} PbS \downarrow$
 Black
(d) $Hg^{2+} + H_2S \xrightarrow{H^+} HgS \downarrow$
 Black
 $Bi^{3+} + H_2S \xrightarrow{H^+} Bi_2S_3 \downarrow$
 Brown ppt
 Ba^{2+} , Zn^{2+} and Fe^{3+} are not precipitated as sulphide.

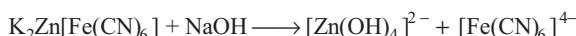
30. $K_3^{+3}[Fe(CN)_6] + KI$ (excess) \longrightarrow



or $K_2Zn[Fe(CN)_6]$
 White ppt



$K_2Zn[Fe(CN)_6]$ reacts with NaOH as



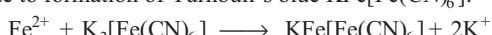
31. $NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O$



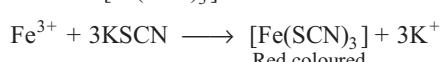
32. When mixture of NaCl is heated with $K_2Cr_2O_7$ in concentrated H_2SO_4 , red vapour of chromyl chloride (CrO_2Cl_2) is produced. Vapours of chromyl chloride when passed through NaOH, solution turns yellow due to formation of Na_2CrO_4 . Some chlorine gas is also evolved owing to the following side reaction:



33. The blue precipitate of Fe^{2+} ion with potassium ferricyanide is due to formation of Turnbull's blue $KFe[Fe(CN)_6]$.



The red colour of Fe^{3+} ion with potassium thiocyanate is due to formation of $[Fe(SCN)_3]$.

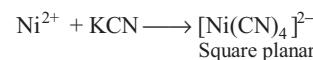


34. Both Al^{3+} and Bi^{3+} are precipitated as their hydroxides.
35. As $MgSO_4$ is soluble in water, so not used for estimation of SO_4^{2-} ion.
36. Cation Cd^{2+} belongs to group II while Ni^{2+} belongs to group III of analytical group. Group II radicals are precipitated by passing $H_2S(g)$ through acidic solution of salt but radicals of group III are precipitated by passing $H_2S(g)$ in NH_3/NH_4Cl buffer solution of salt due to greater solubility products of later salts.

37. **PLAN** This problem can be solved by using concept of chemical reactions of transition metal ions (.) colour and structure of transition metal compounds.

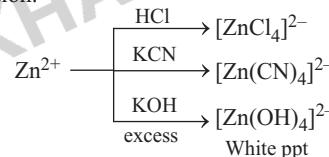
Here, among given four option Ni^{2+} and Zn^{2+} has ability to form tetrahedral as well as square planar complex depending upon types of reagent used.

Ni^{2+} on reaction with KCN forms square planar complex $[Ni(CN)_4]^{2-}$ due to strong field strength of CN.

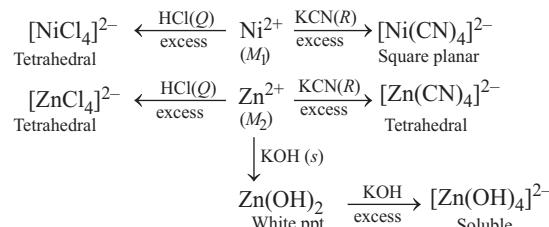


While on reaction with HCl, Ni^{2+} forms stable tetrahedral complex $[Ni(Cl)_4]^{2-}$.

Zn^{2+} , on the other hand, on reaction with KCN as well as HCl produces tetrahedral complex because of its d^{10} electronic configuration.



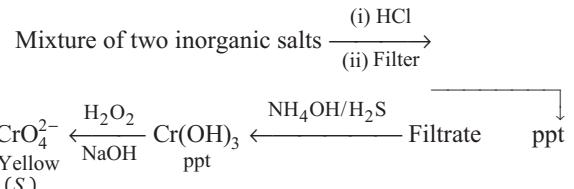
Complete reaction sequence can be shown as



38. Zn^{2+} on treatment with excess of KOH produces $[Zn(OH)_4]^{2-}$.

39, 40. **PLAN** $PbCl_2$ is soluble in hot water.

In ammoniacal medium, cations of group III and IV may be precipitated as hydroxide or sulphide and dissolved in H_2O_2 due to oxidation.

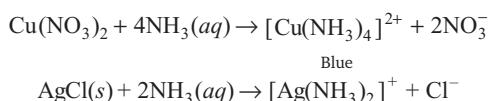


Thus, Q. 38. P is Pb^{2+} . Q. 39. S is Na_2CrO_4 .

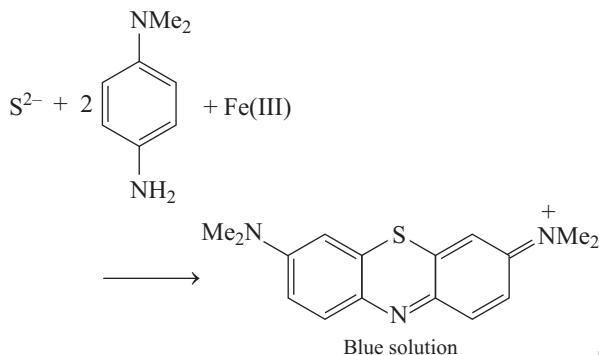
- 41.** Appearance of blue colour on addition of the metal rod M to the solution of N is an indication that metal may be Cu. Later formation of white precipitate on addition of NaCl and dissolution of this precipitate in aqueous ammonia confirm that while precipitate is of AgCl. This implies that the solution N is of AgNO_3 . This confirm that the metal M is only Cu.

- 42.** The compound N is AgNO_3 , explained above.

- 43.** Since, in the beginning, concentrated AgNO_3 solution was taken, some AgNO_3 remain in solution which gives white precipitate of AgCl on addition of NaCl. The precipitate finally dissolve in ammonia and Cu^{2+} present in solution also forms complex with ammonia as



The comprehension describing methylene-blue test.



Therefore,

- 44.** X is Na_2S .

- 45.** Y is FeCl_3 .

- 46.** Compound Z is $\text{Fe}[\text{Fe}(\text{CN})_6]$.

- 47.** Heating chloride salt with $\text{K}_2\text{Cr}_2\text{O}_7$ in conc. H_2SO_4 gives off a deep vapour of chromyl chloride (CrO_2Cl_2).

- 48.** Because $\text{Fe}(\text{OH})_2$ is soluble.

- 49.** ZnS is soluble in dil. HCl but CuS does not dissolve in dil. HCl.

- 50.** In absence of NH_4Cl , both $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ will be precipitated.

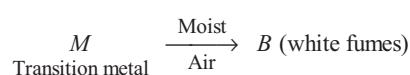
- 51.** From qualitative analysis of the different metal ions it is found that PbS , CuS , HgS , Ag_2S , NiS , CoS are black coloured.

MnS — dirty pink/buff coloured, SnS_2 — yellow coloured.

Bi_2S_3 — brown/black (brownish black) coloured.

Hence, correct integer is (6 or 7).

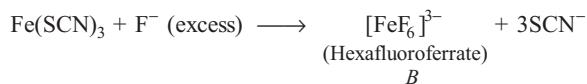
- 52.** $\text{MCl}_4 \xrightarrow{\text{Zn}} \text{Purple coloured compound } (A)$
Colourless



$$\Rightarrow M = \text{Ti}, A = [\text{Ti}(\text{H}_2\text{O})_6]^{3+}; B = \text{TiO}_2$$

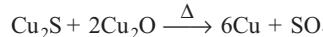
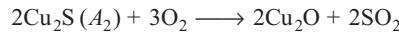
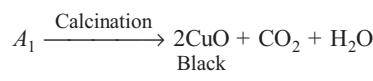
Ti (IV) contains no d -electron, while $d-d$ transition of single electron of Ti (III) will cause colour change.

- 53.** (i) $\text{Fe}^{3+} + 3\text{SCN}^- \longrightarrow \text{Fe}(\text{SCN})_3$ (blood red colouration)
Iron (III)
thiocyanate
 A

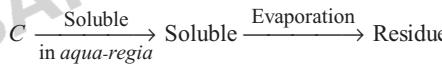
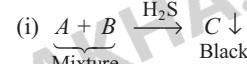


$$\begin{aligned}\text{(ii) Magnetic moment } (\mu_S) &= \sqrt{n(n+2)} \text{ BM} \\ &= \sqrt{35} \text{ BM} = 5.92 \text{ BM}\end{aligned}$$

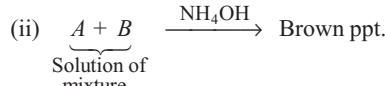
- 54.** $A_1 = \text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ and $A_2 = \text{Cu}_2\text{S}$



- 55.** $\underbrace{A + B}_{\text{Mixture}} \longrightarrow$ lilac colour in flame



$$\Rightarrow C \text{ is HgS.}$$

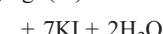
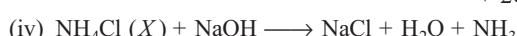
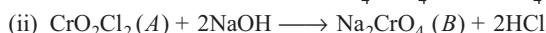
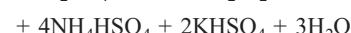
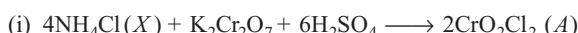


$$\Rightarrow A = \text{KI} \text{ and } B = \text{HgI}_2$$

- 56.** $X = \text{NH}_4\text{Cl}$; $A = \text{CrO}_2\text{Cl}_2$; $B = \text{Na}_2\text{CrO}_4$; $C = \text{PbCrO}_4$;

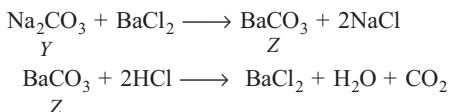


Reactions involved :



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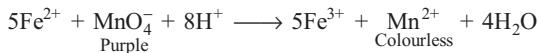
$\text{H}_2\text{O}(g)$ is condensed to liquid water.



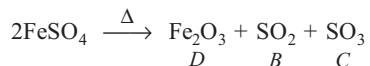
82. Compound A is a light green crystalline solid, so it may be FeSO_4 .

(i) FeSO_4 is a salt of strong acid and weak base, so it hydrolyses in dil. H_2SO_4 but no gas is evolved.

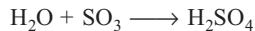
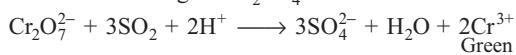
(ii) FeSO_4 is a strong reducing agent, thus decolourises KMnO_4 solution :



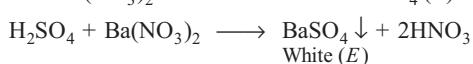
(iii) FeSO_4 on strong heating gives both SO_2 (*B*) and SO_3 (*C*) gases alongwith a residue of Fe_2O_3 (*D*).



(iv) The gaseous mixture reduced dichromate solution to green solution and also gives H_2SO_4 in solution :



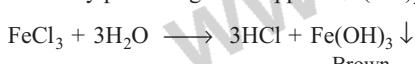
(v) The sulphuric acid (formed in previous step) gives white ppt. with $\text{Ba}(\text{NO}_3)_2$, due to formation of BaSO_4 (E) :



(vi) The residue D when heated on charcoal in a reducing flame reduces to iron (Fe) which is a magnetic substance.

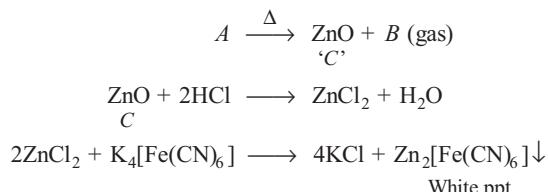
Hence, $A = \text{FeSO}_4$, $B = \text{SO}_2$, $C = \text{SO}_3$, $D = \text{Fe}_2\text{O}_3$ and $E = \text{BaSO}_4$.

83. FeCl_3 is a salt of strong acid and weak base. In water, it hydrolyzes slowly producing brown ppt of $\text{Fe}(\text{OH})_3$.

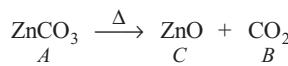
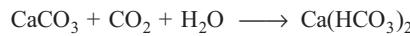
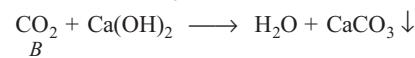


84. Nitric acid is a strong oxidising agent, oxidises H_2S to S.

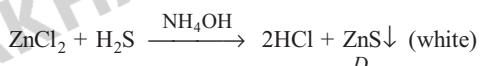
- 85.** (i) The compound C produced by heating A is white in colour and changes to yellow on heating, thus compound C may be ZnO . C with dil. HCl and $\text{K}_4[\text{Fe}(\text{CN})_6]$ gives white ppt. This confirms that the compound C must be ZnO .



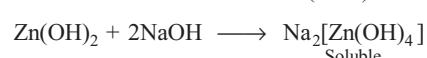
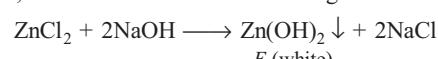
(ii) The gas B turns lime water milky and milkiness disappear with continuous passage of gas. Hence, the gas is CO_2 and compound A in ZnCO_3 .



(iii) The solution of A gives white ppt of ZnS D with NH_4OH and excess of H_2S .



(iv) The solution of A also gives initially a white ppt E with NaOH , which dissolve in excess of reagent.



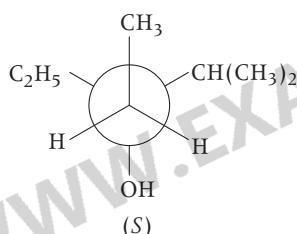
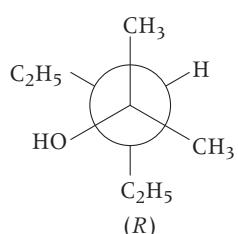
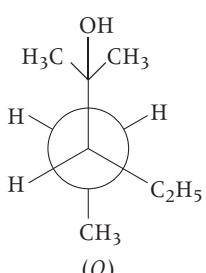
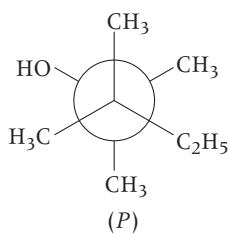
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Organic Chemistry Basics

Topic 1 Nomenclature and Isomerism

Objective Questions I (Only one correct option)

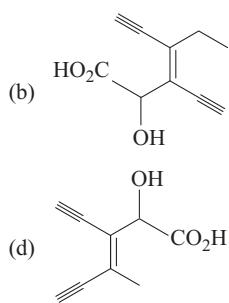
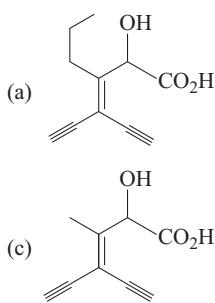
- 1.** Newman projections P , Q , R and S are shown below :



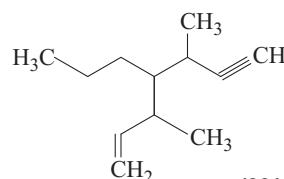
Which one of the following options represents identical molecules? (2020 Adv.)

- (a) P and Q (b) Q and S
 (c) O and R (d) R and S

- 2.** Which one of the following structures has the IUPAC name 3-ethynyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid?



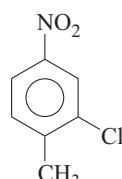
- 3.** The IUPAC name for the following compound is



(2019 Main, 12 April II)

- (a) 3-methyl-4-(3-methylprop-1-enyl)-1-heptene
 - (b) 3, 5-dimethyl-4-propylhept-6-en-1-yne
 - (c) 3-methyl-4-(1-methylprop-2-enyl)-1-heptene
 - (d) 3, 5-dimethyl-4-propylhept-1-en-6-yne

4. The correct IUPAC name of the following compound is



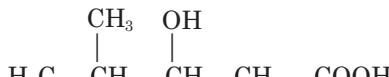
(2019 Main, 9 April I)

- (a) 2-methyl-5-nitro-1-chlorobenzene
 - (b) 3-chloro-1-methyl-1-nitrobenzene
 - (c) 2-chloro-1-methyl 1-4-nitrobenzene
 - (d) 5-chloro-4-methyl 1-1-nitrobenzene

5. Which of the following compounds will show the maximum 'enol' content? (2019 Main, 8 April II)

- (a) CH_3COCH_3
 - (b) $\text{CH}_3\text{COCH}_2\text{COCH}_3$
 - (c) $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$
 - (d) $\text{CH}_3\text{COCH}_2\text{CONH}_3$

6. The IUPAC name of the following compound is

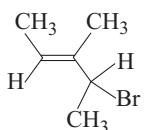


(2019 Main, 8 April I)

- (a) 4,4 - dimethyl -3-hydroxybutanoic acid
 - (b) 2-methyl-3-hydroxypentan-5-oic acid
 - (c) 3- hydroxy -4- methylpentanoic acid
 - (d) 4-methyl-3-hydroxypentanoic acid

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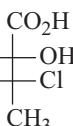
7. What is the IUPAC name of the following compound?



(2019 Main, 10 Jan II)

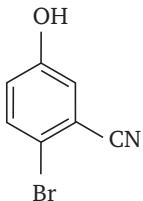
- (a) 3-bromo-3-methyl-1,2-dimethylprop-1-ene
- (b) 3-bromo-1,2-dimethylbut-1-ene
- (c) 2-bromo-3-methylpent-3-ene
- (d) 4-bromo-3-methylpent-2-ene

8. The absolute configuration of is (2016 Main)



- (a) (2S, 3R)
- (b) (2S, 3S)
- (c) (2R, 3R)
- (d) (2R, 3S)

9. The IUPAC name of the following compound is



(2009)

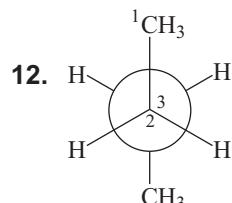
- (a) 4-bromo-3-cyanophenol
- (b) 2-bromo-5-hydroxybenzonitrile
- (c) 2-cyano-4-hydroxybromobenzene
- (d) 6-bromo-3-hydroxybenzonitrile

10. The number of stereoisomers obtained by bromination of *trans*-2-butene is (2007, 3M)

- (a) 1
- (b) 2
- (c) 3
- (d) 4

11. The IUPAC name of C_6H_5COCl is (2006, 3M)

- (a) benzoyl chloride
- (b) benzene chloro ketone
- (c) benzene carbonyl chloride
- (d) chloro phenyl ketone



C_2 is rotated anti-clockwise 120° about C_2-C_3 bond. The resulting conformer is (2004, 1M)

- (a) partially eclipsed
- (b) eclipsed
- (c) gauche
- (d) staggered

13. Which of the following compounds exhibits stereoisomerism? (2002, 3M)

- (a) 2-methylbutene-1
- (b) 3-methylbutyne-1
- (c) 3-methylbutanoic acid
- (d) 2-methylbutanoic acid

14. The number of isomers for the compound with molecular formula $C_2BrClFI$ is (2001, 1M)

- (a) 3
- (b) 4
- (c) 5
- (d) 6

15. Which of the following compounds will exhibit geometrical isomerism? (2000, 1M)

- (a) 1-phenyl-2-butene
- (b) 3-phenyl-1-butene
- (c) 2-phenyl-1-butene
- (d) 1,1-diphenyl-1-propene

16. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive (1999, 2M)

- (a) optical rotation and is derived from D-glucose
- (b) pH in organic solvent
- (c) optical rotation and is derived from D-(+)-glyceraldehydes
- (d) optical rotation when substituted by deuterium

17. How many optically active stereoisomers are possible for butane-2, 3-diol? (1997, 1M)

- (a) 1
- (b) 2
- (c) 3
- (d) 4

18. Isomers which can be interconverted through rotation around a single bond are (1992, 1M)

- (a) conformers
- (b) diastereomers
- (c) enantiomers
- (d) positional isomers

19. The enolic form of acetone contains (1990, 1M)

- (a) 9 sigma bonds, 1 pi bond and 2 lone pairs
- (b) 8 sigma bonds, 2 pi bonds and 2 lone pairs
- (c) 10 sigma bonds, 1 pi bond and 1 lone pair
- (d) 9 sigma bonds, 2 pi bonds and 1 lone pair

20. The number of isomers of C_6H_{14} is (1987, 2007, 3M)

- (a) 4
- (b) 5
- (c) 6
- (d) 7

21. If two compounds have the same empirical formula but different molecular formulae, they must have (1987, 1M)

- (a) different percentage composition
- (b) different molecular weight
- (c) same velocity
- (d) same vapour density

22. Which of the following will have least hindered rotation about carbon-carbon bond? (1987, 1M)

- (a) Ethane
- (b) Ethylene
- (c) Acetylene
- (d) Hexachloroethane

23. The IUPAC name of the compound

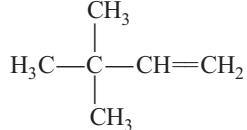


- (a) 1,1-dimethyl-2-butene
- (b) 3-methyl-1-butene
- (c) 2-vinyl propane
- (d) None of these

24. An isomer of ethanol is (1986, 1M)

- (a) methanol
- (b) diethyl ether
- (c) acetone
- (d) dimethyl ether

25. The IUPAC name of the compound having the formula is



(1984, 1M)

- (a) 3, 3, 3-trimethyl-1-propene
- (b) 1, 1, 1-trimethyl-2-propene
- (c) 3, 3-dimethyl-1-butene
- (d) 2, 2-dimethyl-3-butene

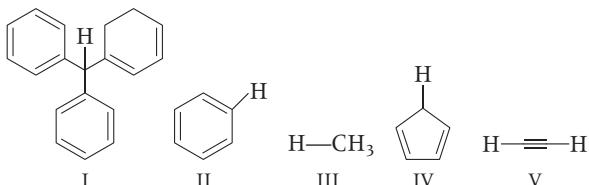
- 26.** Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism ? (1983, 1M)
- 2-butene
 - 2-butyne
 - 2-butanol
 - butanal

- 27.** The compound which is not isomeric with diethyl ether is (1981, 1M)
- n*-propyl methyl ether
 - butane-1-ol
 - 2-methyl propane-2-ol
 - butanone

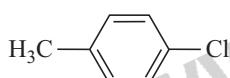
Objective Questions II

(One or more than one correct option)

- 28.** With respect to the compounds I-V. Choose the correct statement(s). (2020 Adv.)

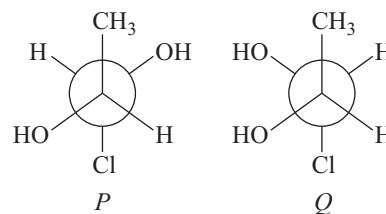
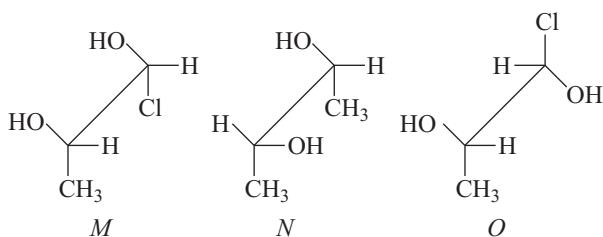


- (a) The acidity of compound I is due to delocalisation in the conjugate base.
 (b) The conjugate base of compound IV is aromatic.
 (c) Compound II becomes more acidic, when it has a $-\text{NO}_2$ substituent.
 (d) The acidity of compounds follows the order
 $I > \text{IV} > \text{V} > \text{II} > \text{III}$.
- 29.** The IUPAC name(s) of the following compound is (are) (2017 Adv.)



- (a) 4-methylchlorobenzene
 (b) 4-chlorotoluene
 (c) 1-chloro-4-methylbenzene
 (d) 1-methyl-4-chlorobenzene
- 30.** The correct combination of names for isomeric alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ is/are (2014 Adv.)
- tert*-butanol and 2-methylpropan-2-ol
 - tert*-butanol and 1,1-dimethylethan-1-ol
 - n*-butanol and butan-1-ol
 - iso*-butyl alcohol and 2-methylpropan-1-ol

- 31.** Which of the given statement(s) about *N*, *O*, *P* and *Q* with respect to *M* is/are correct? (2012)



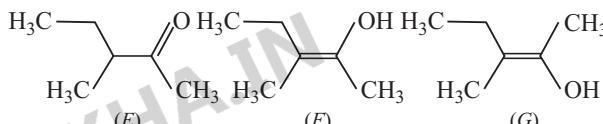
- M* and *N* are non-mirror image stereoisomers
- M* and *O* are identical
- M* and *P* are enantiomers
- M* and *Q* are identical

- 32.** The correct statement(s) about the compound (2009)



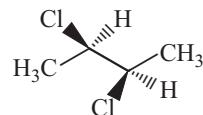
- The total number of stereoisomers possible for *X* is 6
- The total number of diastereomers possible for *X* is 3
- If the stereochemistry about the double bond in *X* is *trans*, the number of enantiomers possible for *X* is 4
- If the stereochemistry about the double bond in *X* is *cis*, the number of enantiomers possible for *X* is 2

- 33.** The correct statement(s) concerning the structures *E*, *F* and *G* is/are



- E*, *F* and *G* are resonance structures
 - E*, *F* and *E*, *G* are tautomers
 - F* and *G* are geometrical isomers
 - F* and *G* are diastereomers
- (2008, 4M)

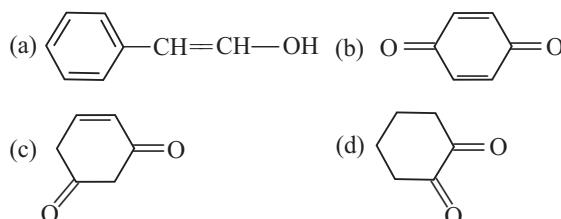
- 34.** The correct statement(s) about the compound given below is/are



(2008, 4M)

- the compound is optically active
- the compound possesses centre of symmetry
- the compound possesses plane of symmetry
- the compound possesses axis of symmetry

- 35.** Tautomerism is exhibited by (1998, 2M)

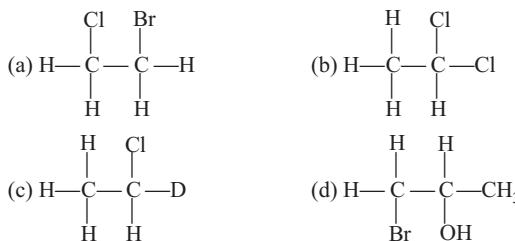


- 36.** Which of the following compounds will show geometrical isomerism ? (1998, 2M)

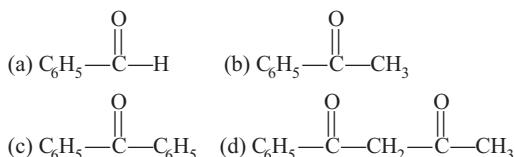
- 2-butene
- propene
- 1-phenyl propene
- 2-methyl-2-butene

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37. Which of the following have asymmetric carbon atom?
(1989, 1M)



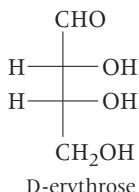
38. Keto-enol tautomerism is observed in
(1988, 2M)



39. Only two isomeric monochloro derivatives are possible for
(1986, 1M)
- | | |
|----------------------|---------------------------|
| (a) <i>n</i> -butane | (b) 2, 4-dimethyl pentane |
| (c) benzene | (d) 2-methyl propane |

Match the Columns

40. The Fischer projection of D-erythrose is shown below :



D-erythrose and its isomers are listed as P, Q, R, and S in Column-I. Choose the correct relationship of P, Q, R, and S with D-erythrose from Column II.
(2020 Adv.)

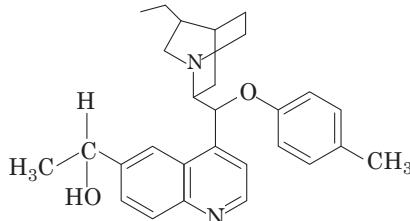
	Column I	Column II	
P.		1.	Diastereomer
Q.		2.	Identical
R.		3.	Enantiomer
S.			

Codes

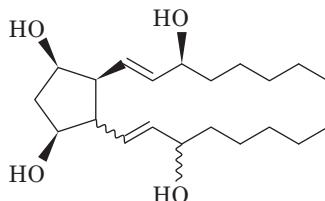
P	Q	R	S
(a) 2	3	2	2
(b) 3	1	1	2
(c) 2	1	1	3
(d) 2	3	3	1

Numerical Answer Type Questions

41. The number of chiral carbons present in the molecule given below is
(2020 Main, 2 Sep I)



42. For the given compound X, the total number of optically active stereoisomers is
X:



→ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed

~~~ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is not fixed

(2018 Adv.)

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I  
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I  
 (c) Statement I is correct; Statement II is incorrect  
 (d) Statement I is incorrect; Statement II is correct

43. **Statement I** Molecules that are non-superimposable on their mirror images are chiral.

**Statement II** All chiral molecules have chiral centres.

(2007, 3M)

### Fill in the Blank

44. Isomers which are ..... mirror images are known as ..... (superimposable, non-superimposable, enantiomers, diastereomers, epimers)  
(1988, 1M)

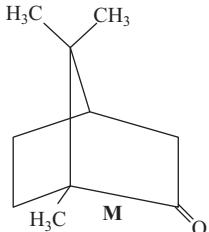
### True/False

45. 2, 3, 4-trichloropentane has three asymmetric carbon atoms.  
(1990, 1M)

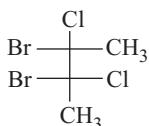
46. *m*-chlorobromobenzene is an isomer of *m*-bromochlorobenzene.  
(1985,  $\frac{1}{2}$ M)

**Integer Answer Type Questions**

47. The total number of stereoisomers that can exist for  $M$  is (2015 Adv.)



48. The total number(s) of stable conformers with non-zero dipole moment for the following compound is/are



(2014 Adv.)

**Subjective Questions**

49. Give the total number of cyclic structural as well as stereoisomers possible for a compound with the molecular formula  $\text{C}_5\text{H}_{10}$ . (2009)

50.  $\mu_{\text{obs}} = \sum \mu_i x_i$

where  $\mu_i$  is the dipole moment of stable conformer and  $x_i$  is the mole fraction of that conformer.

- (a) Write stable conformer for  $Z-\text{CH}_2-\text{CH}_2-Z$  in Newman's projection.

If  $\mu_{\text{solution}} = 1.0 \text{ D}$  and mole fraction of *anti* form = 0.82, find  $\mu_{\text{gauche}}$

- (b) Write most stable *meso* conformer of  $(\text{CHD}_Y)_2$ . If

- (i)  $Y = \text{CH}_3$  about  $\text{C}_2-\text{C}_3$  rotation and  
(ii)  $Y = \text{OH}$  about  $\text{C}_1-\text{C}_2$  rotation. (2005, 6M)

51. (a) Draw Newman's projection for the less stable staggered form of butane.

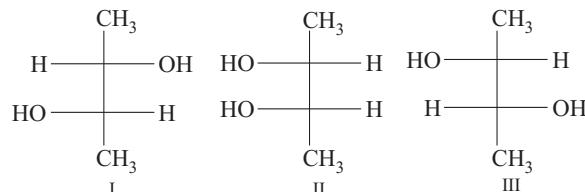
- (b) Relatively less stability of the staggered form is due to

- (i) Torsional strain  
(ii) van der Waals' strain  
(iii) Combination of the above two

(2004, 5M)

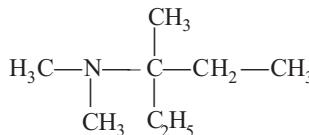
52. Glycerine contain one ..... hydroxy group. (2004)

53. Identify the pairs of enantiomers and diastereomers from the following (2000, 2M)



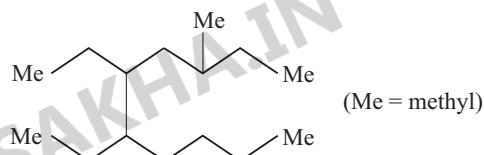
54. Write tautomeric forms of phenol. (1992, 1M)

55. Write the IUPAC name of the following compound:



(1991, 1M)

56. Give the IUPAC name of the following compound :



( $\text{Me} = \text{methyl}$ )

57. Write the IUPAC name of  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}-\text{COOH}$ . (1986, 1M)

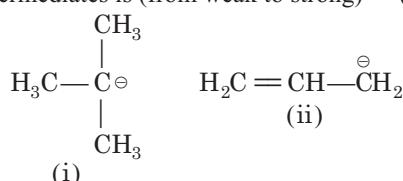
58. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment ? (1985, 2M)

59. Write structural formulae for the isomeric alcohols having the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ . (1984, 2M)

## Topic 2 General Organic Chemistry

### Objective Questions I (Only one correct option)

1. The increasing order of basicity for the following intermediates is (from weak to strong) (2020 Main, 9 Jan I)



- (a) (v) < (iii) < (ii) < (iv) < (i) (b) (iii) < (i) < (ii) < (iv) < (v)  
(c) (v) < (i) < (iv) < (ii) < (iii) (d) (iii) < (iv) < (ii) < (i) < (v)

2. 25 g of an unknown hydrocarbon upon burning produces 88 g of  $\text{CO}_2$  and 9 g of  $\text{H}_2\text{O}$ . This unknown hydrocarbon contains (2019 Main, 12 April II)

- (a) 20 g of carbon and 5 g of hydrogen  
(b) 22 g of carbon and 3 g of hydrogen  
(c) 24 g of carbon and 1 g of hydrogen  
(d) 18 g of carbon and 7 g of hydrogen

3. An organic compound  $A$  is oxidised with  $\text{Na}_2\text{O}_2$  followed by boiling with  $\text{HNO}_3$ . The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate. Based on above observation, the element present in the given compound is (2019 Main, 12 April II)

- (a) nitrogen (b) phosphorus (c) fluorine (d) sulphur

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4. The increasing order of nucleophilicity of the following nucleophiles is  
 (2019 Main, 10 April II)

- (1)  $\text{CH}_3\text{CO}_2^-$  (2)  $\text{H}_2\text{O}$  (3)  $\text{CH}_3\text{SO}_3^-$  (4)  $\ddot{\text{O}}\text{H}$   
 (a) (1) < (4) < (3) < (2) (b) (2) < (3) < (1) < (4)  
 (c) (4) < (1) < (3) < (2) (d) (2) < (3) < (4) < (1)

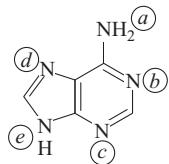
5. In chromatography, which of the following statements is incorrect for  $R_f$ ?  
 (2019 Main, 10 April II)

- (a)  $R_f$  value depends on the type of chromatography  
 (b) Higher  $R_f$  value means higher adsorption  
 (c)  $R_f$  value is dependent on the mobile phase  
 (d) The value of  $R_f$  can not be more than one

6. The principle of column chromatography is  
 (2019 Main, 10 April I)

- (a) differential absorption of the substances on the solid phase  
 (b) differential adsorption of the substances on the solid phase  
 (c) gravitational force  
 (d) capillary action

7. In the following compound,



the favourable site/s for protonation is/are  
 (2019 Main, 11 Jan II)

- (a) (a) and (e) (b) (b), (c) and (d)  
 (c) (a) and (d) (d) (a)

8. The correct match between items I and II is

|    | Item - I<br>(Mixture)          | Item II<br>(Separation method) |
|----|--------------------------------|--------------------------------|
| A. | $\text{H}_2\text{O}$ : Sugar   | P. Sublimation                 |
| B. | $\text{H}_2\text{O}$ : Aniline | Q. Recrystallisation           |
| C. | $\text{H}_2\text{O}$ : Toluene | R. Steam distillation          |
|    |                                | S. Differential extraction     |

(2019 Main, 11 Jan I)

- (a) (A) → (Q); (B) → (R); (C) → (S)  
 (b) (A) → (Q); (B) → (R); (C) → (P)  
 (c) (A) → (S); (B) → (R); (C) → (P)  
 (d) (A) → (R); (B) → (P); (C) → (S)

9. An organic compound is estimated through Dumas method and was found to evolved 6 moles of  $\text{CO}_2$ , 4 moles of  $\text{H}_2\text{O}$  and 1 mole of nitrogen gas. The formula of the compound is  
 (2019 Main, 11 Jan I)

- (a)  $\text{C}_6\text{H}_8\text{N}$  (b)  $\text{C}_{12}\text{H}_8\text{N}$  (c)  $\text{C}_{12}\text{H}_8\text{N}_2$  (d)  $\text{C}_6\text{H}_8\text{N}_2$

10. If dichloromethane (DCM) and water ( $\text{H}_2\text{O}$ ) are used for differential extraction, which one of the following statements is correct?  
 (2019 Main, 10 Jan I)

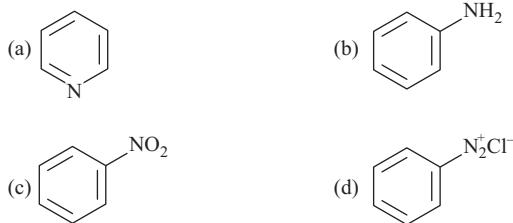
- (a) DCM and  $\text{H}_2\text{O}$  would stay as lower and upper layer respectively in the S.F.  
 (b) DCM and  $\text{H}_2\text{O}$  would stay as upper and lower layer respectively in the separating funnel (S.F.)  
 (c) DCM and  $\text{H}_2\text{O}$  will be miscible clearly  
 (d) DCM and  $\text{H}_2\text{O}$  will make turbid/colloidal mixture

11. Which amongst the following is the strongest acid?

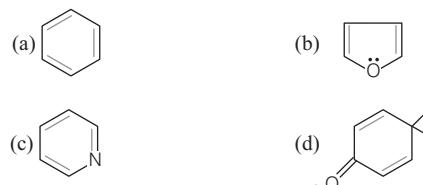
(2019 Main, 9 Jan I)

- (a)  $\text{CHBr}_3$  (b)  $\text{CHI}_3$   
 (c)  $\text{CHCl}_3$  (d)  $\text{CH}(\text{CN})_3$

12. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation?  
 (2018 Main)



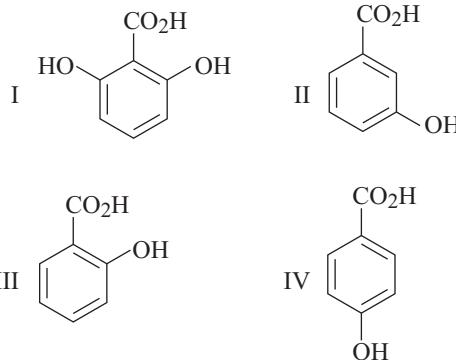
13. Which of the following molecules is least resonance stabilised?  
 (2017 Main)



14. The distillation technique most suited for separating glycerol from spent lye in the soap industry is  
 (2016 Main)

- (a) fractional distillation  
 (b) steam distillation  
 (c) distillation under reduced pressure  
 (d) simple distillation

15. The correct order of acidity for the following compounds is  
 (2016 Adv.)



- (a) I > II > III > IV  
 (c) III > IV > II > I

16. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of  $M/10$  sulphuric acid. The unreacted acid required 20 mL of  $M/10$  sodium hydroxide for complete neutralisation. The percentage of nitrogen in the compound is  
 (2014 Main)

- (a) 6% (b) 10%  
 (c) 3% (d) 5%

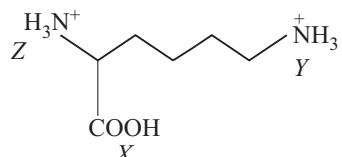


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31. For 1-methoxy-1, 3-butadiene, which of the following resonating structure is least stable? (2005, 1M)

- (a)  $\text{CH}_2=\overset{\ominus}{\text{C}}\text{H}-\overset{\oplus}{\text{C}}\text{H}=\text{CH}-\text{O}-\text{CH}_3$
- (b)  $\text{CH}_2-\overset{\ominus}{\text{C}}\text{H}=\text{CH}-\text{CH}=\overset{\oplus}{\text{O}}-\text{CH}_3$
- (c)  $\text{CH}_2=\text{CH}-\overset{\oplus}{\text{C}}\text{H}-\overset{\ominus}{\text{C}}\text{H}-\text{O}-\text{CH}_3$
- (d)  $\text{CH}_2=\text{CH}-\overset{\ominus}{\text{C}}\text{H}-\text{CH}=\overset{\oplus}{\text{O}}-\text{CH}_3$

32.



Arrange in order of increasing acidic strength (2004, 1M)

- (a)  $X > Z > Y$
- (b)  $Z < X > Y$
- (c)  $X > Y > Z$
- (d)  $Z > X > Y$

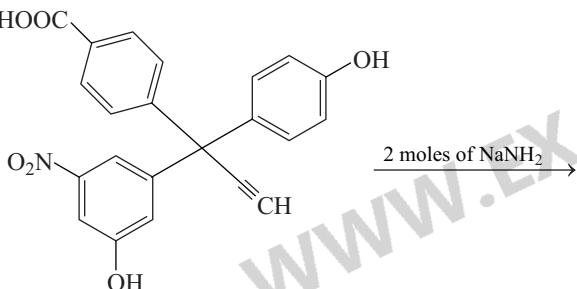
33. Among the following, the molecule with the highest dipole moment is (2003, 1M)

- (a)  $\text{CH}_3\text{Cl}$
- (b)  $\text{CH}_2\text{Cl}_2$
- (c)  $\text{CH}_2\text{Cl}_2$
- (d)  $\text{CCl}_4$

34. Which of the following represent the given mode of hybridisation  $sp^2 - sp^2 - sp - sp$  from left to right? (2003, 1M)

- (a)  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$
- (b)  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$
- (c)  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$
- (d)

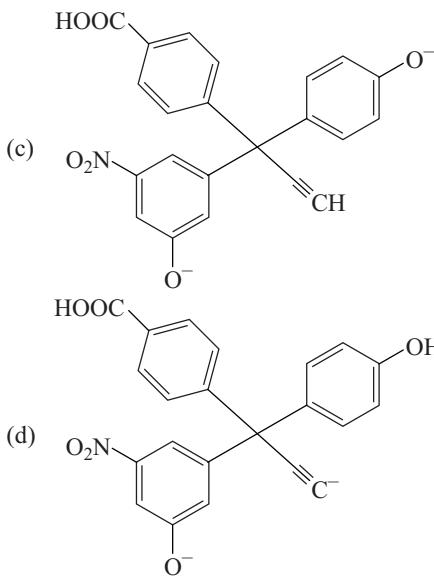
35.



The product A will be

- (a)
- (b)

(2003)



36. Which of the following acids has the smallest dissociation constant? (2002)

- (a)  $\text{CH}_3\text{CHFCOOH}$
- (b)  $\text{FCH}_2\text{CH}_2\text{COOH}$
- (c)  $\text{BrCH}_2\text{CH}_2\text{COOH}$
- (d)  $\text{CH}_3\text{CHBrCOOH}$

37. Identify the correct order of boiling points of the following compounds:

- |                                                             |                                                   |
|-------------------------------------------------------------|---------------------------------------------------|
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (1) | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (2) |
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (3)          | (2002)                                            |
| (a) $1 > 2 > 3$                                             | (b) $3 > 1 > 2$                                   |
| (c) $1 > 3 > 2$                                             | (d) $3 > 2 > 1$                                   |

38. Which of the following hydrocarbons has the lowest dipole moment? (2002)

- (a) *cis*-2-butene
- (b) 2-butyne
- (c) 1-butyne
- (d)  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{CH}$

39. The correct order of basicities of the following compounds is

- |                                                                                           |                                         |
|-------------------------------------------------------------------------------------------|-----------------------------------------|
| $\text{H}_3\text{C}-\overset{\text{NH}}{\underset{\text{NH}_2}{\text{C}}} \text{H}_3$ (1) | $\text{CH}_3\text{CH}_2\text{NH}_2$ (2) |
| $(\text{CH}_3)_2\text{NH}$ (3)                                                            | $\text{CH}_3\text{CONH}_2$ (4)          |
| (a) $2 > 1 > 3 > 4$                                                                       | (b) $1 > 3 > 2 > 4$                     |
| (c) $3 > 1 > 2 > 4$                                                                       | (d) $1 > 2 > 3 > 4$                     |

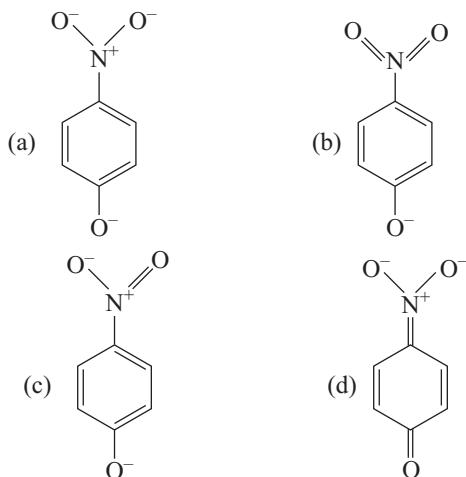
40. Among the following, the strongest base is (2000)

- (a)  $\text{C}_6\text{H}_5\text{NH}_2$
- (b)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$
- (c)  $m\text{-NO}_2\text{---C}_6\text{H}_4\text{NH}_2$
- (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

41. Which of the following, has the most acidic hydrogen? (2000)

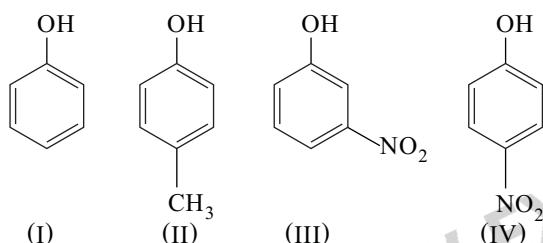
- (a) 3-hexanone
- (b) 2, 4-hexanedione
- (c) 2, 5-hexanedione
- (d) 2, 3-hexanedione

- 42.** The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is  
(1999)



- 43.** Among the following compounds, the strongest acid is  
(1998)
- (a)  $\text{HC}\equiv\text{CH}$       (b)  $\text{C}_6\text{H}_6$   
 (c)  $\text{C}_2\text{H}_6$       (d)  $\text{CH}_3\text{OH}$

- 44.** In the following compounds  
(1997)



The order of acidity is

- (a) III > IV > I > II  
 (b) I > IV > III > II  
 (c) II > I > III > IV  
 (d) IV > III > I > II

- 45.** What is the decreasing order of strength of the bases?

$\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{H}-\text{C}\equiv\text{C}^-$  and  $\text{CH}_3-\text{CH}_2^-$   
(1997)

- (a)  $\text{CH}_3-\text{CH}_2^- > \text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{OH}^-$   
 (b)  $\text{H}-\text{C}\equiv\text{C}^- > \text{CH}_3-\text{CH}_2^- > \text{NH}_2^- > \text{OH}^-$   
 (c)  $\text{OH}^- > \text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{CH}_3-\text{CH}_2^-$   
 (d)  $\text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{OH}^- > \text{CH}_3-\text{CH}_2^-$

- 46.** The hybridisation of carbon atoms in  $\text{C}-\text{C}$  single bond  $\text{H}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$  is  
(1991, 1M)

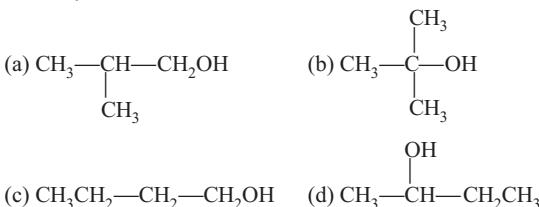
- (a)  $sp^3 - sp^3$       (b)  $sp^2 - sp^3$   
 (c)  $sp - sp^2$       (d)  $sp^3 - sp$

- 47.** Amongst the following, the most basic compound is  
(1990, 1M)
- (a) benzylamine      (b) aniline  
 (c) acetanilide      (d) *p*-nitroaniline

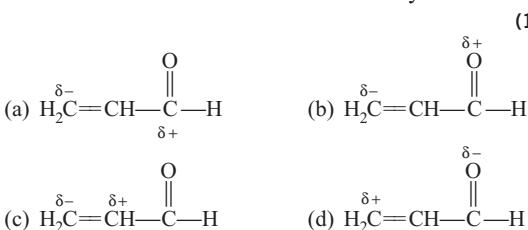
- 48.** The number of sigma and pi-bonds in 1-butene 3-yne are  
(1989, 1M)

- (a) 5 sigma and 5 pi      (b) 7 sigma and 3 pi  
 (c) 8 sigma and 2 pi      (d) 6 sigma and 4 pi

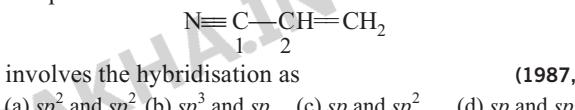
- 49.** The compound which gives the most stable carbonium ion on dehydration is  
(1989, 1M)



- 50.** Polarisation of electrons in acrolein may be written as  
(1988, 1M)



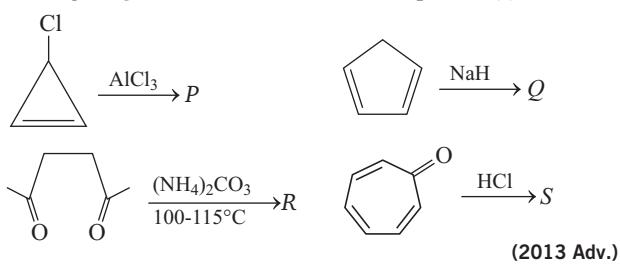
- 51.** The bond between carbon atom (1) and carbon atom (2) in compound  
(1987, 1M)



### Objective Questions II

(One or more than one correct option)

- 52.** Among *P*, *Q*, *R* and *S*, the aromatic compounds(s) is/are

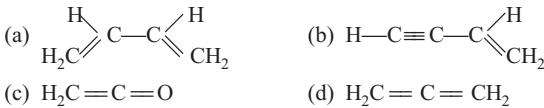


- (a) *P*      (b) *Q*      (c) *R*      (d) *S*

- 53.** The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are due to  
(2013 Adv.)

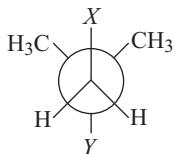
- (a)  $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi^*$  electron delocalisations  
 (b)  $\sigma \rightarrow \sigma^*$  and  $\sigma \rightarrow \pi$  electron delocalisations  
 (c)  $\sigma \rightarrow p$  (filled) and  $\sigma \rightarrow \pi$  electron delocalisations  
 (d)  $p$  (filled)  $\rightarrow \sigma$  and  $\sigma \rightarrow \pi^*$  electrons delocalisations

- 54.** Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is/are  
(2011)



## 316 Organic Chemistry Basics

55. In the Newman's projection for 2,2-dimethylbutane



X and Y can respectively be

- (a) H and H
- (b) H and C<sub>2</sub>H<sub>5</sub>
- (c) C<sub>2</sub>H<sub>5</sub> and H
- (d) CH<sub>3</sub> and CH<sub>3</sub>

(2010)

56. The molecules that will have dipole moment are (1992, 1M)

- (a) 2, 2-dimethyl propane
- (b) *trans*-2-pentene
- (c) *cis*-3-hexene
- (d) 2,2,3,3-tetramethyl butane

57. The compound in which C uses its *sp*<sup>3</sup>-hybrid orbitals for bond formation is (2000, 1M)

- (a) HCOOH
- (b) (H<sub>2</sub>N)<sub>2</sub>CO
- (c) (CH<sub>3</sub>)<sub>3</sub>COH
- (d) CH<sub>3</sub>CHO

58. Phenol is less acidic than

(1986)

- (a) acetic acid
- (b) *p*-methoxy phenol
- (c) *p*-nitrophenol
- (d) ethanol

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I

- (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I

- (c) Statement I is correct; Statement II is incorrect

- (d) Statement I is incorrect; Statement II is correct

59. **Statement I** *p*-hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.

**Statement II** *o*-hydroxybenzoic acid has intramolecular hydrogen bonding.

60. **Statement I** *p*-nitrophenol is a stronger acid than *o*-nitrophenol.

**Statement II** Intramolecular hydrogen bonding make the *o*-isomer weaker acid than *p*-isomer.

### Match the Columns

61. Match the reactions in Column I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column II. (2011)

|    | Column I | Column II                                |
|----|----------|------------------------------------------|
| A. |          | p. Nucleophilic substitution             |
| B. |          | q. Electrophilic substitution            |
| C. |          | r. Dehydration                           |
| D. |          | s. Nucleophilic addition<br>t. Carbanion |

- 62.** Match the reaction in Column I with appropriate options in Column II.

(2010)

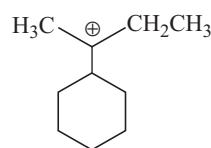
|    | Column I                                                                                                                                                                                                                                                                 | Column II                                           |
|----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|
| A. | <br>$\text{C}_6\text{H}_5-\text{N}_2\text{Cl} + \text{C}_6\text{H}_5-\text{OH} \xrightarrow[0^\circ\text{C}]{\text{NaOH}/\text{H}_2\text{O}} \text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5-\text{OH}$                                                      | p. Racemic mixture                                  |
| B. | <br>$\begin{array}{c} \text{OH} & \text{OH} \\   &   \\ \text{H}_3\text{C}-\text{C}- & -\text{C}-\text{CH}_3 \end{array} \xrightarrow{\text{H}_2\text{SO}_4} \begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ | q. Addition reaction                                |
| C. | <br>$\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{LiAlH}_4} \text{C}_6\text{H}_5-\text{CH}(\text{OH})-\text{CH}_3$                                                                                                | r. Substitution reaction                            |
| D. | <br>$\text{SH}-\text{C}_6\text{H}_5-\text{Cl} \xrightarrow{\text{Base}} \text{C}_6\text{H}_5-\text{S}-\text{C}_6\text{H}_5$                                                                                                                                              | s. Coupling reaction<br>t. Carbocation intermediate |

### Fill in the Blanks

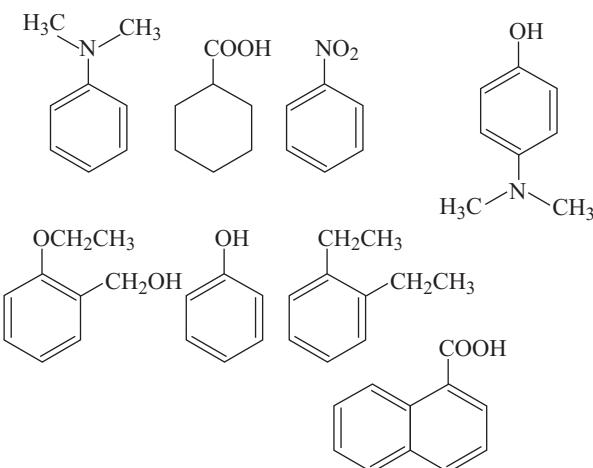
63. The kind of delocalisation involving sigma bond orbitals is called..... (1994, 1M)
64. The bond dissociation energy needed to form the benzyl radical from toluene is ..... than the formation of the methyl radical from methane. (1994, 1M)
65. The structure of the enol form of  $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_3$  with intermolecular hydrogen bonding is ..... (1993, 1M)
66. The IUPAC name of succinic acid is ..... (1990, 1M)
67. The shape of  $(\text{CH}_3)^+$  is ..... (1990, 1M)
68. A..... diol has two hydroxyl groups on ..... carbon atoms. (1985, 1M)
69. The terminal carbon atom in butane is ..... hybridised. (1985, 1M)
70. .....ring is most strained. (cyclopropane, cyclobutane, cyclopentane) (1981, 1M)
71. The compound having both  $sp$  and  $sp^2$ -hybridised carbon atoms is ..... (propane, propene, propadiene). (1981, 1M)
72. In acidic medium, ..... behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981, 1M)
73. Among the given cations, ..... is most stable. (*sec*-butyl carbonium ion, *tert*-butyl carbonium ion, *n*-butyl carbonium ion) (1981, 1M)

### Integer Answer Type Questions

74. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is (2011)



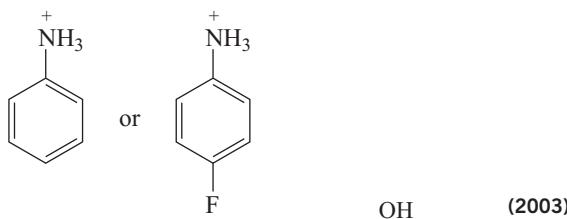
75. Amongst the following, the total number of compounds soluble in aqueous NaOH is (2010)



## 318 Organic Chemistry Basics

### Subjective Questions

76. Which of the following is more acidic and why?



77. Draw the resonating structures of

(2003)

78. You have an ether solution containing 4-hydroxybenzoic acid and 4-aminobenzoic acid. Explain, how will you separate the two in not more than 3 steps? Give confirmatory tests with reagents and conditions for functional groups of each.

(2003)

79. Match the following with their  $K_a$  values

|                              |                      |
|------------------------------|----------------------|
| Benzoic acid                 | $4.2 \times 10^{-5}$ |
| <i>p</i> -nitrobenzoic acid  | $3.3 \times 10^{-5}$ |
| <i>p</i> -chlorobenzoic acid | $6.4 \times 10^{-5}$ |

*p*-methylbenzoic acid  $36.2 \times 10^{-5}$

*p*-methoxybenzoic acid  $10.2 \times 10^{-5}$

(2003)

80. Give reasons for the following:

$\text{CH}_2=\text{CH}^-$  is more basic than  $\text{HC}\equiv\text{C}^-$ .

(2000)

81. Explain, why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid?

(1999)

82. Discuss the hybridisation of carbon atoms in allene ( $\text{C}_3\text{H}_4$ ) and show the  $\pi$ -orbital overlaps.

(1999, 3M)

83. Give reasons for the following in one or two sentences.

The central carbon-carbon bond in 1, 3-butadiene is shorter than that of *n*-butane.

(1998)

84. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why?

(1997)

85. Arrange the following in the order of their increasing basicity.

*p*-toluidine, N,N-dimethyl-*p*-toluidine, *p*-nitroaniline,

aniline.

(1985, 1M)

### Answers

#### Topic 1

- |                                       |             |             |             |
|---------------------------------------|-------------|-------------|-------------|
| 1. (c)                                | 2. (d)      | 3. (d)      | 4. (c)      |
| 5. (b)                                | 6. (c)      | 7. (d)      | 8. (a)      |
| 9. (b)                                | 10. (a)     | 11. (c)     | 12. (c)     |
| 13. (d)                               | 14. (d)     | 15. (a)     | 16. (c)     |
| 17. (b)                               | 18. (a)     | 19. (a)     | 20. (b)     |
| 21. (b)                               | 22. (a)     | 23. (b)     | 24. (d)     |
| 25. (c)                               | 26. (a)     | 27. (d)     | 28. (a,b,c) |
| 29. (b,c)                             | 30. (a,c,d) | 31. (a,b,c) | 32. (a,d)   |
| 33. (b,c,d)                           | 34. (a,d)   | 35. (a,c,d) | 36. (a,c)   |
| 37. (c,d)                             | 38. (b,d)   | 39. (d)     | 40. (c)     |
| 41. (5)                               | 42. (7)     | 43. (c)     |             |
| 44. (Non-superimposable, Enantiomers) |             |             | 45. (False) |
| 46. (False)                           | 47. (2)     | 48. (3)     | 49. (7)     |

#### Topic 2

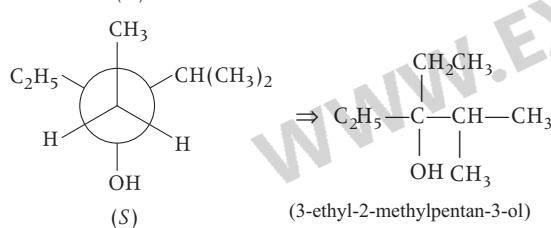
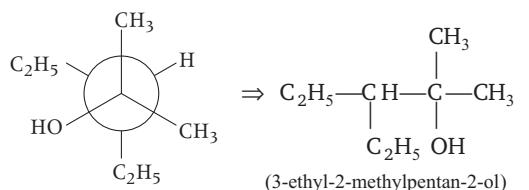
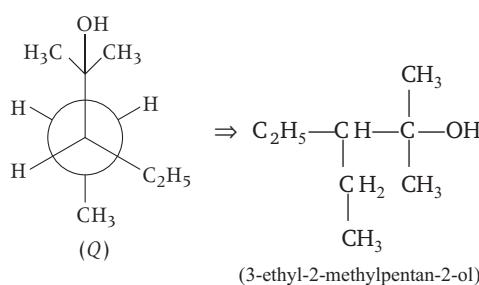
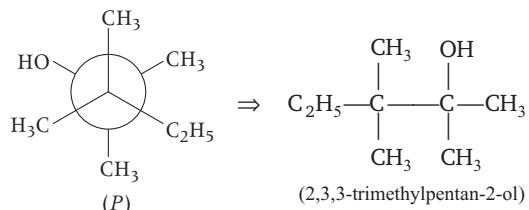
- |        |         |         |         |
|--------|---------|---------|---------|
| 1. (a) | 2. (c)  | 3. (b)  | 4. (c)  |
| 5. (b) | 6. (b)  | 7. (b)  | 8. (a)  |
| 9. (d) | 10. (a) | 11. (d) | 12. (b) |

- |                                                 |                    |                              |               |
|-------------------------------------------------|--------------------|------------------------------|---------------|
| 13. (d)                                         | 14. (c)            | 15. (a)                      | 16. (b)       |
| 17. (d)                                         | 18. (d)            | 19. (c)                      | 20. (c)       |
| 21. (b)                                         | 22. (c)            | 23. (b)                      | 24. (d)       |
| 25. (a)                                         | 26. (b)            | 27. (d)                      | 28. (a)       |
| 29. (d)                                         | 30. (c)            | 31. (c)                      | 32. (a)       |
| 33. (a)                                         | 34. (a)            | 35. (a)                      | 36. (c)       |
| 37. (b)                                         | 38. (b)            | 39. (b)                      | 40. (d)       |
| 41. (b)                                         | 42. (b)            | 43. (d)                      | 44. (d)       |
| 45. (a)                                         | 46. (d)            | 47. (a)                      | 48. (b)       |
| 49. (b)                                         | 50. (d)            | 51. (c)                      | 52. (a,b,c,d) |
| 53. (a)                                         | 54. (b,c)          | 55. (b,d)                    | 56. (b,c)     |
| 57. (c,d)                                       | 58. (a,c)          | 59. (d)                      | 60. (a)       |
| 61. (A → r, s, t; B → p, s; C → r, s; D → q, r) |                    |                              |               |
| 62. (A → r, s; B → t; C → p, q; D → r)          |                    |                              |               |
| 63. (hyperconjugation)                          |                    |                              |               |
| 64. (less)                                      | 65. (cyclic)       | 66. (butanedioic acid)       |               |
| 67. (triangular planar)                         |                    | 68. ( <i>geminal</i> , same) |               |
| 69. ( $sp^3$ )                                  | 70. (cyclopropane) | 71. (propene)                | 72. (aniline) |
| 73. ( <i>tert</i> -butyl carbonium ion),        | 74. (6)            | 75. (4)                      |               |

# Hints & Solutions

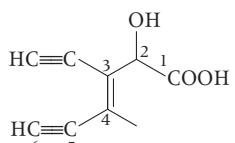
## Topic 1 Nomenclature and Isomerism

1. IUPAC name of *P*, *Q*, *R* and *S* are :



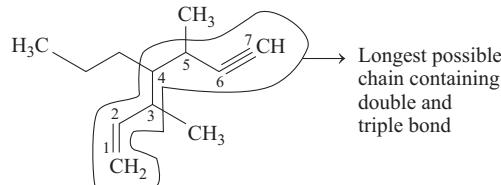
IUPAC name of compounds *Q* and *R* are same, thus the correct option is (c).

2. According to the IUPAC rules, first of all select the longest carbon chain (6-carbon atoms) then numbering should start from most prior functional group, which is carboxylic acid in the given compound, thus



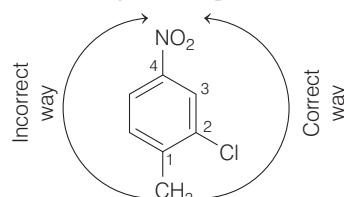
3-ethynyl-2-hydroxy-4-methylhex-3-en-5-yoic acid

3. The IUPAC name for the given compound is 3, 5-dimethyl-4-propylhept-1-en-6-yne.



If both double and triple bonds are present in the compound, the endings like-en-yne, a (numeral) dien-(numeral)-yne etc., are used. Numbers as low as possible are given to double and triple bonds as a set.

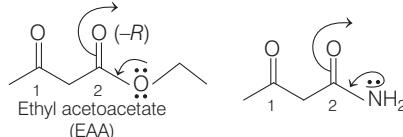
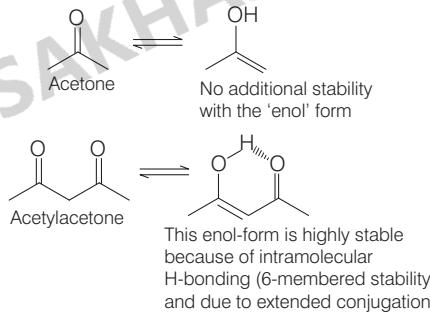
4. The IUPAC name of the given compound is



2- chloro-1-methyl-4-nitrobenzene

Here, the given compound contains two or more functional groups. So, the numbering is done in such a way that the sum of the locants is the lowest.

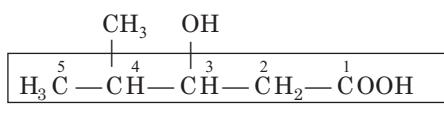
- 5.



In both of the compounds, C-2 of  $\text{C}=\text{O}$  group is a part of the acid

$\text{O}$  derivative (ester,  $-\text{C}=\text{O}-\text{OEt}$  and acid amide,  $-\text{C}=\text{O}-\text{NH}_2$ ). So,  $\text{C}^2=\text{O}$  does not take part in enolisation, because it is already in resonance ( $-R$ ) with the derivative group itself.

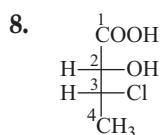
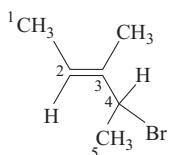
6. The IUPAC name of the given compound is 3-hydroxy-4-methylpentanoic acid.



## 320 Organic Chemistry Basics

While naming the compound, the longest chain that have principal functional group —COOH is chosen and numbered in such a manner that the principal functional group gets the lowest possible number. —OH act as substituent and used as prefix in nomenclature.

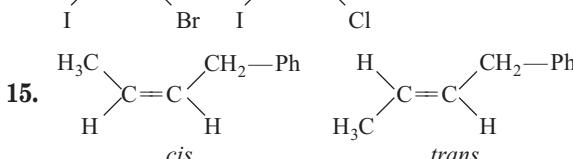
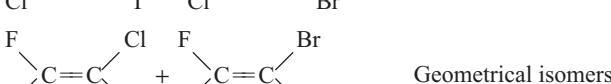
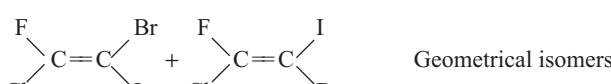
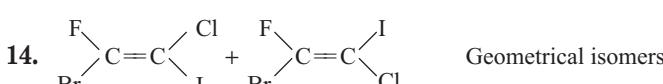
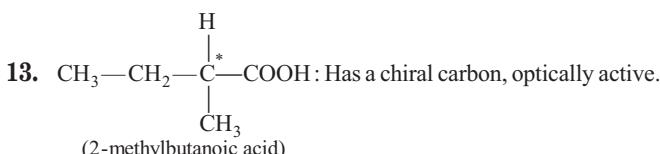
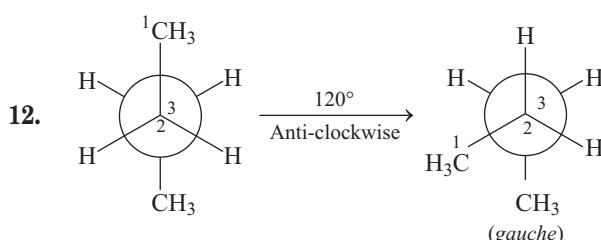
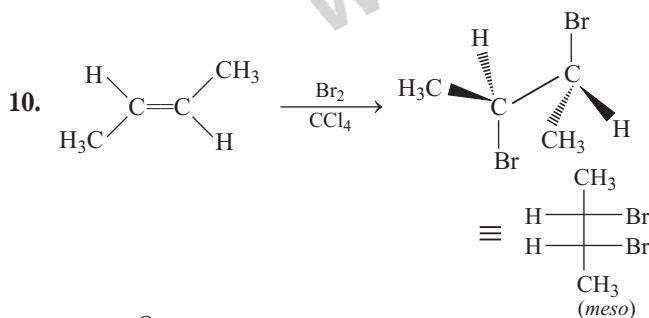
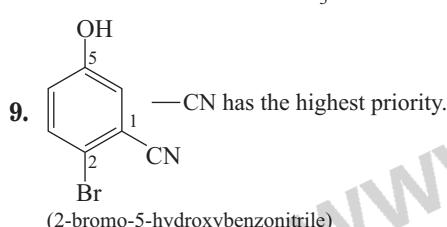
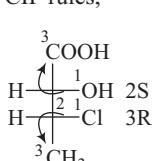
7. While naming the compound, alkene gets priority over functional group (—Br) and numbering starts from alkene side. Hence, IUPAC name: 4-bromo-3-methyl pent-2-ene



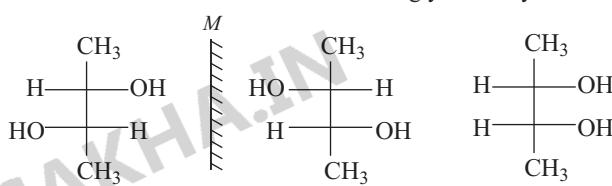
For C-2, order of priority of substituents is OH > CH(Cl)(CH<sub>3</sub>) > COOH

For C-3, order of priority of substituents is Cl > CH(OH)COOH > CH<sub>3</sub>

Hence, according to CIP rules,

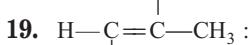


16. The 'D' term in name is derived from D-glyceraldehyde.



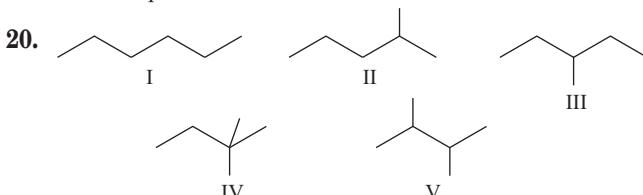
I and II are optically active while III is optically inactive (meso form).

18. Conformers can be interconverted through rotation about C—C bond.

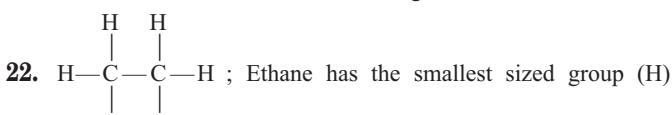


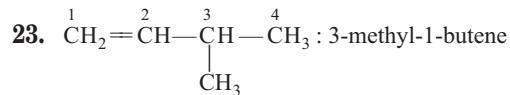
Enol of acetone

It has 9 σ (6 with H, two C—C and one C—O), one π-bond and two lone-pairs.



21. Compounds with same empirical formula but different molecular formula have same percentage composition of elements but different molecular weight.

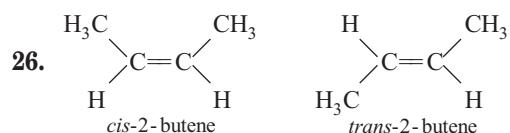
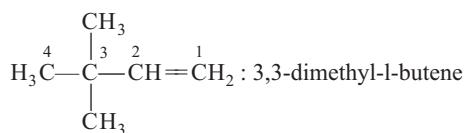




24. Ethers and alcohols (saturated, acyclic) with same number of carbons are always isomeric.

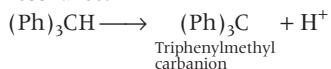
$\text{CH}_3-\text{O}-\text{CH}_3$  and  $\text{CH}_3-\text{CH}_2-\text{OH}$  are functional isomers.

25. Double bond has preference over alkyl group hence :

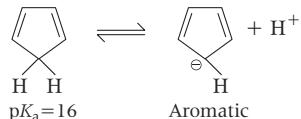


27. Diethyl ether ( $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ) will be isomeric with all 4-carbon saturated alcohols. Butanone ( $\text{CH}_3\text{CH}_2\text{COCH}_3$ ) is unsaturated, has two hydrogen less than the diethylether.

28. Triphenylmethane (I) is acidic because its conjugate base is stabilised by resonance.

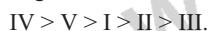


Cyclopentadiene (IV) is acidic because its conjugate base is aromatic.



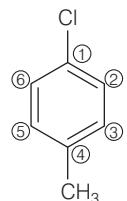
Nitrobenzene is more acidic than benzene because nitro group is electron withdrawing. It will stabilise the conjugate base of benzene by  $-R$  and  $-I$  effect.

The acidic strength order on the basis of  $pK_a$  data is



Hence, the correct options are (a), (b) and (c) only.

29. Since, there is no principal functional groups, numbering of disubstituted benzene is done in alphabetical order as



Hence IUPAC name of this compound is 1-chloro-4-methyl benzene.

Also, toluene is an acceptable name in IUPAC, hence this compound can also be named as 4-chloro toluene.

30. **PLAN** This problem is based on structure and nomenclature of organic compound.

Draw structure of each compound and write IUPAC name of the given compound.

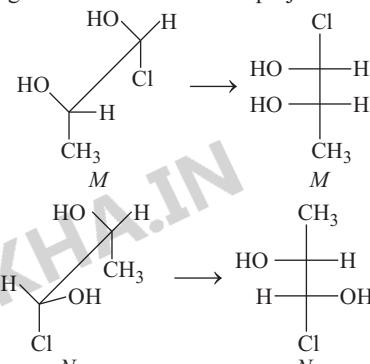
Match the molecular formula of given compound with molecular formula of compound given in choices.

The combination of names for possible isomeric alcohols with molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  is/are

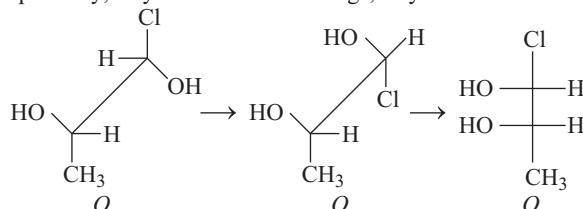
| Formula                                                                                               | Names                                                               |
|-------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$                                               | <i>n</i> -butyl alcohol / <i>n</i> -butanol / butan-1-ol            |
| $\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{OH} \\   \\ \text{CH}_3 \end{array}$        | <i>Iso</i> -butyl alcohol / 2-methyl propan-1-ol                    |
| $\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{OH} \\   \\ \text{CH}_3 \end{array}$        | Secondary butyl alcohol / butan-2-ol                                |
| $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$ | Tertiary butyl alcohol / <i>tert</i> butanol / 2-methyl propan-2-ol |

Hence, choices (a), (c) and (d) are correct.

31. Converting all of them into Fischer projection.



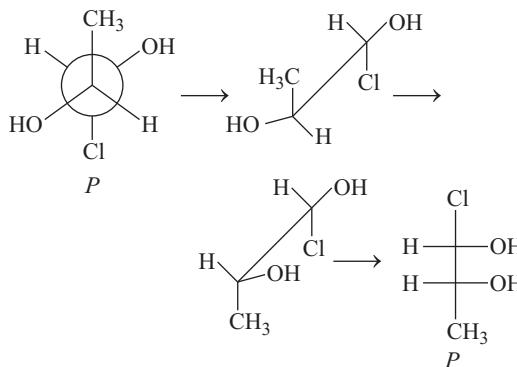
Since, *M* and *N* have  $-\text{OH}$  on same side and opposite side respectively, they cannot be mirror image, they are diastereomers.



*M* and *O* are identical.

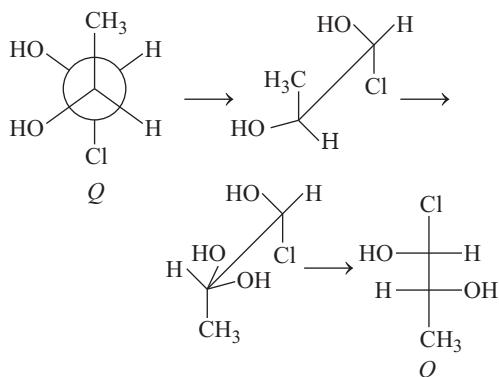
**NOTE** Fischer projection represents eclipse form of Sawhorse projection.

For comparision purpose, similar types of eclipse conformers must be drawn i.e. both vertically up or both vertically down.

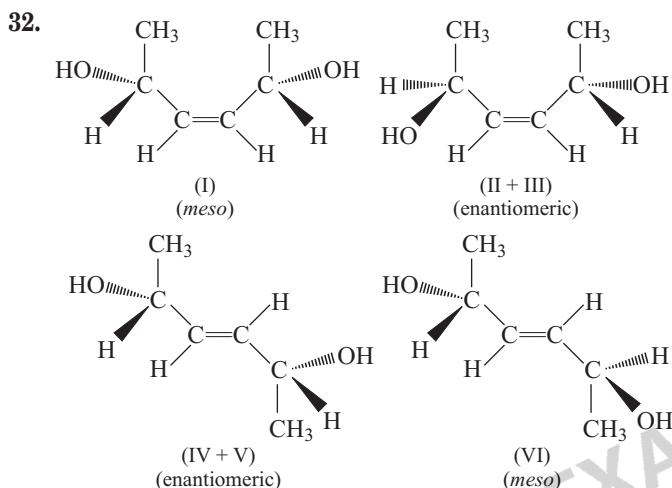


## 322 Organic Chemistry Basics

*M* and *P* are non-superimposable mirror images, hence, enantiomers.



*M* and *Q* are non-identical they are distereomers.



Total six isomers. In both *cis* and *trans* forms, there are two enantiomers each.

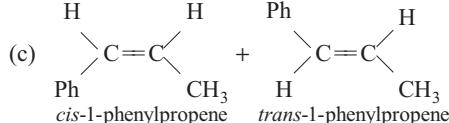
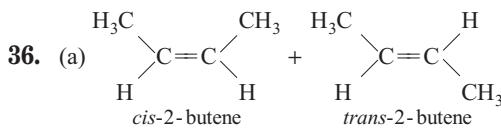
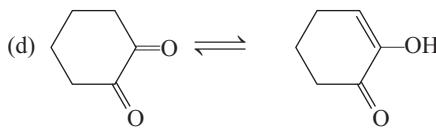
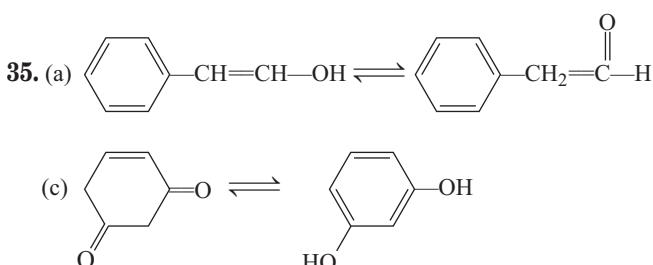
33. *E*, *F* and *G* are not resonance structures because movement of hydrogen between *E* and *F* are involved.

*E*, *F* and *E*, *G* are tautomers in which *E* is keto form and both *F* and *G* are enol form of the same *E*.

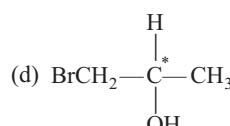
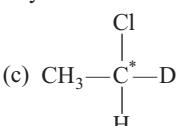
*F* and *G* are geometrical isomers.

*F* and *G* are distereomers as they are stereo isomers but not related by mirror image relationship.

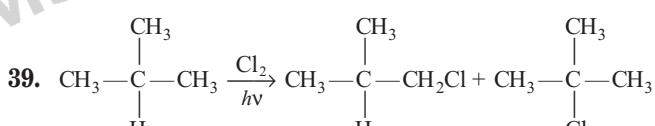
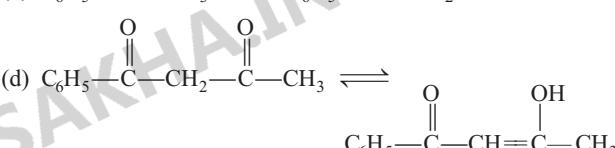
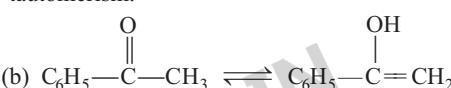
34. The compound is optically active as well as it possesses a two-fold axis of symmetry.



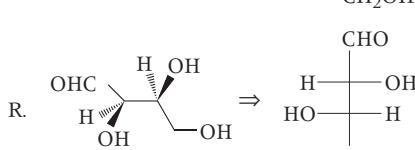
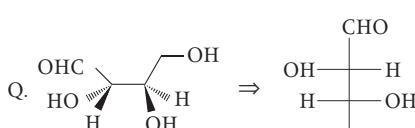
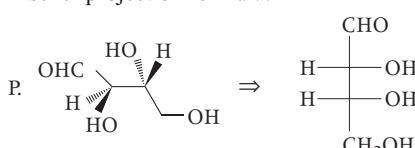
37. A carbon bonded to four different atoms or groups is called asymmetric carbon :

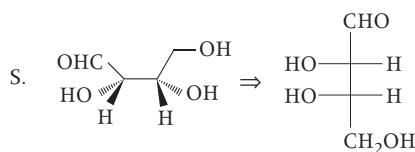


38. Carbonyl compounds containing  $\alpha$ -H show keto-enol tautomerism.



40. (c) First of all, we need to convert wedge-dash formula into Fischer projection formula.





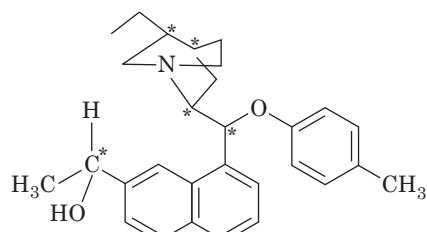
Now we can clearly see, that compound P is same as given compound, thus compound P is identical to D-erythrose. Compound Q and D-erythrose are not mirror images of one another and are non-superimposable on one another. Thus, they are diastereomers.

Compound R and D - erythrose are also not mirror images of one another and are non-superimposable on one another. Thus, they are diastereomers.

Compound S and D-erythrose are chiral molecules. They are mirror images of one another. Furthermore, the molecules are non-superimposable on one another. This means that the molecules cannot be placed on top of one another and give the same molecule. Chiral molecules with one or more stereocenters can be enantiomers.

Hence, the correct option is (c).

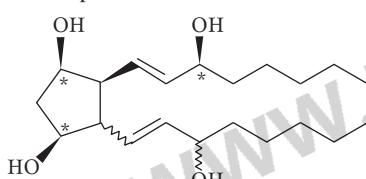
41.



The molecule contains five chiral carbon ( $C^*$ ) atoms.

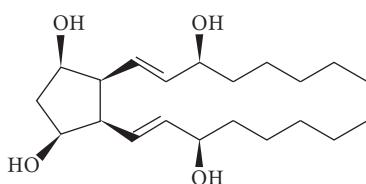
42.

(7) As given in the question 3 stereocentres are visible, i.e.



Hence, the total number of stereoisomers =  $2^3 = 8$

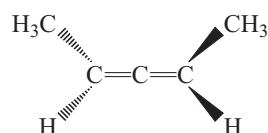
But out of these the following one is optically inactive due to symmetry



Hence, total number of optically active stereoisomers=7

43.

Molecules that are non-superimposable on its mirror image are optically active and known as chiral molecule. However, for chirality of molecule, presence of chiral centre is not essential, e.g.



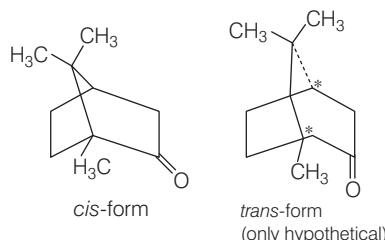
Molecule is chiral but does not possess any chiral carbon.

44.

Non-superimposable, Enantiomers.

### True / False

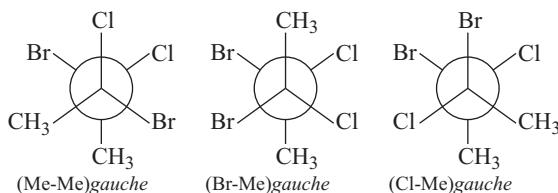
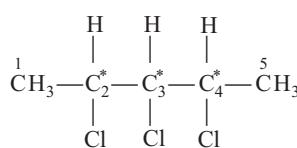
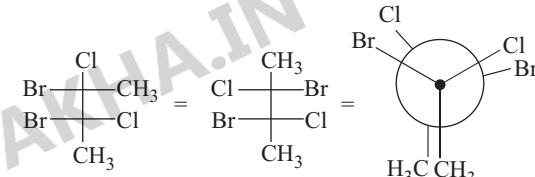
45. It has only two asymmetric carbon, carbon no.3 is not asymmetric.
46. They are identical.
47. Although the compound has two chiral carbons (indicated by stars), it does not have four optically active isomers as expected. It is due to its existence in *cis*-form only.



The above shown transformation does not exist due to restricted rotation about the bridge head carbons, hence only *cis*-form and its mirror image exist.

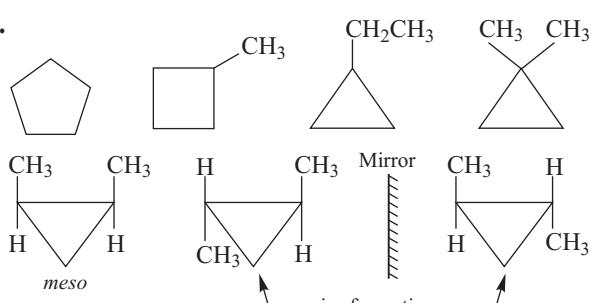
48. PLAN This problem can be solved by using concept of conformational analysis of given organic compound. To solve the question draw the stable conformational structures of organic compound and determine the net resultant dipole moment.

The conformations of the given compound are as follows



These three have non-zero dipole moment due to non-cancellation of all dipole moment created by C—Cl and C—Br bond.

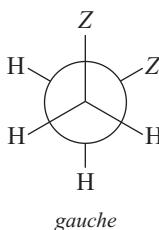
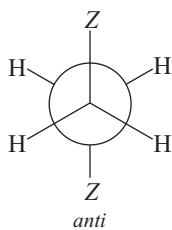
49.



$\Rightarrow$  Total seven isomers

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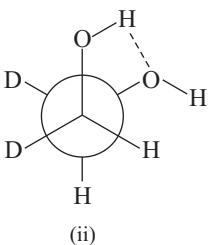
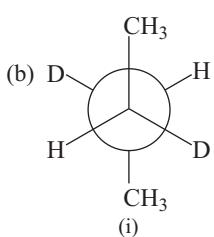
50. (a)



Mole fraction of *anti* form = 0.82

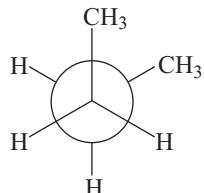
Mole fraction of *gauche* form = 0.18

$$\begin{aligned}\mu_{\text{obs}} &= 1 \text{ D} \Rightarrow 1 = \mu_{\text{anti}} \times 0.82 + \mu_{\text{gauche}} \times 0.18 \\ \therefore \mu_{\text{anti}} &= 0 \Rightarrow 1 = \mu_{\text{gauche}} \times 0.18 \\ \Rightarrow \mu_{\text{gauche}} &= \frac{1}{0.18} = 5.55 \text{ D}\end{aligned}$$



Structure (ii) is more stable than its *anti* conformer because of intramolecular H-bonding.

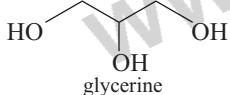
51. (a)



less stable staggered form of butane

(b) The less stability of above mentioned conformer is due to van der Waals' repulsion between the adjacent methyl groups.

52.



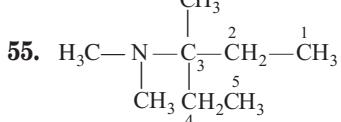
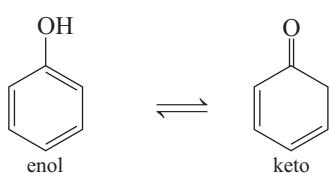
It contains a secondary ( $2^\circ$ ) hydroxy group.

53. I and III are mirror images of one another as well as they are non-superimposable while II is a *meso* form.

$\Rightarrow$  (I + III) = Enantiomers

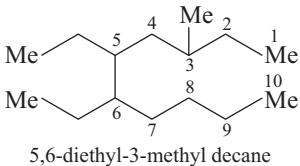
I + II and II + III = Diastereomers

54.



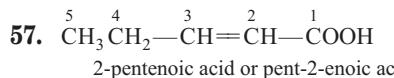
3-(N, N-dimethyl)-3-methyl pentanamine  
or 3-methyl-3-(N, N-dimethyl) pentanamine

56.



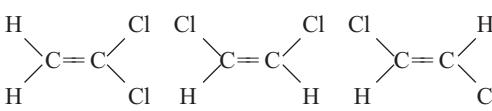
5,6-diethyl-3-methyl decane

57.



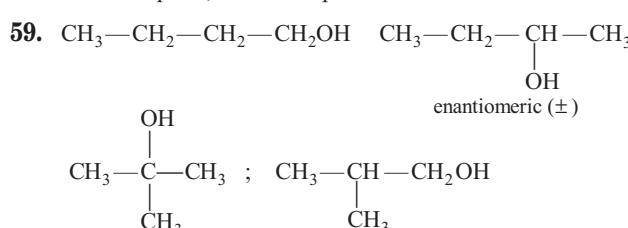
2-pentenoic acid or pent-2-enoic acid

58.



III is non-polar, has zero dipole moment.

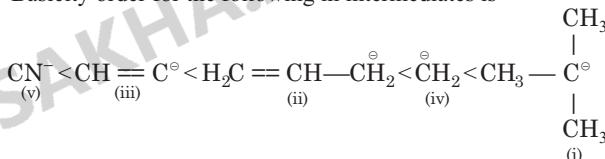
59.



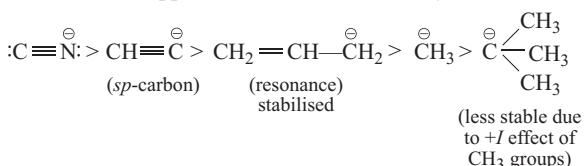
Total number of isomers (including stereoisomers) = 5

## Topic 2 General Organic Chemistry

1. Basicity order for the following in intermediates is



which is also the opposite of the order of stability of carbanions.



2. Hydrocarbon containing C and H upon burning produces  $\text{CO}_2$  and water vapour respectively. The equation is represented as



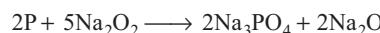
$$\text{Mass of carbon} = \frac{12}{44} \times \text{mass of CO}_2$$

$$= \frac{12}{44} \times 88 \text{ g} = 24 \text{ g}$$

$$\text{Mass of hydrogen} = \frac{2}{18} \times \text{mass of H}_2\text{O} = \frac{2}{18} \times 9 = 1 \text{ g}$$

So, the unknown hydrocarbon contains 24 g of carbon and 1 g of hydrogen.

3. Organic compound 'A' contain phosphorus as it gives positive test with ammonium molybdate. Phosphorus present in organic compound 'A' get oxidised with  $\text{Na}_2\text{O}_2$  and form  $\text{Na}_3\text{PO}_4$ .



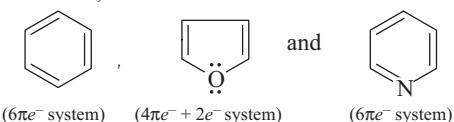
Compound Sodium phosphate



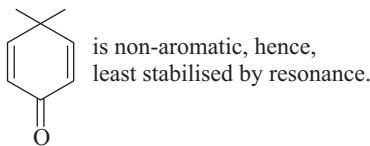
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$(\text{NH}_4)_2\text{SO}_4$  during the process. Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.

13. Aromatic compounds are stable due to resonance while non-aromatics are not. According to Huckel's rule (or  $4n + 2$  rule), "For a planar, cyclic compound to be aromatic, its  $\pi$  cloud must contain  $(4n + 2)\pi$  electrons, where,  $n$  is any whole number." Thus,



are aromatic and stabilised by resonance.  
They follow Huckel's rule.



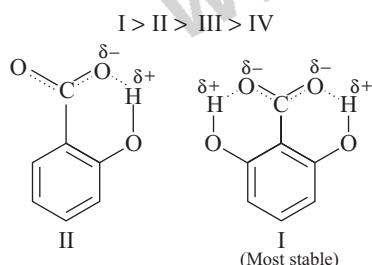
14. Glycerol with high boiling point ( $290^\circ\text{C}$ ) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

15. —OH group displays both kinds of effect; an electron withdrawing acid-strengthening inductive effect from the *meta*-position and an electron-releasing acid weakening resonance effect from the *para*-position (at this position, resonance effect outweighs the inductive effect).

Thus, III > IV.

*o*-hydroxybenzoic acid (II) is far stronger than the corresponding *meta* and *para* isomers as the carboxylate ion is stabilised by intramolecular H-bonding.

2,6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramolecular H-bonding, Thus, correct order is



16. **THINKING PROCESS** This problem is based on the estimation of percentage of N in organic compound using Kjeldahl's method. Use the concept of stoichiometry and follow the steps given below to solve the problem.

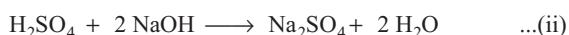
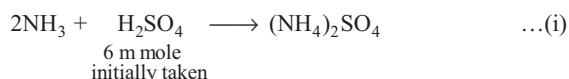
- (a) Write the balanced chemical reaction for the conversion of N present in organic compound to ammonia, ammonia to ammonium sulphate and ammonium sulphate to sodium sulphate.
- (b) Calculate millimoles ( $m$  moles) of N present in organic compound followed by mass of N present in organic compound using the concept of stoichiometry.

- (c) At last, calculate % of N present in organic compound using formula

$$\% \text{ of N} = \frac{\text{Mass of N} \times 100}{\text{Mass of organic compound}}$$

$$\text{Mass of organic compound} = 1.4 \text{ g}$$

Let it contain  $x$  m mole of N atom.



2 m mole NaOH reacted.

Hence, m moles of  $\text{H}_2\text{SO}_4$  reacted in Eq. (ii) = 1

$\Rightarrow$  m moles of  $\text{H}_2\text{SO}_4$  reacted from Eq. (i) =  $6 - 1 = 5$  m moles

$\Rightarrow$  m moles of  $\text{NH}_3$  in Eq. (i) =  $2 \times 5 = 10$  m moles

$\Rightarrow$  m moles of N atom in the organic compound = 10 m moles

$\Rightarrow$  Mass of N =  $10 \times 10^{-3} \times 14 = 0.14 \text{ g}$

$$\% \text{ of N} = \frac{\text{Mass of N present in organic compound}}{\text{Mass of organic compound}} \times 100$$

$$\Rightarrow \% \text{ of N} = \frac{0.14}{1.4} \times 100 = 10\%$$

17. 18 g  $\text{H}_2\text{O}$  contains 2 g H

$$\therefore 0.72 \text{ g } \text{H}_2\text{O} \text{ contains } 0.08 \text{ g H}$$

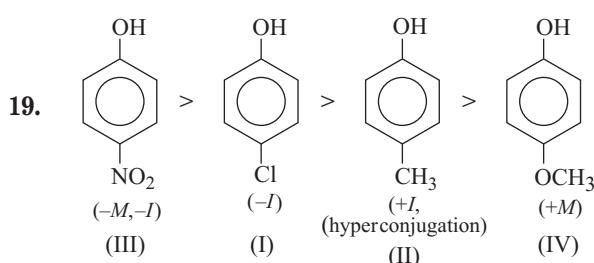
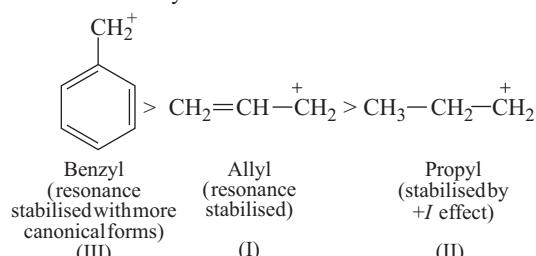
$$44 \text{ g } \text{CO}_2 \text{ contains } 12 \text{ g C}$$

$$\therefore 3.08 \text{ g } \text{CO}_2 \text{ contains } 0.84 \text{ g C}$$

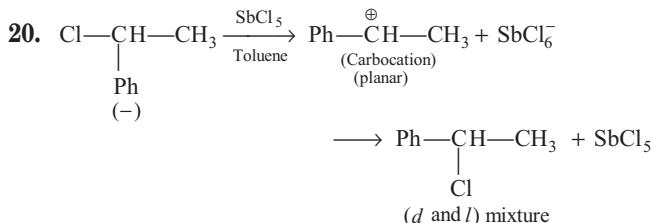
$$\therefore \text{C : H} = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$$

$$\therefore \text{Empirical formula} = \text{C}_7\text{H}_8$$

18. The order of stability of carbocation will be



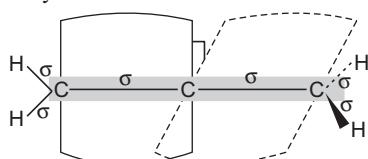
Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.





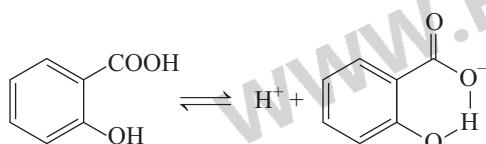

Hybridisation of an atom is determined by determining the number of hybrid orbitals at that atom which is equal to the number of sigma ( $\sigma$ ) bonds plus number of lone pairs at the concerned atom.

$\Pi(\pi)$  bonds are not formed by hybrid orbitals, therefore, not counted for hybridisation.



Here, the terminal carbons have only three sigma bonds associated with them, therefore, hybridisation of terminal carbons is  $sp^3$ . The central carbon has only two sigma bonds associated, hence hybridisation at central carbon is  $sp$ .

- 22.** A mono-substituted benzoic acid is stronger than a mono-substituted phenol as former being a carboxylic acid. Among the given substituted benzoic acid, *ortho*-hydroxy acid is strongest acid although  $-\text{OH}$  causes electron donation by resonance effect which tends to decrease acid strength. It is due to a very high stabilisation of conjugate base by intramolecular H-bond which outweigh the electron donating resonance effect of  $-\text{OH}$ .

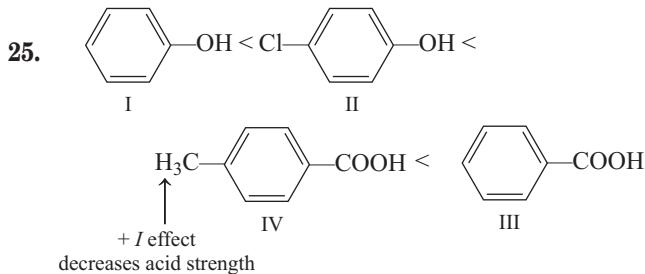
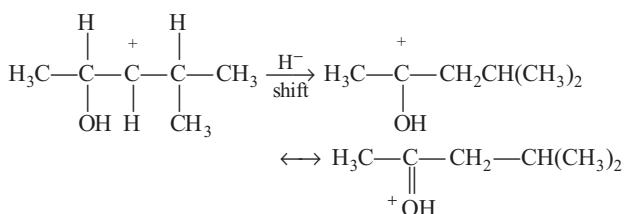


The overall order of acid-strength of given four acids is *ortho*-hydroxybenzoic acid ( $pK_a = 2.98$ ) > Toluic acid ( $pK_a = 4.37$ ) > *p*-hydroxybenzoic acid ( $pK_a = 4.58$ ) > *p*-nitrophenol ( $pK_a = 7.15$ )

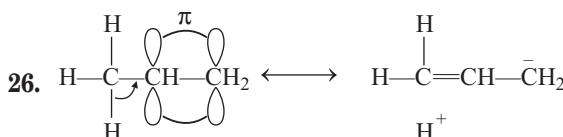
- 23.** I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen. III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is



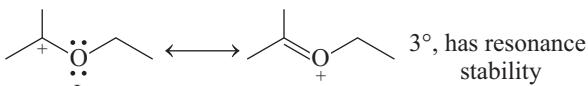
- 24.** H at C<sub>2</sub> will migrate giving resonance stabilised carbocation.



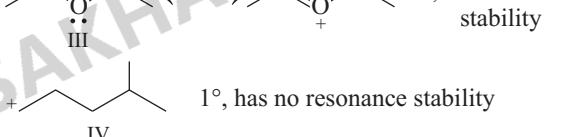
Cl has overall electron withdrawing effect, increases acid strength.



27. The  $\sigma$ -electron of C—H bond is delocalised with  $p$ -orbitals of  $\pi$ -bond.

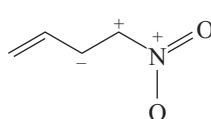


$2^\circ$ , has resonance

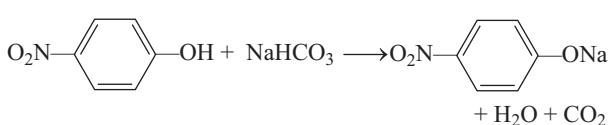


Therefore, overall stability order is : I  $\geq$  III  $\geq$  II  $\geq$  IV

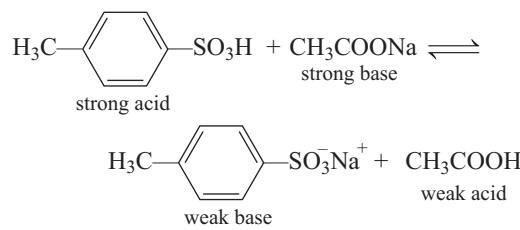
- 28.** The following structure has like charge on adjacent atoms, therefore least stable



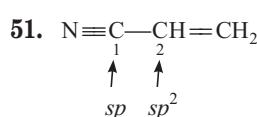
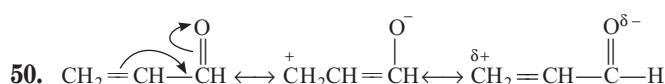
- 29.**  + NaHCO<sub>3</sub> →  + H<sub>2</sub>O + CO<sub>2</sub>



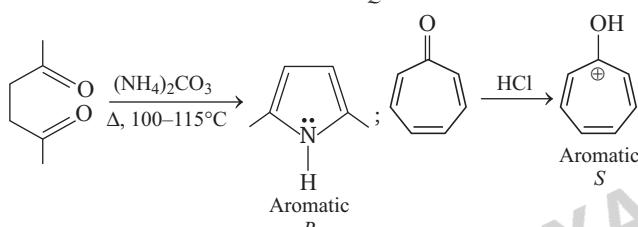
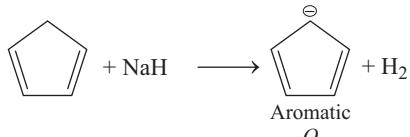
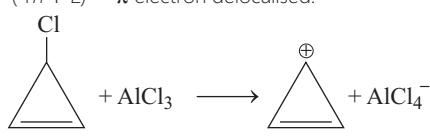
- 30.** A spontaneous neutralisation will occur between strong acid and strong base as







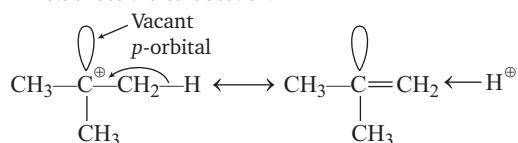
52. **PLAN** A species is said to have aromatic character if  
 (a) ring is planar  
 (b) there is complete delocalisation of  $\pi$ -electrons  
 (c) Hückel rule i.e.  $(4n + 2)$  rule is followed.  
 where,  $n$  is the number of rings  
 $(4n + 2) = \pi$  electron delocalised.



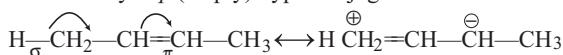
|   | $n$ | $(4n + 2)$ | $\pi$ electrons              |
|---|-----|------------|------------------------------|
| P | -   | 0          | 2                            |
| Q | -   | 1          | 6 (including lone pair)      |
| R | -   | 1          | 6 (including lone pair on N) |
| S | -   | 1          | 6                            |

In all cases there is complete delocalisation of  $\pi$ -electrons.

53. **PLAN** Spreading out charge by the overlap of an empty  $p$ -orbital with an adjacent  $\sigma$ -bond is called hyperconjugation. This overlap (the hyperconjugation) delocalises the positive charge on the carbocation, spreading it over a larger volume, and this stabilises the carbocation.

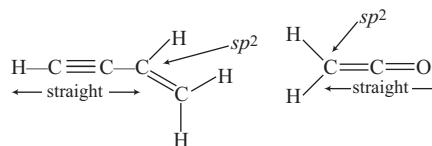


tertiary butyl carbocation has one vacant  $p$ -orbital, hence, it is stabilised by  $\sigma-p$  (empty) hyperconjugation.



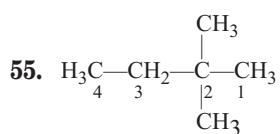
In 2-butene, stabilisation is due to hyperconjugation between  $\sigma - \pi^*$  electron delocalisation.

54. In both (b) and (c), all the atoms are present in one single plane

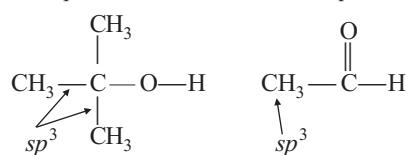
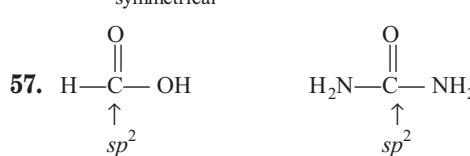
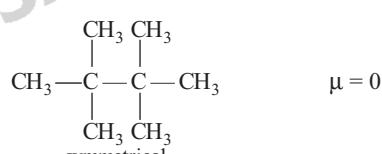
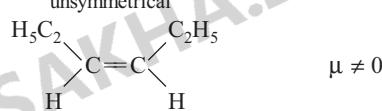
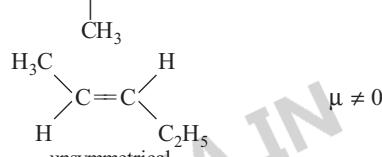
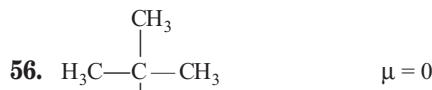


In (a) 1, 3-butadiene, conformational change is possible between  $\text{C}_2 - \text{C}_3$  bond in which atoms will be present in more than one single plane.

In (d) allene, the terminals  $\text{H}-\text{C}-\text{H}$  planes are perpendicular to one another.



On  $\text{C}_2 - \text{C}_3$  axis,  $X = \text{CH}_3$ ,  $Y = \text{CH}_3$   
 On  $\text{C}_1 - \text{C}_2$  axis,  $X = \text{H}$ ,  $Y = \text{C}_2\text{H}_5$



58. Phenol is less acidic than a carboxylic acid (acetic acid). Nitro group from *para* position exert electron withdrawing resonance effect, increases acid strength. Therefore, phenol is less acidic than *p*-nitrophenol.

On the other hand, methoxy group from *para* position, donate electrons by resonance effect, decreases acid strength of phenol. Also ethanol is weaker acid than phenol due to resonance stabilisation in phenoxide ion.

Hence,

ethanol < *p*-methoxyphenol < phenol < *p*-nitrophenol < acetic acid

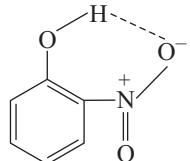
—increasing acid strength—

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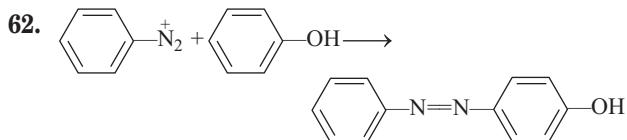
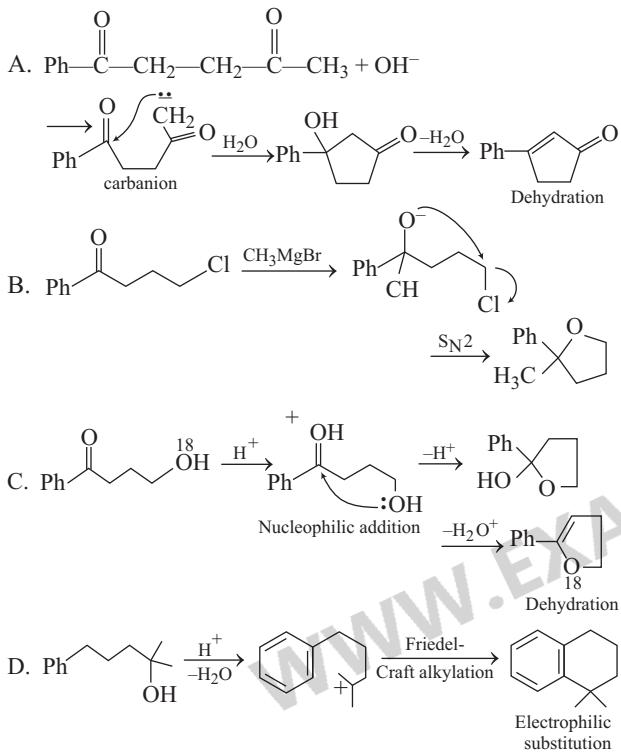
59. Statement I is incorrect; Statement II is correct. Intramolecular H-bonding in *ortho*-hydroxy benzoic acid lowers the boiling point.

60. Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.

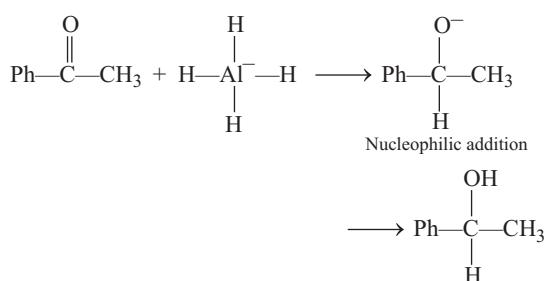
Intramolecular H-bonding discourage release of  $H^+$  to some extent, hence weaker acid than its *para* isomer.



61.

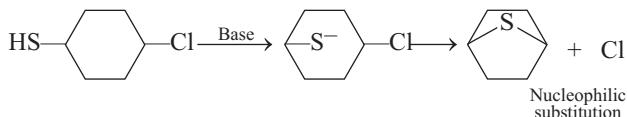


this is an example of electrophilic substitution at *para* position of phenol, giving a coupling product.



Pianacol-pinacolone rearrangement, occur through carbocation intermediate.

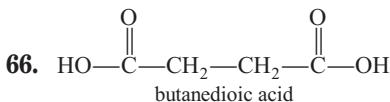
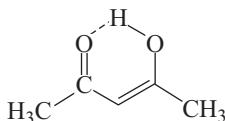
Nucleophilic addition occur at  $sp^2$  (planar) carbon, generating a chiral centre, hence product will be a racemic mixture.



63. Hyperconjugation.

64. Less, stable free radical is formed.

65. Cyclic

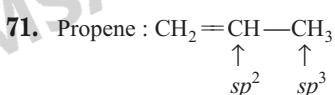


67. Triangular planar; carbon is  $sp^2$ -hybridised

68. *geminal*, same

69.  $sp^3$ -hybridised

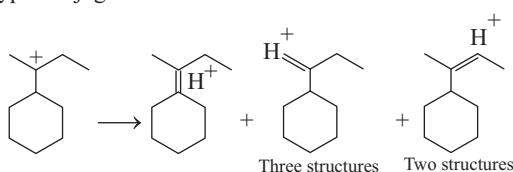
70. Cyclopropane: here the C—C—C bond angle is  $60^\circ$  while the requirement is  $109^\circ$ .



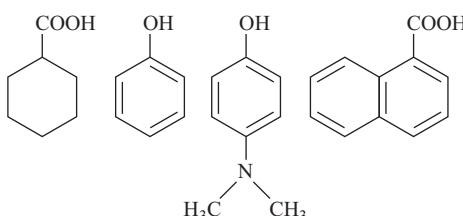
72. Aniline

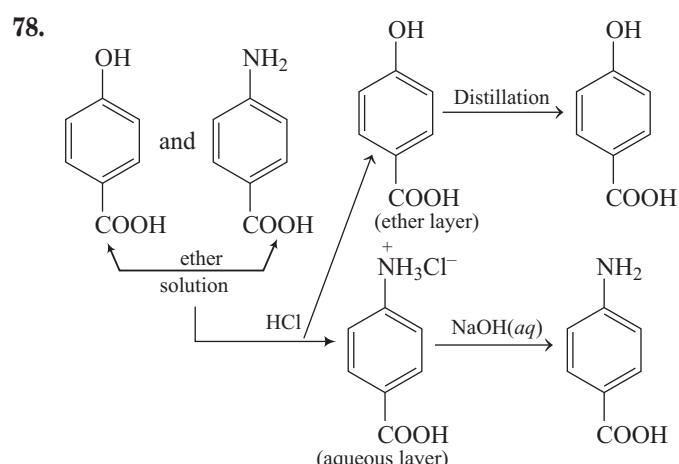
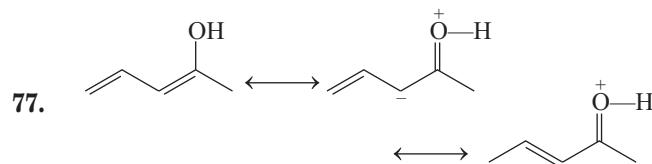
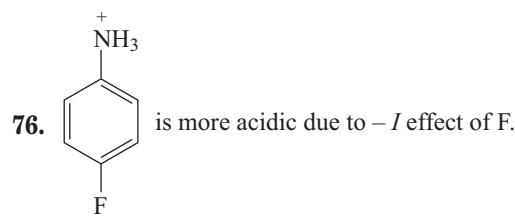
73. *Tert*-butyl carbonium ion because the three methyl group stabilises carbocation by *+I* effect.

74. These are total  $6\alpha$ -H to  $sp^2$  carbon and they all can participate in hyperconjugation.

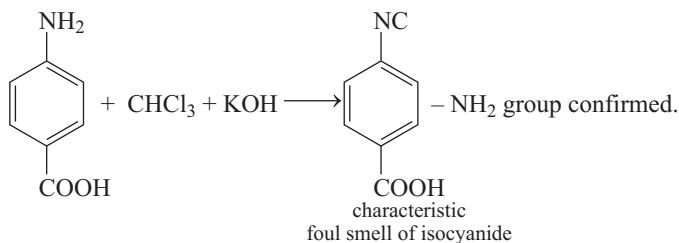
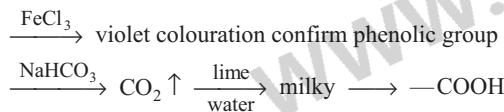


75. Aromatic alcohols and carboxylic acids forms salt with NaOH, will dissolve in aqueous NaOH :





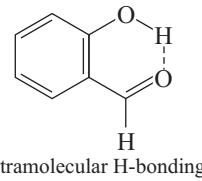
#### Tests of functional groups



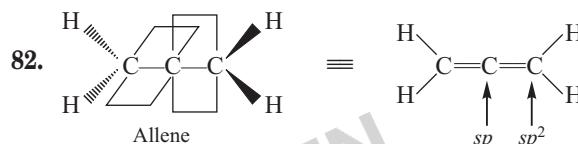
79. *p*-methoxy benzoic acid is the weakest and *p*-nitrobenzoic acid is the strongest acid among these acids. Chloro group has overall electron withdrawing effect on ring, therefore, increases acid strength of benzoic acid. Methyl group decreases acid strength of benzoic acid by  $+I$  effect. Therefore,

|                                | $K_a$                 |
|--------------------------------|-----------------------|
| <i>p</i> -methoxy benzoic acid | $3.3 \times 10^{-5}$  |
| <i>p</i> -methyl benzoic acid  | $4.2 \times 10^{-5}$  |
| benzoic acid                   | $6.4 \times 10^{-5}$  |
| <i>p</i> -chlorobenzoic acid   | $10.2 \times 10^{-5}$ |
| <i>p</i> -nitrobenzoic acid    | $36.2 \times 10^{-5}$ |

80.  $\text{H}-\text{C}\equiv\text{C}-\text{H}$  is more acidic than  $\text{CH}_2=\text{CH}_2$ .
81. Intramolecular H-bonding in *ortho*-hydroxybenzaldehyde decreases its melting point as well as boiling point. Molecules of *p*-hydroxybenzaldehyde is symmetrical, associated together by intermolecular H-bonds, has higher boiling point and melting point.

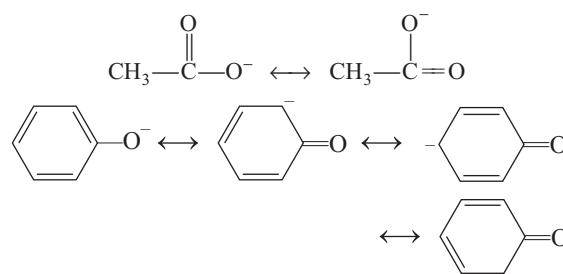


Intramolecular H-bonding



The above shown resonance introduces some double bond character to central C=C bond. Therefore, the central C=C bond in 1, 3-butadiene is shorter (stronger) than C=C bond in butane.

84. In case of acetate ion, both the resonance structures are equivalent and negative charge always remains on electronegative oxygen. These factors makes acetate ion more stable than phenoxide ion in which negative charge also moves on carbon atoms.



85. *p*-nitroaniline < aniline < *p*-toluidine < N,N-dimethyl-*p*-toluidine. Nitro group, by electron withdrawing resonance effect decreases the basic strength. Methyl group by electron donating inductive effect, increases basic strength.

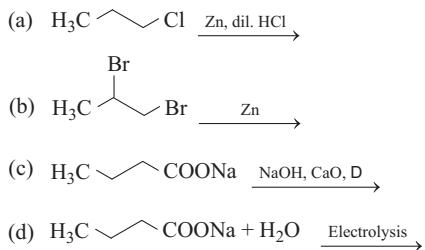
# 22

## Hydrocarbons

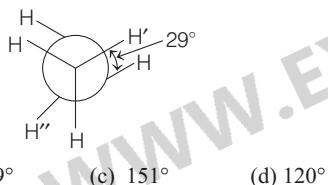
### Topic 1 Saturated Hydrocarbons

#### Objective Questions I (Only one correct option)

1. Which of the following reactions produce(s) propane as a major product? (2019 Adv.)



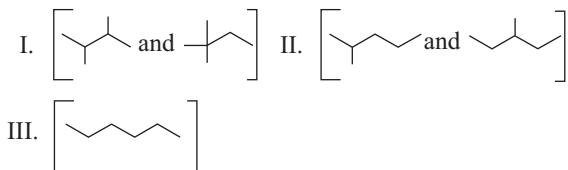
2. In the following skew conformation of ethane,  $\text{H}'-\text{C}-\text{C}-\text{H}''$  dihedral angle is (2019 Main, 12 April II)



3. Which of these factors does not govern the stability of a conformation in acyclic compounds? (2019 Main, 10 April II)

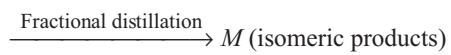
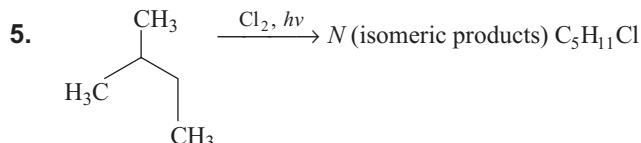
- (a) Electrostatic forces of interaction  
 (b) Torsional strain  
 (c) Angle strain  
 (d) Steric interactions

4. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (2014 Adv.)



The correct order of their boiling point is

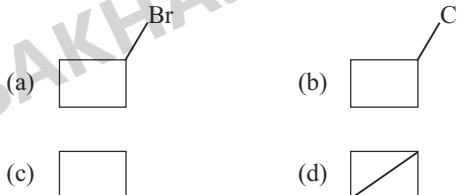
- (a) I > II > III  
 (b) III > II > I  
 (c) II > III > I  
 (d) III > I > II



What are N and M? (2006, 5M)

- (a) 6, 6  
 (b) 6, 4  
 (c) 4, 4  
 (d) 3, 3

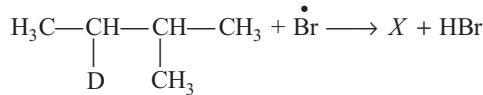
6. 1-bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? (2005, 1M)



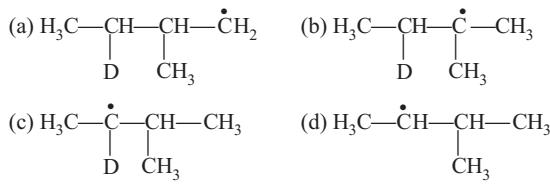
7. How many chiral compounds are possible on mono chlorination of 2-methyl butane? (2004, 1M)

- (a) 2  
 (b) 4  
 (c) 6  
 (d) 8

8. Consider the following reaction



Identify the structure of the major product X (2002, 3M)



9. Benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ) can be prepared from toluene by chlorination with (1998)

- (a)  $\text{SO}_2\text{Cl}_2$   
 (b)  $\text{SOCl}_2$   
 (c)  $\text{Cl}_2$   
 (d)  $\text{NaOCl}$

10.  $(\text{CH}_3)_3\text{CMgCl}$  on reaction with  $\text{D}_2\text{O}$  produces (1997)

- (a)  $(\text{CH}_3)_3\text{CD}$   
 (b)  $(\text{CH}_3)_3\text{OD}$   
 (c)  $(\text{CD}_3)_3\text{CD}$   
 (d)  $(\text{CD}_3)_3\text{OD}$

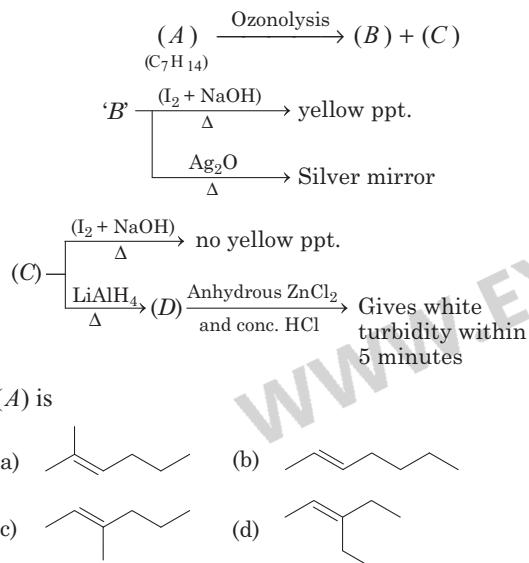
## **Integer Answer Type Question**

- 18.** The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compound, is  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2$ . (2011)

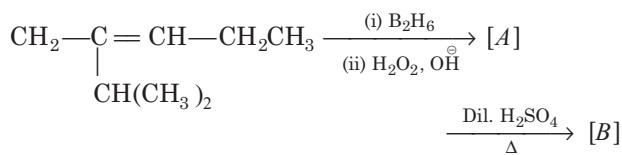
## **Topic 2 Unsaturated Hydrocarbons**

### **Objective Questions I (Only one correct option)**

1. Consider the following reactions: (2020 Main, 6 Sep I)

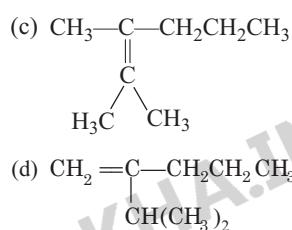


- 2.** The major product [B] in the following sequence of reactions is **(2020 Main, 8 Jan II)**

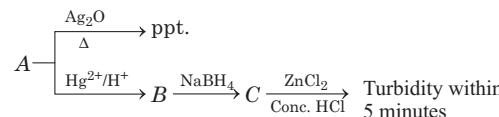


- (a)  $\text{CH}_3 - \underset{\text{CH}(\text{CH}_3)_2}{\underset{|}{\text{C}}} - \text{CH} = \text{CH} - \text{CH}_3$

(b)  $\text{CH}_3 - \underset{\text{CH}(\text{CH}_3)_2}{\underset{|}{\text{C}}} = \text{CH} - \text{CH}_2\text{CH}_3$



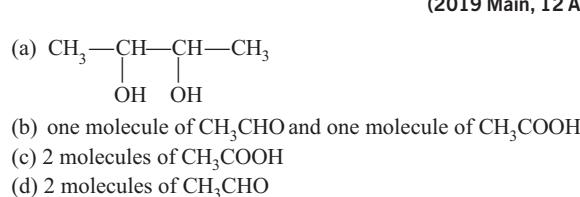
- 3.** Consider the following reactions,



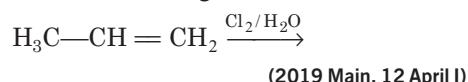
- A* is (2019 Main, 12 April II)

(a)  $\text{CH} \equiv \text{CH}$       (b)  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$   
 (c)  $\text{CH}_3 - \text{C} \equiv \text{CH}$       (d)  $\text{CH}_2 = \text{CH}_2$

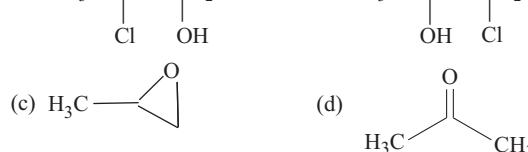
4. But-2-ene on reaction with alkaline  $\text{KMnO}_4$  at elevated temperature followed by acidification will give



5. The major product of the following addition reaction is

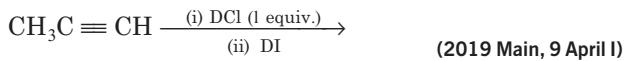


- (a)  $\text{CH}_3 - \text{CH} - \text{CH}_2$       (b)  $\text{CH}_3 - \text{CH}$



## 334 Hydrocarbons

6. The major product of the following reaction is



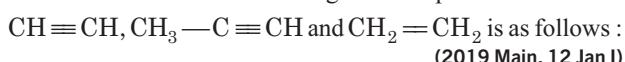
- (a)  $\text{CH}_3\text{CD}(\text{Cl})\text{CHD}(\text{I})$       (b)  $\text{CH}_3\text{CD}_2\text{CH}(\text{Cl})(\text{I})$   
 (c)  $\text{CH}_3\text{CD}(\text{I})\text{CHD}(\text{Cl})$       (d)  $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$

7. Which one of the following alkenes when treated with HCl yields majorly an anti Markownikov product?

(2019 Main, 8 April II)

- (a)  $\text{Cl}-\text{CH}=\text{CH}_2$       (b)  $\text{H}_2\text{N}-\text{CH}=\text{CH}_2$   
 (c)  $\text{CH}_3\text{O}-\text{CH}=\text{CH}_2$       (d)  $\text{F}_3\text{C}-\text{CH}=\text{CH}_2$

8. The correct order for acid strength of compounds



- (a)  $\text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{HC}\equiv\text{CH}$   
 (b)  $\text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2$   
 (c)  $\text{HC}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_2=\text{CH}_2$   
 (d)  $\text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{C}\equiv\text{CH}$

9. The *trans*-alkenes are formed by the reduction of alkynes with

(2018 Main)

- (a)  $\text{H}_2\text{-Pd/C, BaSO}_4$       (b)  $\text{NaBH}_4$   
 (c)  $\text{Na/liq. NH}_3$       (d)  $\text{Sn-HCl}$

10. The reaction of propene with  $\text{HOCl} (\text{Cl}_2 + \text{H}_2\text{O})$  proceeds through the intermediate

(2016 Main)

- (a)  $\text{CH}_3-\overset{+}{\text{CH}}-\text{CH}_2-\text{Cl}$   
 (b)  $\text{CH}_3-\text{CH}(\text{OH})-\overset{+}{\text{CH}}_2$   
 (c)  $\text{CH}_3-\text{CHCl}-\overset{+}{\text{CH}}_2$   
 (d)  $\text{CH}_3-\overset{+}{\text{CH}}-\text{CH}_2-\text{OH}$

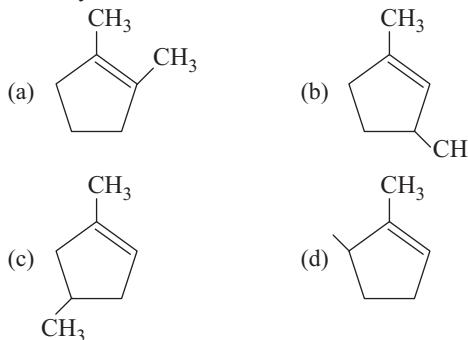
11. Which of the following compounds will exhibit geometrical isomerism?

(2015 Main)

- (a) 1-phenyl-2-butene  
 (b) 3-phenyl-1-butene  
 (c) 2-phenyl-1-butene  
 (d) 1, 1-diphenyl-1-propane

12. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?

(2015 Main)



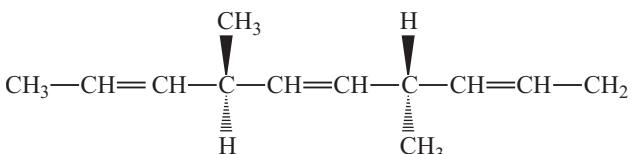
13. The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is

(2014 Main)

- (a) acetylene      (b) ethene  
 (c) 2-butyne      (d) 2-butene

14. The number of optically active products obtained from the complete ozonolysis of the given compound, is

(2012)



- (a) 0      (b) 1      (c) 2      (d) 4

15. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are

(2010)

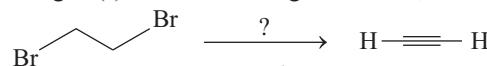
- (a)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$   
 (b)  $\text{BrCH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$   
 (c)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{C}\equiv\text{CH}$   
 (d)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

16. The number of stereoisomers obtained by bromination of *trans*-2-butene is

(2007)

- (a) 1      (b) 2      (c) 3      (d) 4

17. The reagent(s) for the following conversion,

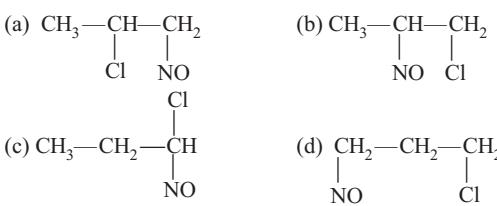


is/are (2007, 3M)

- (a) alcoholic KOH  
 (b) alcoholic KOH followed by  $\text{NaNH}_2$   
 (c) aqueous KOH followed by  $\text{NaNH}_2$   
 (d)  $\text{Zn}/\text{CH}_3\text{OH}$

18.  $\text{CH}_3-\text{CH}\equiv\text{CH}_2 + \text{NOCl} \longrightarrow P$ ; Identify the adduct.

(2006, 3M)



19. Cyclohexene is best prepared from cyclohexanol by which of the following?

(2005)

- (a) conc.  $\text{H}_3\text{PO}_4$       (b) conc.  $\text{HCl}/\text{ZnCl}_2$   
 (c) conc.  $\text{HCl}$       (d) conc.  $\text{HBr}$

20. 2-hexyne gives *trans*-2-hexene on treatment with

(2004, 1M)

- (a)  $\text{Li/NH}_3$       (b)  $\text{Pd/BaSO}_4$       (c)  $\text{LiAlH}_4$       (d)  $\text{Pt/H}_2$

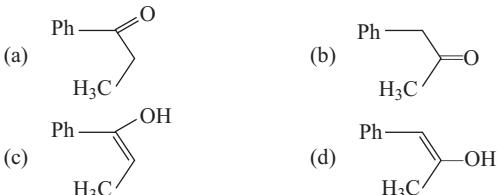
21. 2-phenyl propene on acidic hydration, gives

(2004, 1M)

- (a) 2-phenyl-2-propanol      (b) 2-phenyl-1-propanol  
 (c) 3-phenyl-1-propanol      (d) 1-phenyl-2-propanol

22.  $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow[\text{H}^+]{\text{Hg}^{2+}} A$ ; A is

(2003, 3M)



23. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne. (2002, 3M)

(a) bromine,  $\text{CCl}_4$       (b)  $\text{H}_2$ , Lindlar catalyst  
 (c) dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$       (d) ammoniacal  $\text{CuCl}_2$  solution

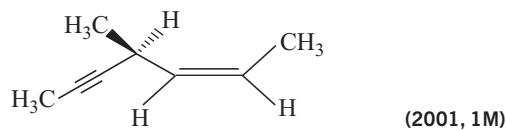
24. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because (2001, 1M)

(a) both are highly ionic  
 (b) one is oxidising and the other is reducing  
 (c) one of the steps is endothermic in both the cases  
 (d) all the steps are exothermic in both the cases

25. The reaction of propene with  $\text{HOCl}$  proceeds via the addition of (2001)

(a)  $\text{H}^+$  in the first step      (b)  $\text{Cl}^+$  in the first step  
 (c)  $\text{OH}^-$  in the first step      (d)  $\text{Cl}^+$  and  $\text{OH}^-$  single step

26. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives (2001, 1M)

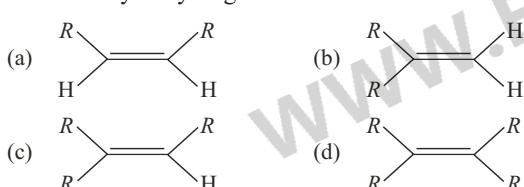


(a) an optically active compound  
 (b) an optically inactive compound  
 (c) a racemic mixture  
 (d) a diastereomeric mixture

27. Propyne and propene can be distinguished by (2000)

(a) conc.  $\text{H}_2\text{SO}_4$       (b)  $\text{Br}_2$  in  $\text{CCl}_4$   
 (c) dil.  $\text{KMnO}_4$       (d)  $\text{AgNO}_3$  in ammonia

28. Which one of the following alkenes will react fastest with  $\text{H}_2$  under catalytic hydrogenation condition? (2000, 1M)



29. The product(s) obtained via oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) of 1-butyne would be (1999, 2M)

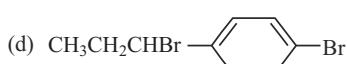
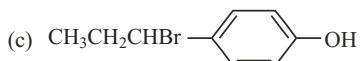
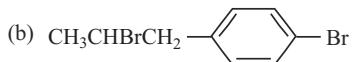
(a)  $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$   
 (b)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$   
 (c)  $\text{CH}_3-\text{CH}_2-\text{CHO} + \text{HCHO}$   
 (d)  $\text{CH}_3-\text{CH}_2-\text{COOH} + \text{HCOOH}$

30. In the compound, , the C2-C3 bond is of the type (1999, 2M)

(a)  $sp-sp^2$       (b)  $sp^3-sp^3$       (c)  $sp-sp^3$       (d)  $sp^2-sp^3$

31. The reaction of  $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_5-\text{OH}$  with  $\text{HBr}$  gives (1998, 2M)

(a)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_5-\text{OH}$



32. Which one of the following has the smallest heat of hydrogenation per mole? (1993, 1M)

(a) 1-butene      (b) *trans*-2-butene  
 (c) *cis*-2-butene      (d) 1, 3-butadiene

33. The number of structural and configurational isomers of a bromo compound,  $\text{C}_5\text{H}_9\text{Br}$ , formed by the addition of  $\text{HBr}$  to 2-pentyne respectively, are (1988, 1M)

(a) 1 and 2      (b) 2 and 4      (c) 4 and 2      (d) 2 and 1

34. Acidic hydrogen is present in (1985, 1M)

(a) ethyne      (b) ethene      (c) benzene      (d) ethane

35. Baeyer's reagent is (1984, 1M)

(a) alkaline permanganate solution  
 (b) acidified permanganate solution  
 (c) neutral permanganate solution  
 (d) aqueous bromine solution

36. When propyne is treated with aqueous  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$ , the major product is (1983, 1M)

(a) propanal      (b) propyl hydrogen sulphate  
 (c) acetone      (d) propanol

37. The compound 1, 2-butadiene has (1983, 1M)

(a) only  $sp$ -hybridised carbon atoms  
 (b) only  $sp^2$ -hybridised carbon atoms  
 (c) both  $sp$  and  $sp^2$ -hybridised carbon atoms  
 (d)  $sp$ ,  $sp^2$  and  $sp^3$ -hybridised carbon atoms

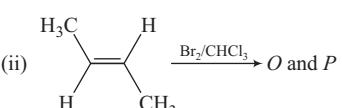
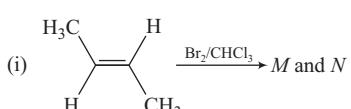
38. Which of the following will decolourise alkaline  $\text{KMnO}_4$  solution? (1980, 1M)

(a)  $\text{C}_3\text{H}_8$       (b)  $\text{CH}_4$       (c)  $\text{CCl}_4$       (d)  $\text{C}_2\text{H}_4$

## Objective Questions II

(One or more than one correct option)

39. The correct statement(s) for the following addition reactions is (are) (2017 Adv.)



(a) (*M* and *O*) and (*N* and *P*) are two pairs of enantiomers  
 (b) Bromination proceeds through *trans*-addition in both the reactions

(c) *O* and *P* are identical molecules  
 (d) (*M* and *O*) and (*N* and *P*) two pairs of diastereomers

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### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct Statement II is correct Statement II is a correct explanation of Statement I.
- (b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I.
- (c) Statement I is correct Statement II is incorrect.
- (d) Statement I is incorrect Statement II is correct.

**40. Statement I** Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromo butane.

**Statement II** Bromine addition to an alkene is an electrophilic addition. (2001, 1M)

**41. Statement I** Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compound.

**Statement II** It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. (2001, 1M)

**42. Statement I** 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

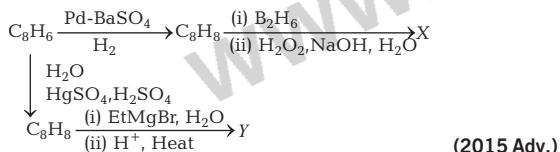
**Statement II** It involves the formation of a primary radical. (2000, 1M)

**43. Statement I** Addition of Br<sub>2</sub> to 1-butene gives two optical isomers.

**Statement II** The product contains one asymmetric carbon. (1998, 1M)

### Passage Based Questions

#### Passage 1



**44. Compound X is**

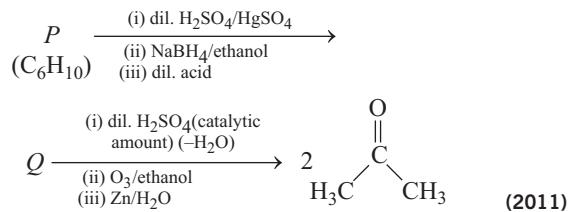
- (a)
- (b)
- (c)
- (d)

**45. The major compound Y is**

- (a)
- (b)
- (c)
- (d)

#### Passage 2

An acyclic hydrocarbon P, having molecular formula C<sub>6</sub>H<sub>10</sub>, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.



**46. The structure of the compound Q is**

- (a)
- (b)
- (c)
- (d)

**47. The structure of compound P is**

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$
- (b)  $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_3$
- (c)
- (d)

#### Passage 3

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.

**48. The correct statement with respect to product Y is**

- (a) it gives a positive Tollen's test and is a functional isomer of X
- (b) it gives a positive Tollen's test and is a geometrical isomer of X
- (c) it gives a positive iodoform test and is a functional isomer of X
- (d) it gives a positive iodoform test and is a geometrical isomer of X

**49. The product X is**

- (a)
- (b)
- (c)
- (d)

**Fill in the Blanks**

50. 1,3-butadiene with bromine in molar ratio of 1 : 1 generate predominantly ..... . (1997, 1M)
51. Addition of water to acetylene compounds is catalysed by ..... and ..... (1993, 1M)
52. Kolbe's electrolysis of potassium succinate gives  $\text{CO}_2$  and ..... . (1993, 1M)
53. The terminal carbon atom in 2-butene is ..... hybridised. (1985, 1M)
54. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is ..... . (1983, 1M)
55. ..... is most acidic. (Ethane, Ethene, Ethyne) (1981, 1M)

**True/False**

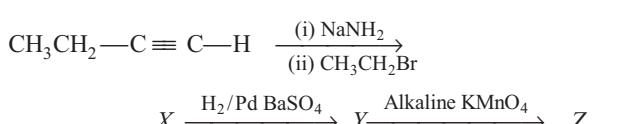
56. Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1981)

**Integer Answer Type Question**

57. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula  $\text{C}_4\text{H}_6$  is (2010)

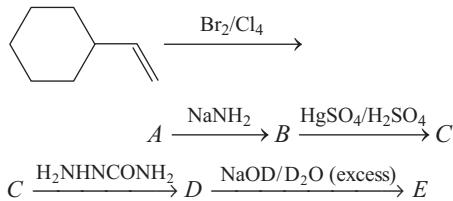
**Subjective Questions**

58. Monomer *A* of a polymer on ozonolysis yields two moles of  $\text{HCHO}$  and one mole of  $\text{CH}_3\text{COCHO}$ .
- Deduce the structure of *A*.
  - Write the structure of all *cis* form of polymer of compound *A*. (2005, 2M)
59. A biologically active compound, Bombykol ( $\text{C}_{16}\text{H}_{30}\text{O}$ ) is obtained from a natural source. The structure of the compound is determined by the following reactions.
- On hydrogenation, Bombykol gives a compound *A*,  $\text{C}_{16}\text{H}_{34}\text{O}$ , which reacts with acetic anhydride to give an ester.
  - Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis ( $\text{O}_3/\text{H}_2\text{O}_2$ ) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.
- Determine the number of double bonds in Bombykol. Write the structures of compound *A* and Bombykol. How many geometrical isomers are possible for Bombykol?
60. Identify *X*, *Y* and *Z* in the following synthetic scheme and write their structures.

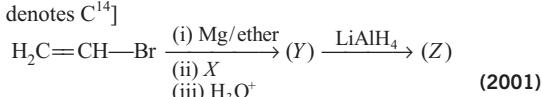


Is the compound *Z* optically active? Justify your answer. (2002)

61. (a) Identify (*A*), (*B*), (*C*), (*D*) and (*E*) in the following schemes and write their structures :

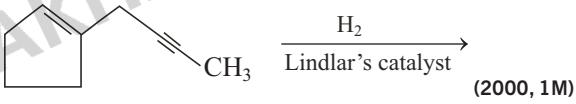


- (b) Identify (*X*), (*Y*) and (*Z*) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde ( $\text{H}_2\text{C}^*\text{O}$ ) as one of the products when compound (*Z*) is treated with  $\text{HBr}$  and subsequently ozonolysed. Mark the  $\text{C}^*$  carbon in the entire scheme.  $\text{BaC}^*\text{O}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{X})$  gas [ $\text{C}^*$  denotes  $\text{C}^{14}$ ]

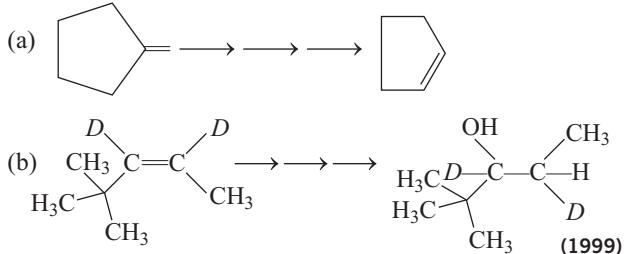


62. An alkene (*A*)  $\text{C}_{16}\text{H}_{16}$  on ozonolysis gives only one product (*B*)  $\text{C}_8\text{H}_8\text{O}$ . Compound (*B*) on reaction with  $\text{NaOH}/\text{I}_2$  yields sodium benzoate. Compound (*B*) reacts with  $\text{KOH}/\text{NH}_2\text{NH}_2$  yielding a hydrocarbon (*C*)  $\text{C}_8\text{H}_{10}$ . Write the structures of compounds (*B*) and (*C*). Based on this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation ( $\text{H}_2/\text{Pd} - \text{C}$ ) gives a racemic mixture. (2001)

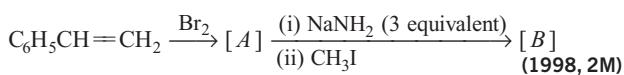
63. What would be the major product in the following reaction?



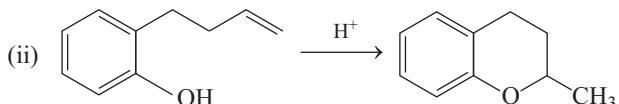
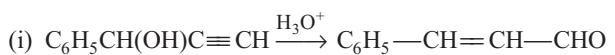
64. Complete the following reactions with appropriate reagents :



65. Complete the following reactions with appropriate structures of products/reagents :



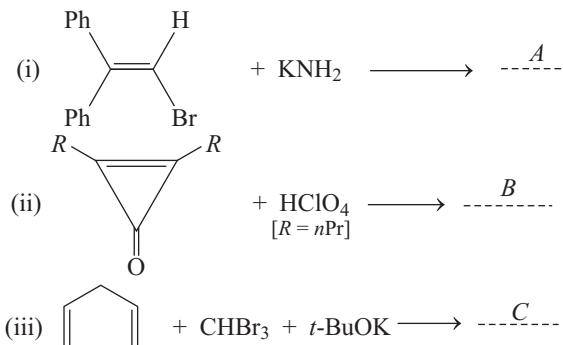
66. Write the intermediate steps for each of the following reactions :



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67. The hydrocarbon *A*, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When *A* is oxidised vigorously with  $\text{KMnO}_4$ , a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of *A* and explain. (1997, 2M)

68. Complete the following, giving the structures of the principal organic products : (1997, 1M)



69. An alkyl halide, *X*, of formula  $\text{C}_6\text{H}_{13}\text{Cl}$  on treatment with potassium tertiary butoxide gives two isomeric alkenes *Y* and *Z* ( $\text{C}_6\text{H}_{12}$ ). Both alkenes on hydrogenation gives 2, 3-dimethyl butane. Predict the structures of *X*, *Y* and *Z*. (1996, 3M)

70. Give the structure of the major organic products obtained from 3-ethyl-2-pentene under each of the following reaction conditions : (1996)

- (a)  $\text{HBr}$  in the presence of peroxide
- (b)  $\text{Br}_2 / \text{H}_2\text{O}$
- (c)  $\text{Hg}(\text{OAc})_2 / \text{H}_2\text{O}$ ,  $\text{NaBH}_4$

71. Write down the structure of the stereoisomers formed when *cis*-2-butene is reacted with bromine. (1995)

72. An organic compound *E* ( $\text{C}_5\text{H}_8$ ) on hydrogenation gives compound *F* ( $\text{C}_5\text{H}_{12}$ ). Compound *E* on ozonolysis gives formaldehyde and 2-keto propanal. Deduce the structure of compound *E*. (1995)

73. When gas *A* is passed through dry KOH at low temperature, a deep red coloured compound *B* and a gas *C* are obtained. The gas *A*, on reaction with but-2-ene, followed by treatment with  $\text{Zn}/\text{H}_2\text{O}$  yields acetaldehyde. Identify *A*, *B* and *C*. (1994, 3M)

74. Give the structures of *A*, *B* and *C* (explanation are not required)
- (i) *A* ( $\text{C}_4\text{H}_8$ ) which adds on  $\text{HBr}$  in the presence and in the absence of peroxide to give same product.
  - (ii) *B* ( $\text{C}_4\text{H}_8$ ) which when treated with  $\text{H}_2\text{O} / \text{H}_2\text{SO}_4$  gives  $\text{C}_4\text{H}_{10}\text{O}$  which cannot be resolved into optical isomers.
  - (iii) *C* ( $\text{C}_6\text{H}_{12}$ ), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound  $\text{C}_6\text{H}_{14}$ .
- (1993, 1M  $\times$  3 = 3M)

75. Write the balanced chemical equation for the following “Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate.” (1991, 1M)

76. Give a chemical test and the reagents used to distinguish between cyclohexane and cyclohexene. (1991, 1M)

77. A white precipitate was formed slowly when silver nitrate was added to compound *A* with molecular formula  $\text{C}_6\text{H}_{13}\text{Cl}$ . Compound *A* on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes *B* and *C*, having formula  $\text{C}_6\text{H}_{12}$ . The mixture of *B* and *C*, on ozonolysis, furnished four compounds

- |                                  |                                                                                  |
|----------------------------------|----------------------------------------------------------------------------------|
| (i) $\text{CH}_3\text{CHO}$      | (ii) $\text{C}_2\text{H}_5\text{CHO}$                                            |
| (iii) $\text{CH}_3\text{COCH}_3$ | (iv) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{CHO}$ |

What are the structures of *A*, *B* and *C*? (1986, 4M)

78. How would you convert acetylene to acetone? (1985, 1M)

79. Give the chemical test to distinguish between 2-butyne and 1-butyne. (1985, 1M)

80. Following statements are true, only under some specific conditions. Write the condition for each subquestion in not more than two sentences :

- (i) 2-methyl propene can be converted into isobutyl bromide by hydrogen bromide.
- (ii) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution.

(1984, 1M  $\times$  2 = 2M)

81. Give reasons for the following in one or two sentences :

- (i) Methane does not react with chlorine in the dark.
- (ii) Propene reacts with  $\text{HBr}$  to give isopropyl bromide but does not give *n*-propyl bromide. (1983, 1M  $\times$  2 = 2M)

82. State with balanced equation, what happens when “propene is bubbled through a hot aqueous solution of potassium permanganate.”? (1982, 1M)

83. One mole of a hydrocarbon *A* reacts with one mole of bromine giving a dibromo compound,  $\text{C}_5\text{H}_{10}\text{Br}_2$ . Compound *A* on treatment with cold dilute alkaline potassium permanganate solution forms a compound,  $\text{C}_5\text{H}_{12}\text{O}_2$ . On ozonolysis *A* gives equimolar quantities of propanone and ethanal. Deduce the structural formula of *A*. (1981, 1M)

84. Write the structural formula of the major product in each of the following cases

- (i) Ethene mixed with air is passed under pressure over a silver catalyst.
- (ii) The compound obtained by hydration of ethyne is treated with dilute alkali. (1981, 2  $\times$  1 / 2 M = 1M)

85. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). (1981, 1M)

86. Give one characteristic test which would distinguish  $\text{CH}_4$  from  $\text{C}_2\text{H}_2$ . (1979, 1M)

## Answers

**Topic 1**

1. (a,c)      2. (b)      3. (c)      4. (b)  
 5. (b)      6. (d)      7. (c)      8. (b)  
 9. (c)      10. (a)      11. (d)      12. (c)  
 13. (d)      14. (b)      15. (c)      16. (d)  
 17. (b)      18. (8)

**Topic 2**

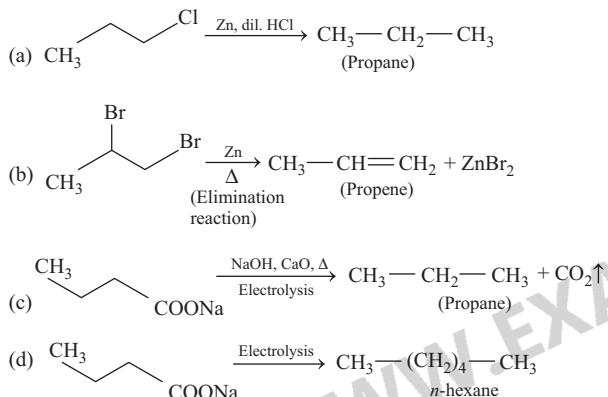
1. (d)      2. (c)      3. (c)      4. (c)  
 5. (b)      6. (d)      7. (d)      8. (c)  
 9. (c)      10. (a)      11. (a)      12. (b)  
 13. (c)      14. (a)      15. (d)      16. (a)

17. (b)      18. (a)      19. (a)      20. (a)  
 21. (a)      22. (a)      23. (d)      24. (c)  
 25. (b)      26. (b)      27. (d)      28. (a)  
 29. (a)      30. (d)      31. (c)      32. (b)  
 33. (b)      34. (a)      35. (a)      36. (c)  
 37. (d)      38. (d)      39. (a,b,d)      40. (b)  
 41. (a)      42. (c)      43. (a)      44. (c)  
 45. (d)      46. (b)      47. (d)      48. (c)  
 49. (a)      50. (3,4-dibromo-1-butene)  
 51.  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$  52. (ethene) 53. ( $sp^3$ ) 54.  
 (2-butyne)  
 55. Terminal alkyne (ethyne) 56. (False) 57. (5)

## Hints & Solutions

**Topic 1 Saturated Hydrocarbons**

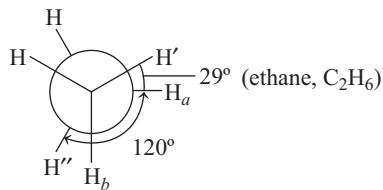
1. The given reactions takes place as follows:



Thus options (a,c) are correct.

2. A dihedral angle is the angle between two C—H bonds projected on a plane orthogonal to the C—C bond. In the given skew conformation, having Newman's projection the dihedral angle is  $\text{H}'—\text{C}—\text{C}—\text{H}''$

$$= (\text{H}'—\text{C}—\text{C}—\text{H}_a) + (\text{H}_a—\text{C}—\text{C}—\text{H}'') \\ = 29^\circ + 120^\circ = 149^\circ$$



3. The four types of strains *viz* (a) electrostatic force of attraction, (b) torsional strain, (c) angle strain, (d) steric stain, are

responsible for the stability or energy barriers of conformers. In cyclic compounds, all types of strains may be present.

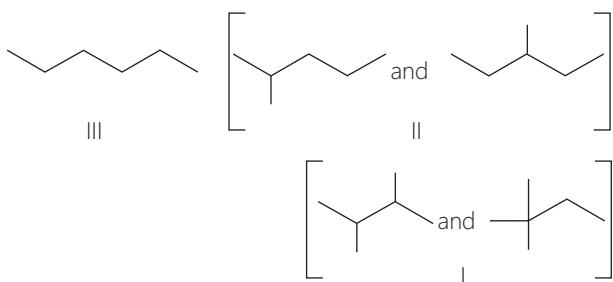
| Compound | Type of strains/forces |
|----------|------------------------|
|          | $a + c$                |
|          | $a + b + c$            |
|          | $a + b + c + d$        |

In a cyclic or open-chain compounds, angle strain (c) is absent. e.g.

| Compound | Types of strains/forces |
|----------|-------------------------|
|          | $a$                     |
|          | $a + b$                 |
|          | $a + b + d$             |

4. **PLAN** This problem is based on boiling point of isomeric alkanes. As we know more the branching in an alkane, lesser will be its surface area and lesser will be the boiling point

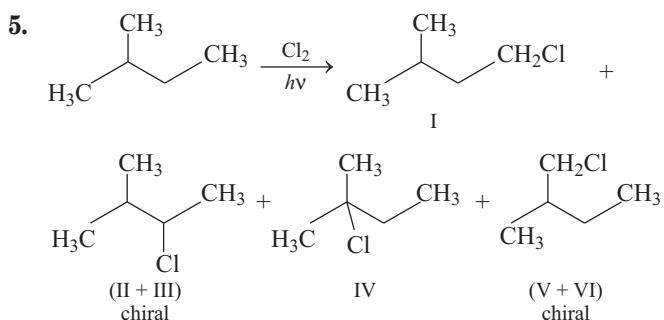
## 340 Hydrocarbons



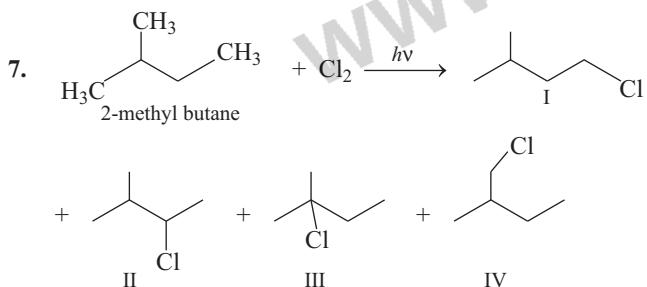
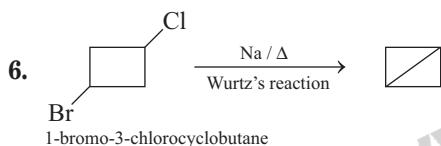
**On moving left to right (III to I)**

- branching increases
- surface area decreases
- boiling point decreases

Hence, correct choice is (b).

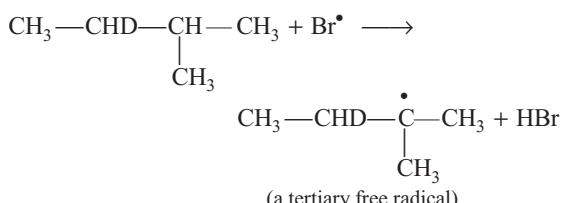


Since, fractional distillation cannot separate enantiomers (II + III and V + VI), M = 4 and N = 6.

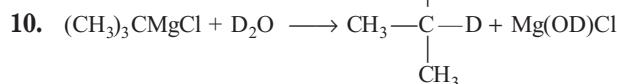
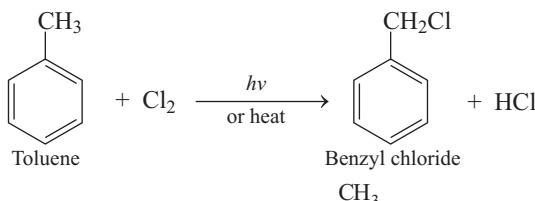


Out of the four products formed above, II and IV are chiral, produced in pairs, giving total of six mono-chlorination products.

8. Bromination is highly selective, occur at the carbon, where the most stable free radical is formed :

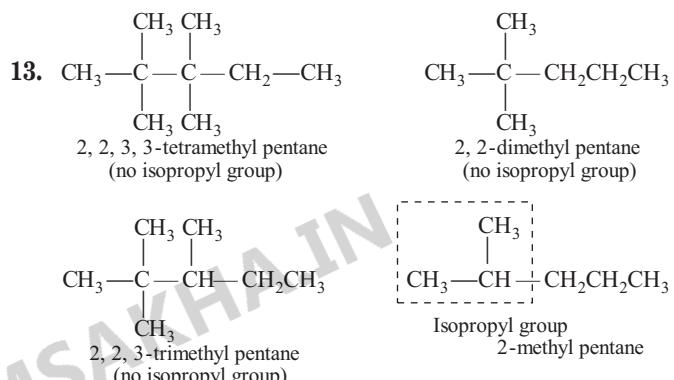


9. Toluene on treatment with  $\text{Cl}_2$  in the presence of heat or light undergo free-radical chlorination at benzylic position, giving benzyl chloride



11. Alkanes are all less dense than water, floats over water.

12. C—H bond with  $sp^3$ -C will be longest in  $\text{C}_2\text{H}_6$ .

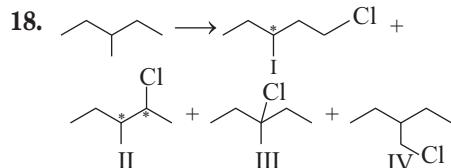


14. Boiling point of alkane increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-octane has highest boiling point, higher than 2, 2, 3, 3-tetramethyl-butane (an isomer of *n*-octane).

15. Ethylene absorb  $\text{H}_2\text{SO}_4$  forming  $\text{CH}_3-\text{CH}_2\text{OSO}_3\text{H}$  and dissolve. Benzene, with warm  $\text{H}_2\text{SO}_4$ , undergo sulphonation and dissolve. Aniline, with  $\text{H}_2\text{SO}_4$ , forms anilinium sulphate salt and dissolve. Hexane, a hydrophobic molecule, does not react with  $\text{H}_2\text{SO}_4$ , remains insoluble.

16. Among alkanes, boiling point increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-hexane has highest boiling point among these.

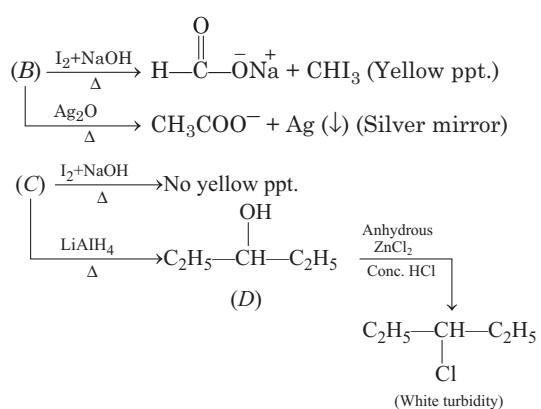
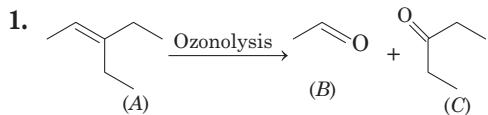
17. Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria. Due to this method of formation, methane is also known as marsh gas.



I has one chiral carbon = two isomers

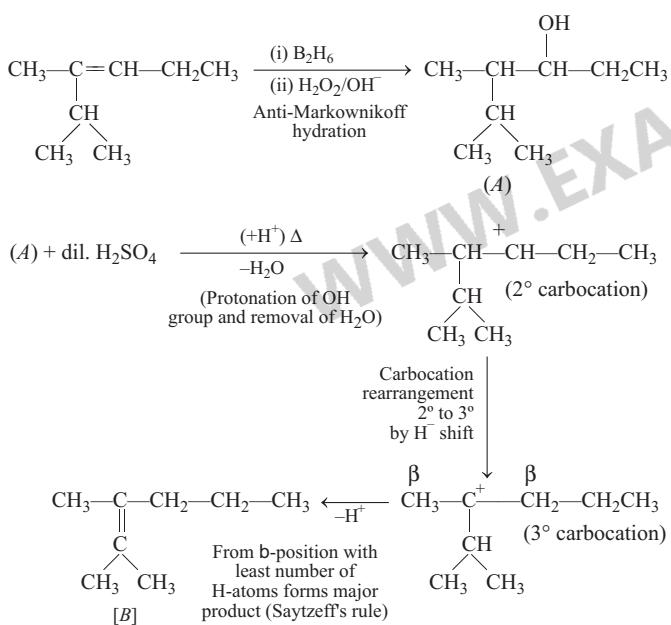
II has two chiral carbons and no symmetry = four isomers.

III and IV have no chiral carbon, no stereoisomers.

**Topic 2 Unsaturated Hydrocarbons**


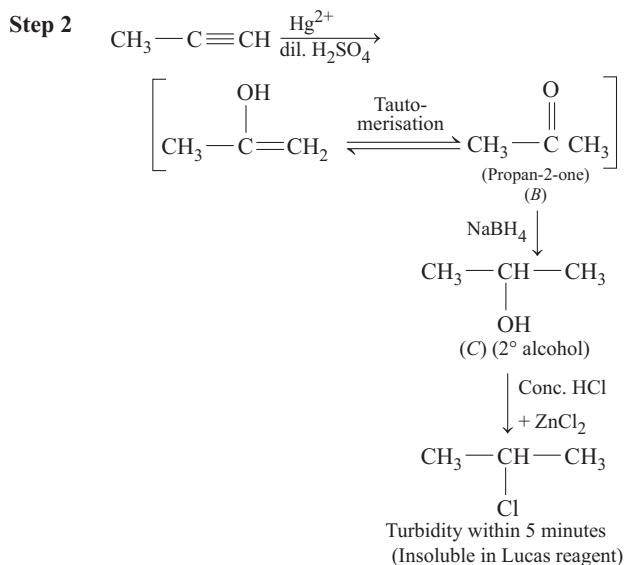
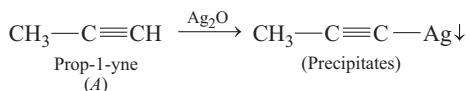
Methyl ketones react with  $I_2 + NaOH$ , so option (a) and (c) are incorrect, while option (b) only gives aldehydes, thus (b) also incorrect. Hence, the correct option is (d).

2.



3. According to the given conditions, the compound should be alkyne with triple bond present at the terminal. The chemical reactions involved are as follows:

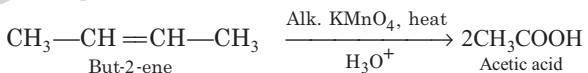
**Step 1**



In step-1, prop-1-yne reacts with  $Ag_2O$  to form  $CH_3-C \equiv C-Ag$  that forms white precipitates.

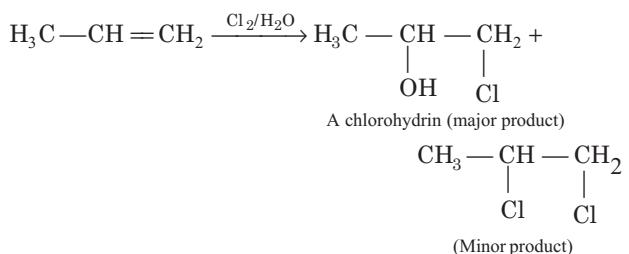
In step 2, prop-1-yne in presence of mercuric sulphate and dil.  $H_2SO_4$  produces carbonyl compound  $(CH_3)_2C=O$  which produces  $(CH_3)_2CH-OH$  in presence of  $NaBH_4$ . 2°alcohol on reaction with Lucas reagent produces turbidity in about 5 min.

4. But-2-ene on reaction with alkaline  $KMnO_4$  at elevated temperature followed by acidification will give acetic acid ( $CH_3COOH$ ). Hot alkaline solution of potassium permanganate followed by acidification oxidatively cleaved alkenes. The reaction proceed as follows :

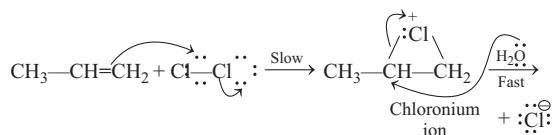


5. The major product of the given addition reaction is
- $$H_3C-CH(OH)-CH_2-Cl$$

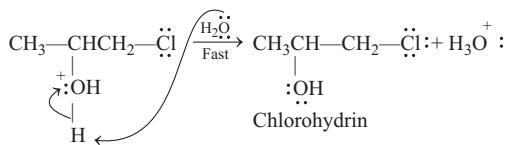
In this reaction,  $H_2O$  is used as a solvent and the major product of the reaction will be a *vicinal* halohydrin. A halohydrin is an organic molecule that contains both OH group and a halogen. In a *vicinal* halohydrin, the OH and halogen are bonded to adjacent carbons.



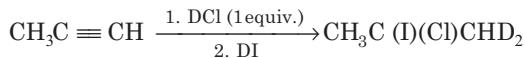
The reaction proceeds through following mechanism :



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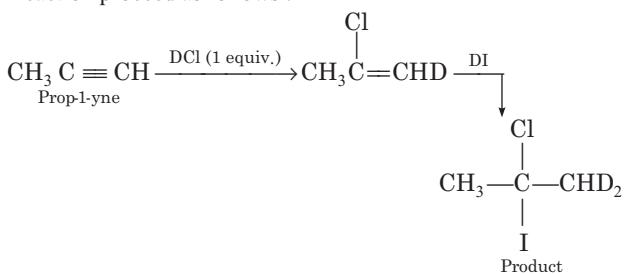


6. The major product obtained in the given reaction is  $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$ .



Addition in unsymmetrical alkynes takes place according to Markovnikov's rule.

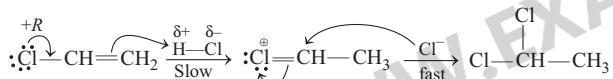
Reaction proceed as follows :



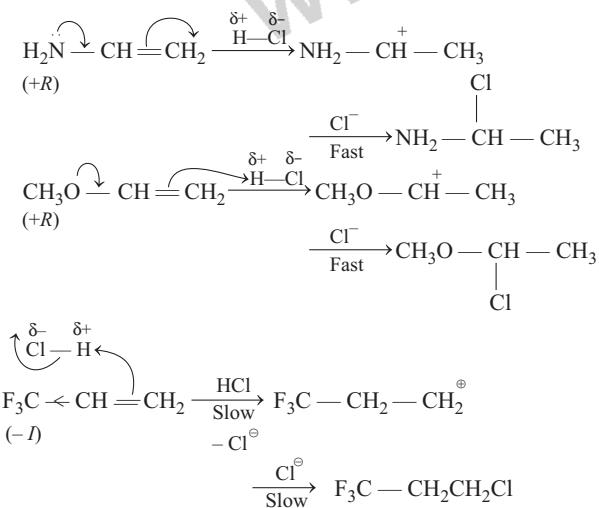
7. Attachment of electron donating group (+ R or + I) with  $sp^2$ -carbon of an unsymmetrical alkene supports Markovnikov's addition rule through electrophilic-addition-pathway.

But, attachment of electron-withdrawing group (- R or - I) for the same will follow anti-Markovnikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway.

The product formed by given alkenes when treated with HCl.

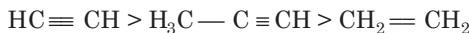


Similarly,



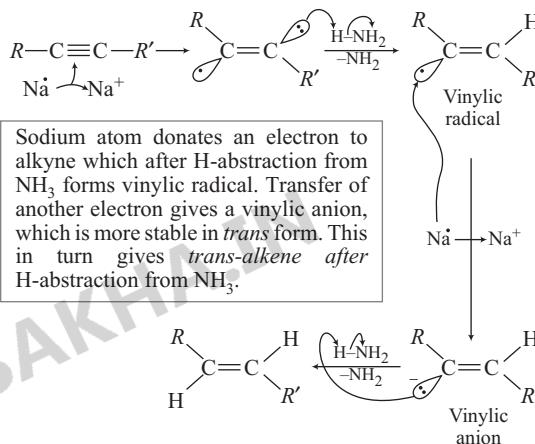
8. Ethene ( $\text{H}_2\text{C}=\text{CH}_2$ ) is  $sp^2$ -hybridised and ethyne ( $\text{HC}\equiv\text{CH}$ ) is  $sp$ -hybridised. In ethyne, the  $sp$ -hybridised carbon atom possesses maximum s-character and hence, maximum electronegativity. Due to which, it attracts the shared electron pair of C—H bond to a greater extent and makes the removal of proton easier. Hence, alkyne is much more acidic than alkene.

Presence of electron donating group in alkyne ( $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$ ) decreases the acidic strength of compound. Hence, the correct order of acidic strength is:

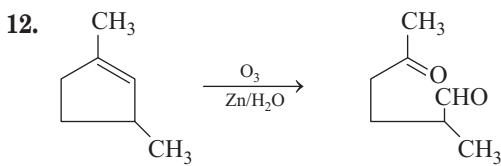
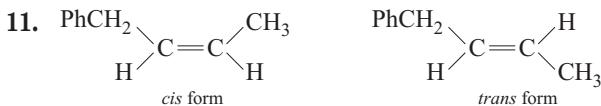
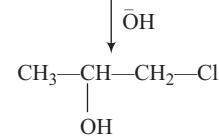
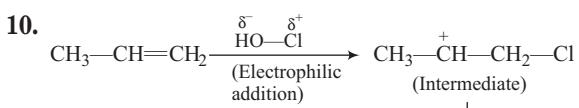


9. Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.

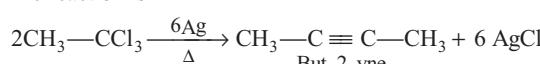
**Mechanism**



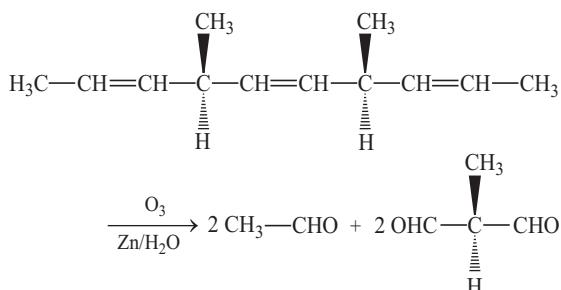
Sodium atom donates an electron to alkyne which after H-abstraction from  $\text{NH}_3$  forms vinylic radical. Transfer of another electron gives a vinylic anion, which is more stable in *trans* form. This in turn gives *trans*-alkene after H-abstraction from  $\text{NH}_3$ .



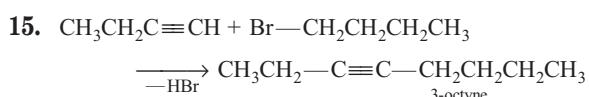
13. The reaction is



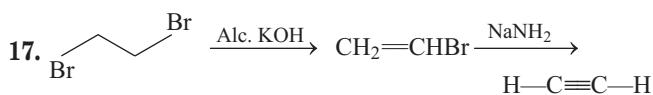
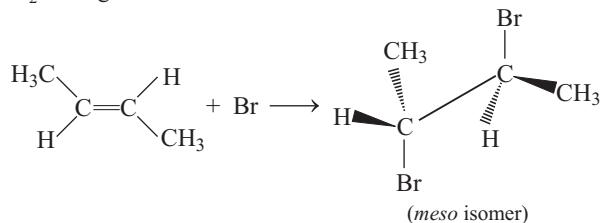
14. Ozonolysis of the given triene occur as follows :



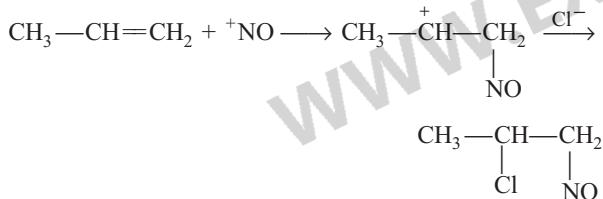
Since, none of the above dial is chiral, no optically active product is obtained.



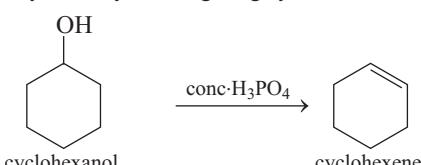
16.  $\text{Br}_2$  undergo anti-addition on  $\text{C=C}$  bonds as:



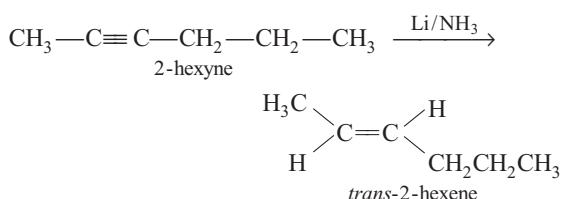
18.  $\text{NOCl}$  undergo electrophilic addition on alkene as:



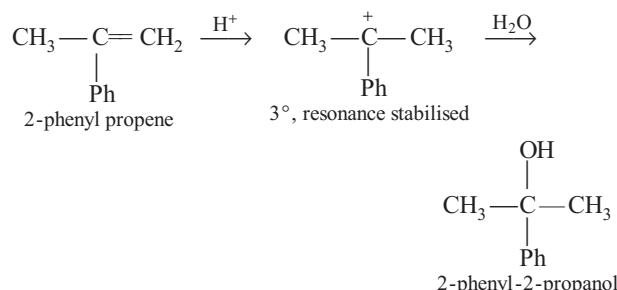
19. Cyclohexanol on treatment with concentrated  $\text{H}_3\text{PO}_4$  undergo acid catalysed dehydration giving cyclohexene.



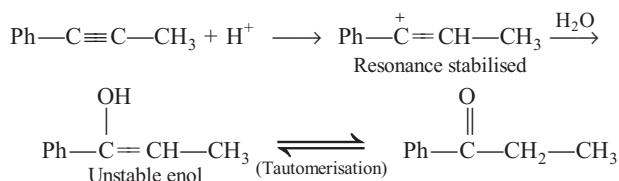
20. Alkynes on treatment with alkali metals in liquid ammonia gives *trans* hydrogenation product:



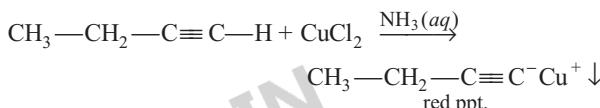
21. Reaction proceeds through carbocation intermediate:



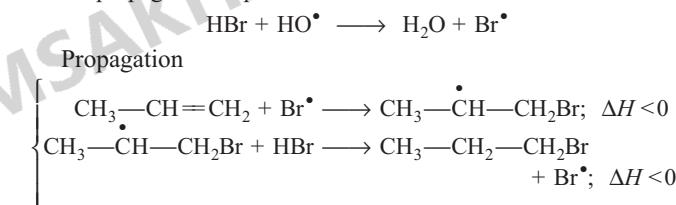
22. Reaction proceeds through carbocation intermediate :



23. Ammoniacal  $\text{CuCl}_2$  forms red precipitate with terminal alkynes, can be used to distinguish terminal alkynes from internal alkynes:

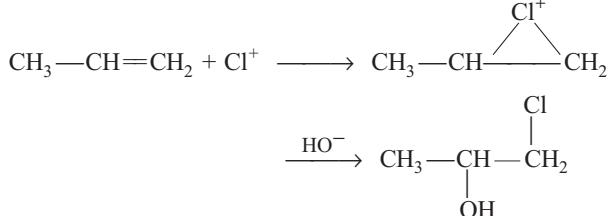


24. In addition of  $\text{HBr}$  to an alkene, in the presence of peroxide, both the propagation steps are exothermic :



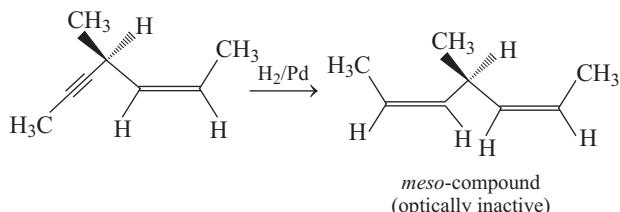
In case of addition of  $\text{HCl}$  and  $\text{HI}$ , one of the propagation step is endothermic, reaction fail to occur.

25.  $\text{HOCl} \longrightarrow \text{HO}^- + \text{Cl}^+$



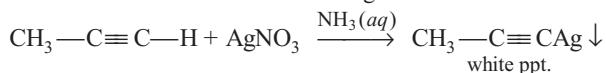
i.e. reaction is initiated by  $\text{Cl}^+$  (chloronium ion electrophile)

26. Hydrogenation with poisoned palladium brings about *cis* hydrogenation of alkyne and does not affect double bonds :



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- 27.** Terminal alkynes forms silver salt with Tollen's reagent while alkene does not react with Tollen's reagent.

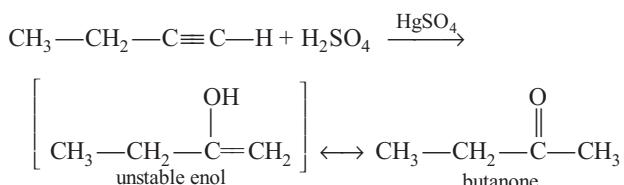


Therefore, Tollen's reagent can be used to distinguish a terminal alkyne like propyne from alkene as well as from internal alkynes.

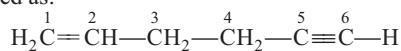
- 28.** Ease of catalytic hydrogenation depends upon the size of groups present at the doubly bonded carbon. Larger the size of groups, difficult the hydrogenation. Therefore, in the given situation, disubstituted reacts at faster rate than tri and tetra substituted alkenes. Among disubstituted, the stability order is :



- 29.** Oxymercuration-demercuration brings about Markownikoff's addition of water as :

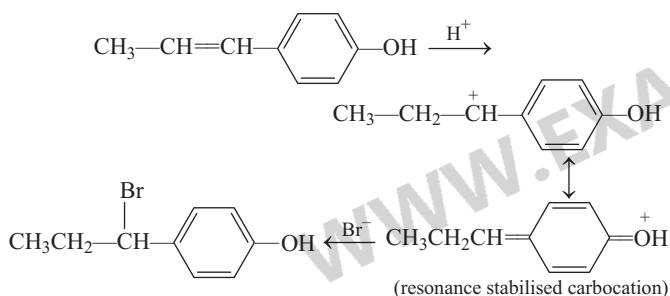


- 30.** According to the IUPAC conventions, compound can be numbered as:



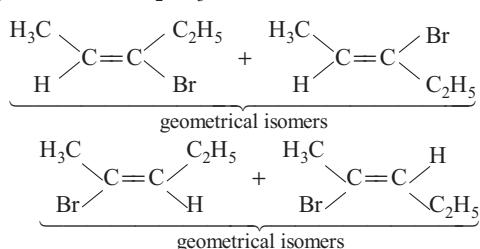
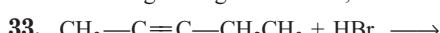
Here, C-2 is  $sp^2$  and C-3 is  $sp^3$ -hybridised.

- 31.** Electrophilic addition on  $\text{C}=\text{C}$  is governed by stability of carbocation:



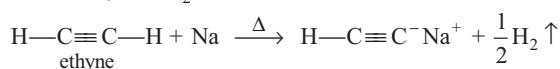
32. Among alkenes-heat of hydrogenation depends on :

  - (a) The number of double bonds-greater, greater the amount of heat evolved in hydrogenation.  
Hence, 1, 3-butadiene has highest heat of hydrogenation among these.
  - (b) Relative stability of alkenes-greater the stability, smaller the heat evolved in hydrogenation. *trans*-2-butene is most stable among three given butenes, has least heat of hydrogenation.



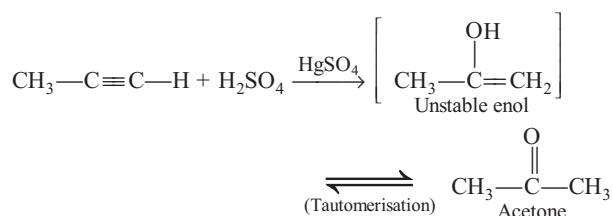
Therefore, two structural and four configurational isomers.

- 34.** Terminal alkynes are slightly acidic, forms salt with very strong base like Na, NaNH, etc.

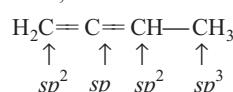


- 35.** Baeyer's reagent is cold, dilute, alkaline permanganate solution, used to detect presence of olefinic bonds.

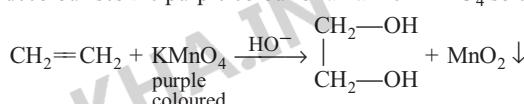
- 36.** Alkynes undergo Markownikoff's addition of water in the presence of  $\text{H}_2\text{SO}_4$  /  $\text{HgSO}_4$ :



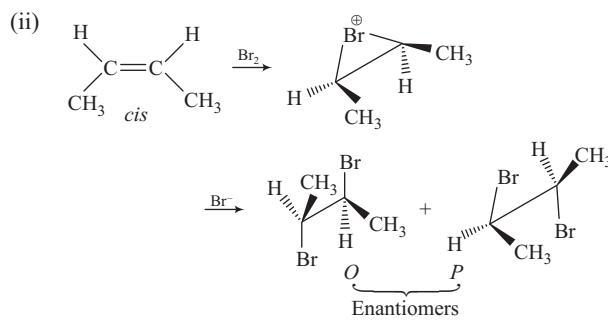
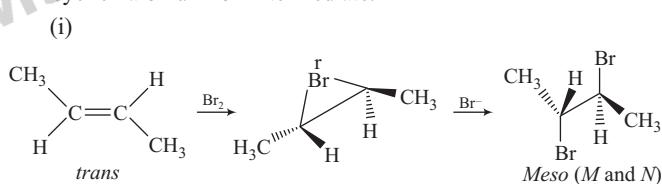
- 37.** Structural formula of 1, 2-butadiene is :



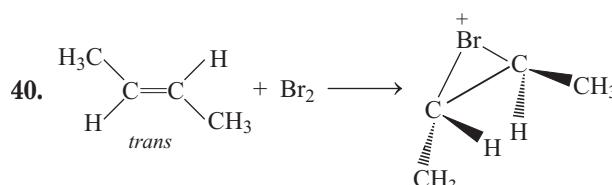
- 38.** Unsaturated compounds which contain  $C=C$  or  $C\equiv C$ , decolourises the purple colour of alkaline  $KMnO_4$  solution.



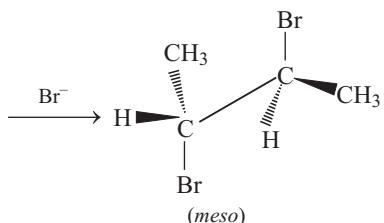
- 39.** Addition of halogen at double bond occur in antiorientation via cyclic halonium ion intermediate.



Here,  $(M + O)$  and  $(N + P)$  are pair of diastereomers.



Statement I is correct. Statement II is also correct. *Meso* form of the product is due to *anti* addition of  $\text{Br}^-$  on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement I.



41. 

Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

- 42.**  $\text{CH}_3\text{---CH}_2\text{---CH=CH}_2 + \text{Br}^\bullet \longrightarrow$

$$\text{CH}_3\text{---CH}_2\text{---}\overset{\bullet}{\text{CH}}\text{---CH}_2\text{Br}$$

a secondary radical

Therefore, Statement I is correct but Statement II is incorrect.

- 43.**  $\text{CH}_3\text{---CH}_2\text{---CH=CH}_2 + \text{Br}_2 \longrightarrow$

$$\text{CH}_3\text{---CH}_2\text{---}\underset{\substack{| \\ \text{Br}}}{\text{CH}}\text{---CH}_2\text{Br}$$

has one chiral carbon

Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

## Passage 1

The reaction condition indicates that starting compound is phenyl acetylene.

- 44.**

$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{H}_2]{\text{Pd/BaSO}_4} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$ 
  
 (2-phenyl ethanol)

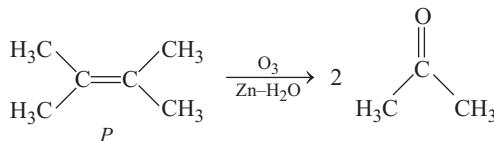
Hydroboration oxidation brings about anti-Markonikoff's hydration of alkene.

- 45.**

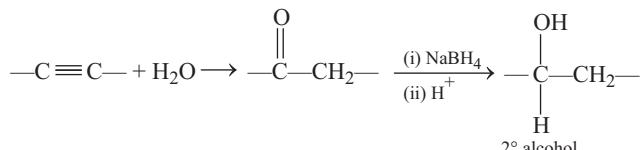
$\text{C}_6\text{H}_5\text{C}\equiv\text{CH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{H}_2\text{O}, \text{HgSO}_4} \text{C}_6\text{H}_5\text{COCH}_3$ 
  
 $\text{C}_6\text{H}_5\text{COCH}_3 + \text{C}_2\text{H}_5\text{MgBr}, \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}^+/\text{D}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CHCH}_3$

## Passage 2

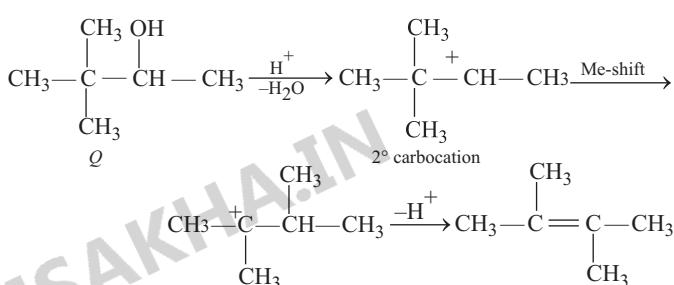
The final ozonolysis product indicates that the alkene before ozonolysis is



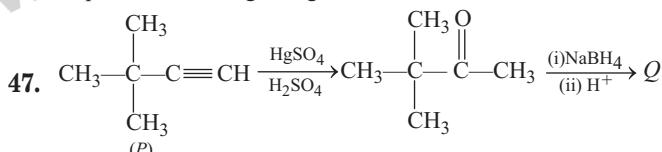
Also  $P(C_6H_{10})$  has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with  $NaBH_4$  gives a  $2^\circ$  alcohol.



The secondary alcohol that can give above shown alkene on acid catalysed dehydration is



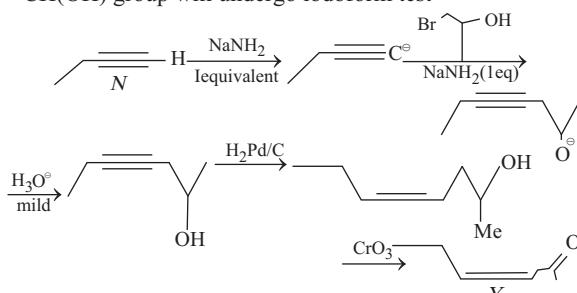
46. Explained in the beginning.



### Passage 3

- 48. PLAN** This problem can be solved by using the concept of iodoform test and functional isomerism.

**Iodoform test** The compound containing  $\text{—COCH}_3$  or  $\text{—CH(OH)}$  group will undergo iodoform test.

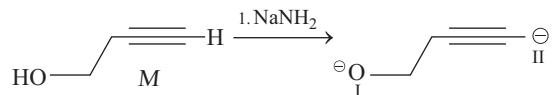


- Thus, X and Y are functional isomers of each other and Y gives iodoform test due to the presence of  $\text{CH}_3\text{CO}$  group as Indicated. Hence, correct choice is (c).

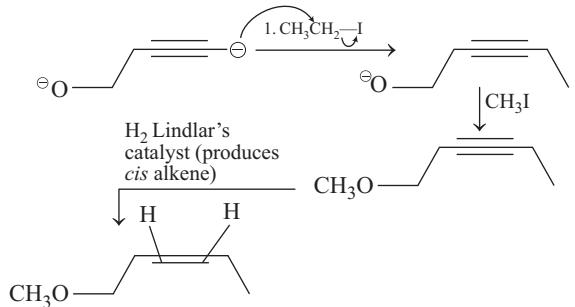
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**49. PLAN** This problem can be solved by using the concept of nucleophilic substitution reaction, oxidation reaction and reduction reaction including strength of nucleophile and regioselectivity.

Reaction of Scheme 1 can be completed as

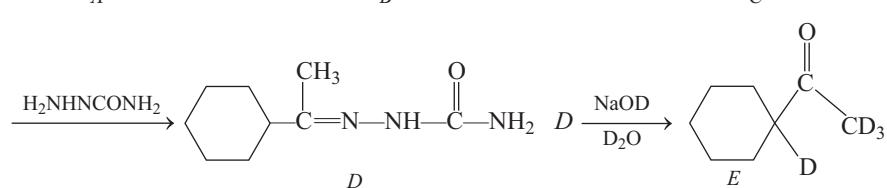
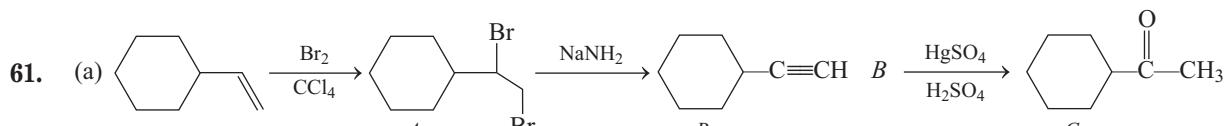
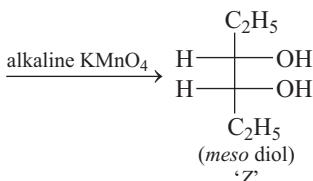
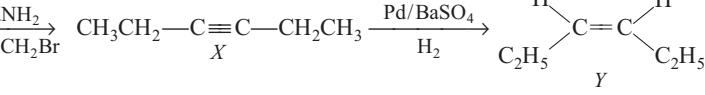
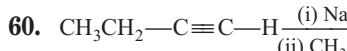
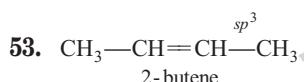
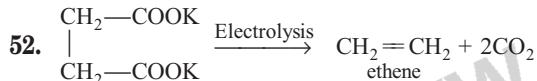
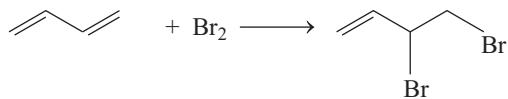


Among two naked nucleophilic group I and II, II is more nucleophilic and then will react selectively as follows

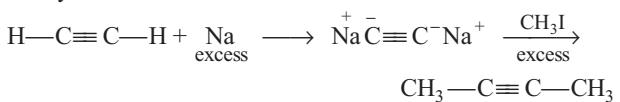


Hence, using the concept of regioselectivity we come on the conclusion that final product is correctly represented by structure (a).

**50. 3, 4-dibromo-1-butene :**

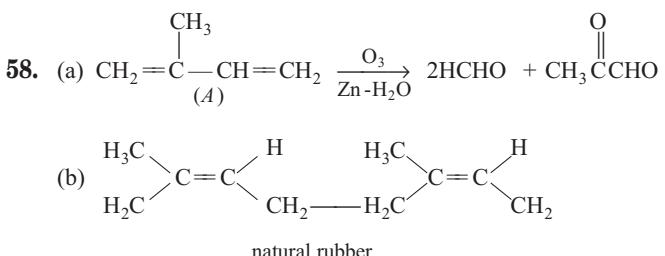
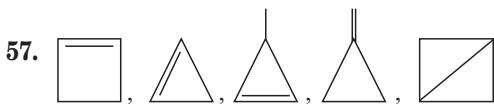


**54. 2-butyne :**

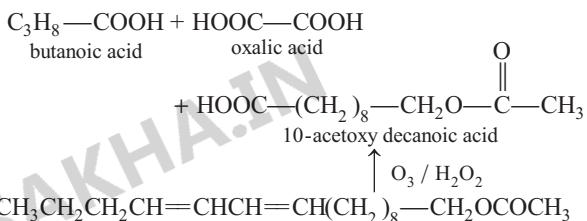


**55.** Terminal alkyne (ethyne) is most acidic among these.

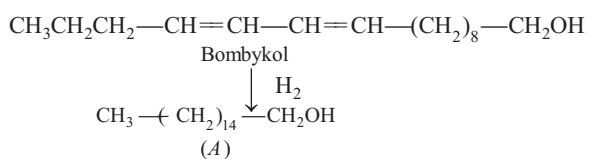
**56.** Sulphuric acid undergo addition to alkene.

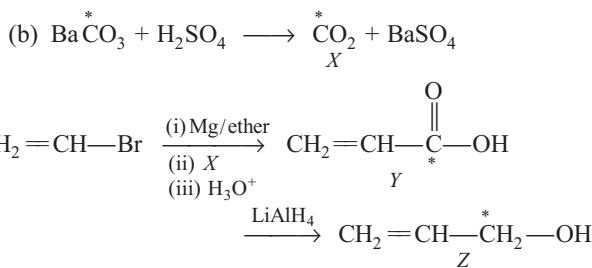


**59.** From oxidation products, structure of starting compound can be deduced as :

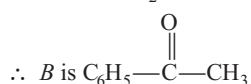


Therefore, Bombykol is :

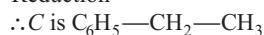




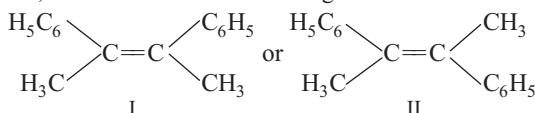
**62.**  $B + \text{NaOH} + \text{I}_2 \longrightarrow \text{C}_6\text{H}_5-\text{COONa}$  (Iodoform reaction)



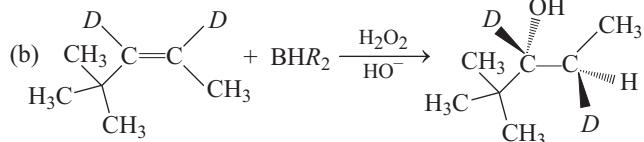
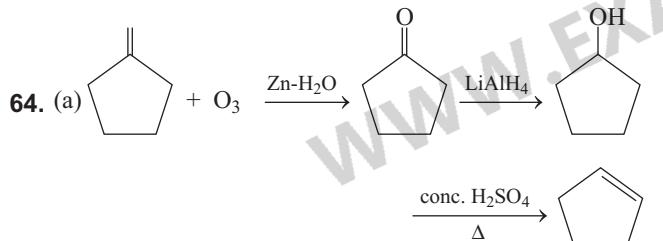
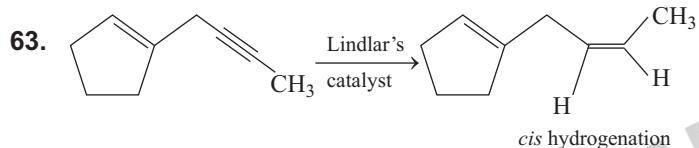
### Reduction”



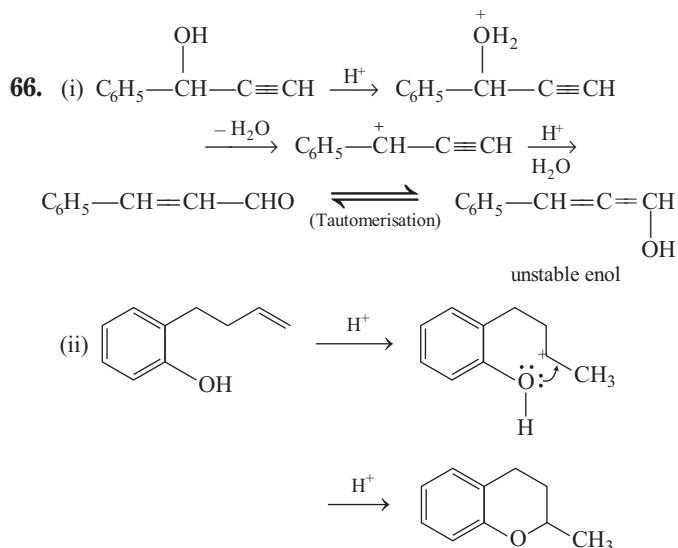
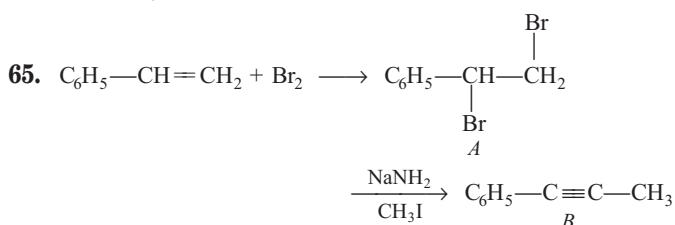
Hence,  $A$  can be one of the following :



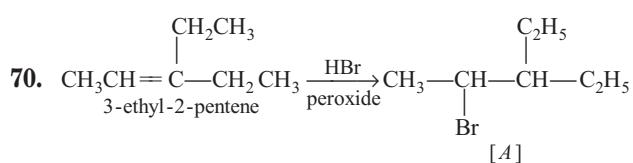
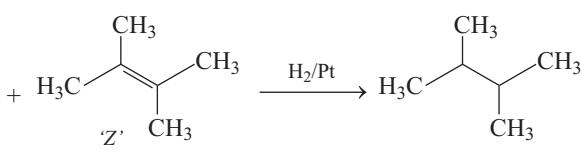
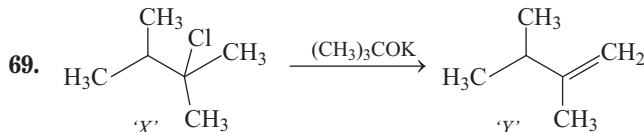
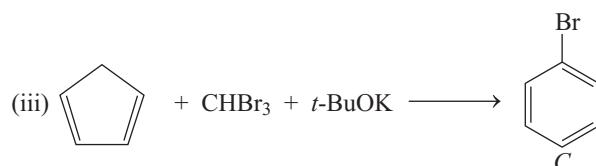
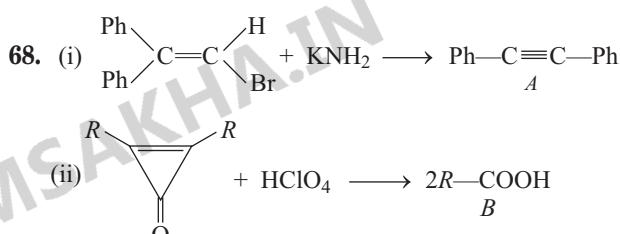
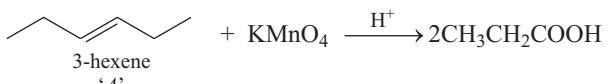
I on catalytic hydrogenation, would give meso compound while II on catalytic hydrogenation, would produce racemic mixtures.



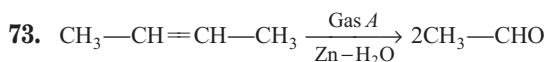
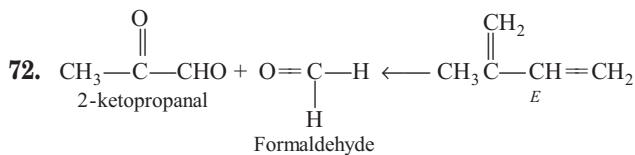
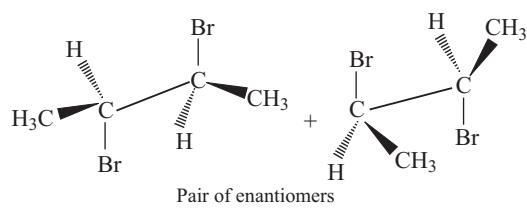
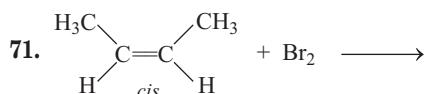
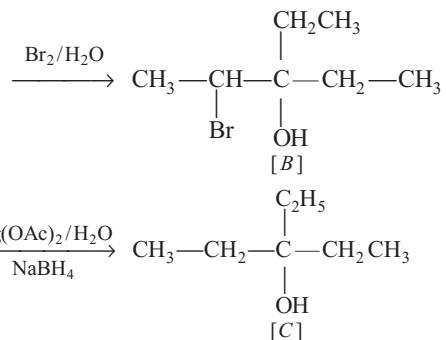
$$R = (\text{CH}_3)_2\text{CHCH}_2$$



**67.** Oxidation product indicates that alkene is symmetrical :



## 348 Hydrocarbons

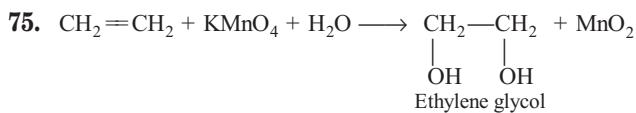
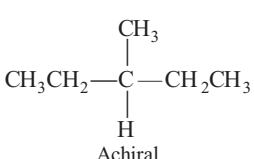
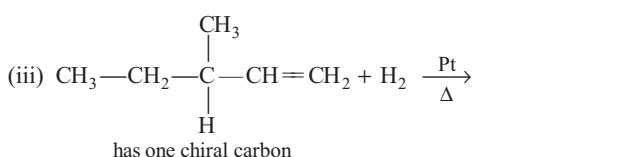
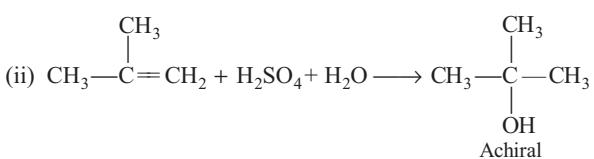
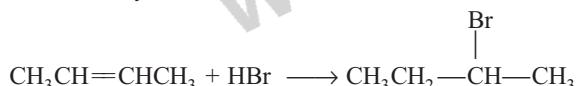


∴ Gas A is ozone ( $\text{O}_3$ )

Also; Gas A + KOH (dry)  $\longrightarrow$   $\begin{array}{c} \text{B} \\ \text{deep red coloured} \end{array} + \text{Gas C}$

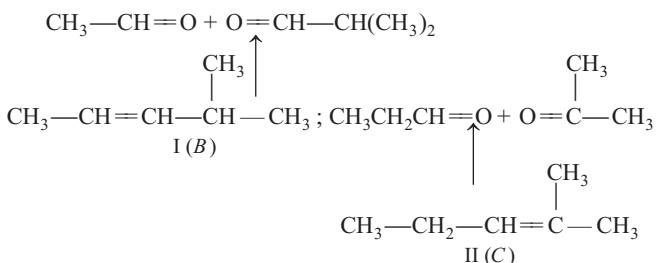
∴  $4\text{O}_3 + 4\text{KOH} \xrightarrow[\text{B}]{\text{C}} 4\text{KO}_3 + 2\text{H}_2\text{O} + \text{O}_2$

74. (i) A must be a symmetrical alkene :

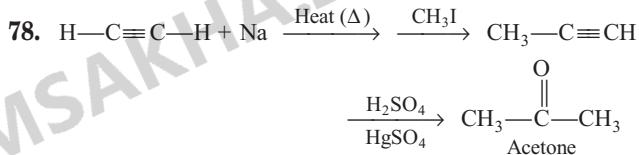
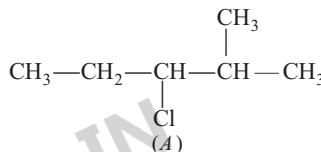


76. Baeyer's reagent (cold, dilute, alkaline permanganate) can be used to distinguish between alkanes and alkenes. Alkenes decolourises purple colour of Baeyer's reagent while alkanes do not.

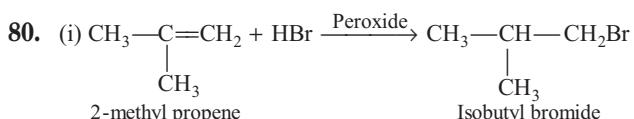
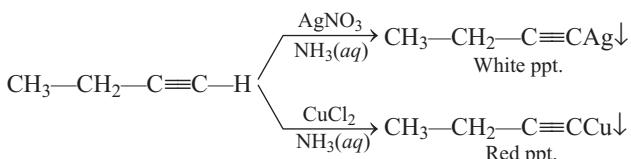
77. The alkenes are :



Since, both alkenes I and II are obtained by  $\beta$ -elimination of same halides, the halides must be :

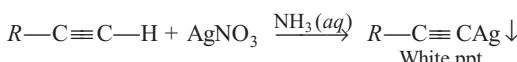


79. 1-butyne (terminal) can be distinguished from 2-butyne (internal) by either Tollen's test or through Fehling's test.



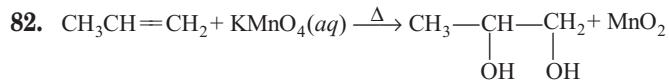
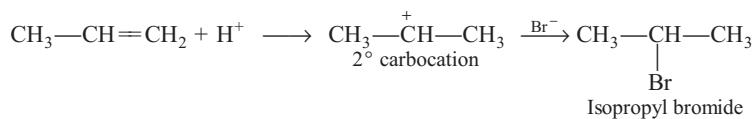
In the absence of peroxide, HBr would be added giving tertiary butyl bromide.

(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate :

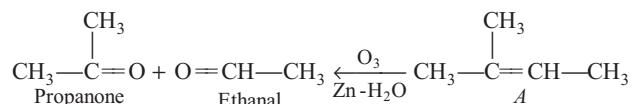


81. (i) Free radical chlorination of alkane require energy which is supplied either in the form of heat or radiation.

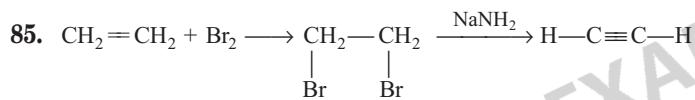
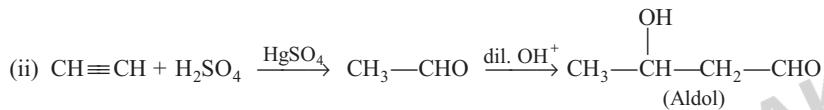
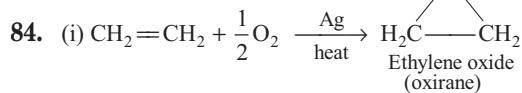
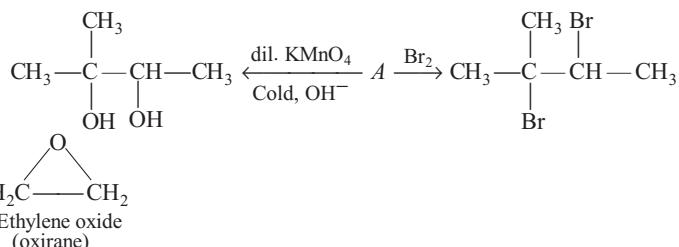
(ii) Addition of HBr proceeds through carbocation intermediates.



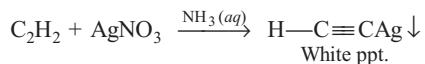
83. Ozonolysis products are the key of identification :



Other products are:



86. Acetylene can be distinguished from methane using Tollen's reagent :



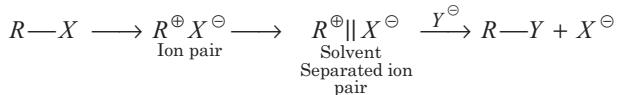
No such reaction occur with methane.

# 23

## Alkyl Halides

1. The mechanism of  $S_N1$  reaction is given as :

(2020 Main, 3 Sep I)



A student writes general characteristics based on the given mechanism as :

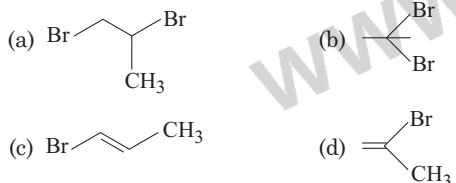
- (A) The reaction is favoured by weak nucleophiles.
- (B)  $R^{\oplus}$  would be easily formed if the substituents are bulky.
- (C) The reaction is accompanied by recemisation.
- (D) The reaction is favoured by non-polar solvents.

Which observations are correct?

- |                      |                 |
|----------------------|-----------------|
| (a) (A) and (B)      | (b) (A) and (C) |
| (c) (A), (B) and (C) | (d) (B) and (D) |

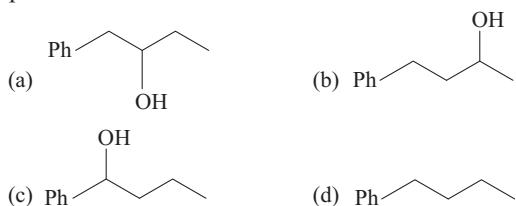
2. 1-methyl ethylene oxide when treated with an excess of HBr produces :

(2020 Main, 7 Jan I)



3. Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives  $X$  as the major product. Reaction of  $X$  with  $Hg(OAc)_2 / H_2O$  followed by  $NaBH_4$  gives  $Y$  as the major product.  $Y$  is

(2019 Main, 12 April II)



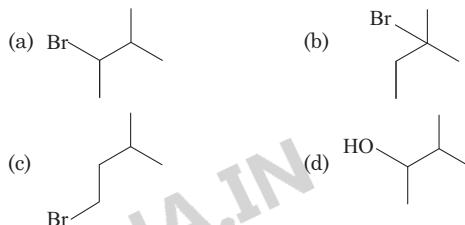
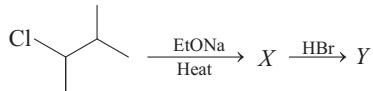
4. Which one of the following is likely to give a precipitate with  $AgNO_3$  solution?

(2019 Main, 12 April II)

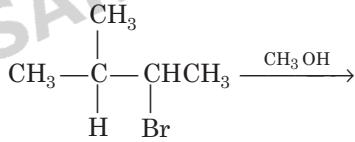
- |                  |                   |
|------------------|-------------------|
| (a) $CH_2=CH-Cl$ | (b) $CCl_4$       |
| (c) $CHCl_3$     | (d) $(CH_3)_3CCl$ |

4. The major product  $Y$  in the following reaction is

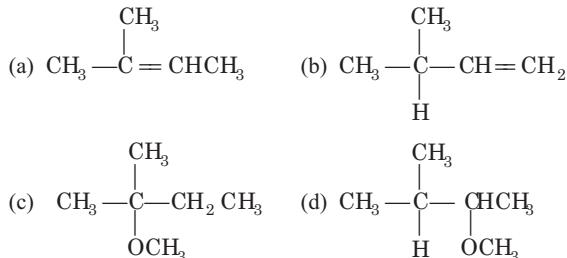
(2019 Main, 10 April II)



6. The major product of the following reaction is

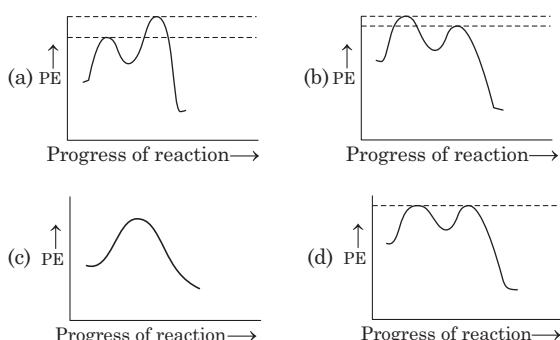


(2019 Main, 10 April I)

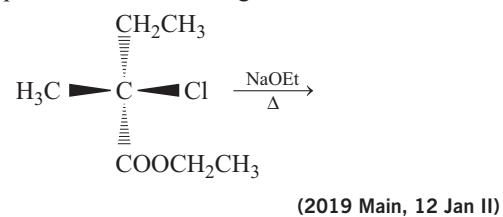


7. Which of the following potential energy (PE) diagrams represents the  $S_N1$  reaction?

(2019 Main, 9 April II)

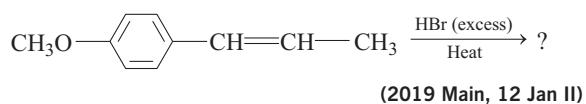


8. The major product of the following reaction is



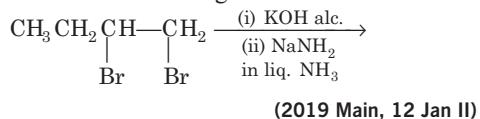
- (a)  $\text{CH}_3\text{CH}_2\text{C}=\text{CH}_2$
- (b)  $\text{CO}_2\text{CH}_2\text{CH}_3$
- (c)  $\text{CH}_3\text{C}=\text{CHCH}_3$
- (d)  $\text{H}_3\text{CH}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_3$

9. The major product in the following conversion is



- (a)  $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}-\text{CH}_2-\text{CH}_3$
- (b)  $\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}-\text{CH}_3$
- (c)  $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}-\text{CH}_3$
- (d)  $\text{HO}-\text{C}_6\text{H}_4-\text{CH}-\text{CH}_2-\text{CH}_3$

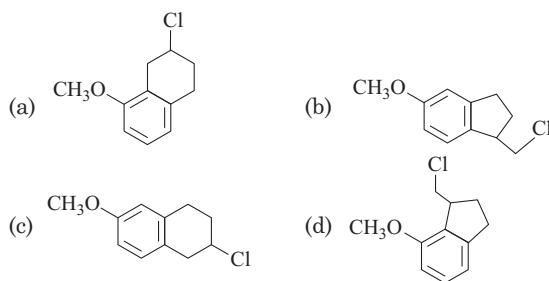
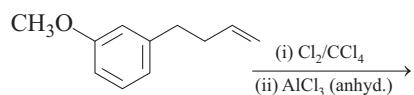
10. The major product of the following reaction is



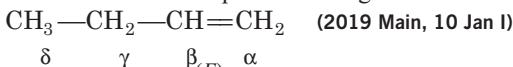
- (a)  $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)-\text{CH}_2$
- (b)  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{NH}_2$
- (c)  $\text{CH}_3\text{CH}=\text{C}=\text{CH}_2$
- (d)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

11. The major product of the following reaction is

**(2019 Main, 12 Jan I)**

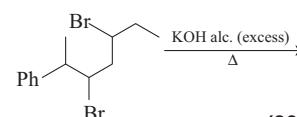


12. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?



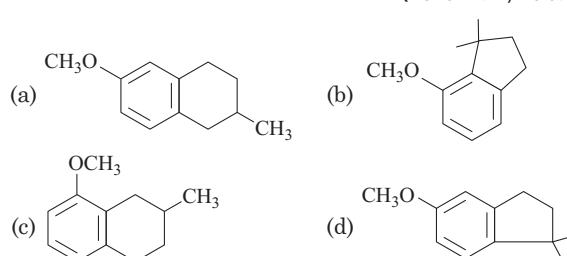
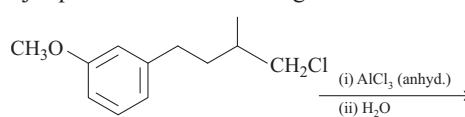
- |                       |                        |                        |                        |
|-----------------------|------------------------|------------------------|------------------------|
| $\delta$              | $\gamma$               | $\beta_{(E)}$          | $\alpha$               |
| (a) $\beta$ -hydrogen | (b) $\delta$ -hydrogen | (c) $\gamma$ -hydrogen | (d) $\alpha$ -hydrogen |

13. The major product of the following reaction is

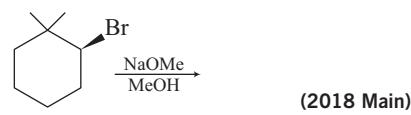


- (a)  $\text{Ph}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2$
- (b)  $\text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$
- (c)  $\text{Ph}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2$
- (d)  $\text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$

14. The major product of the following reaction is



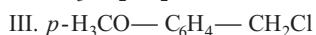
15. The major product of the following reaction is



- (a)  $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{OMe}$
- (b)  $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-\text{CH}_2=\text{CH}_2$
- (c)  $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-\text{CH}=\text{CH}_2$
- (d)  $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}(\text{OMe})_2$

## 352 Alkyl Halides

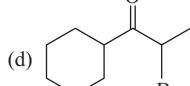
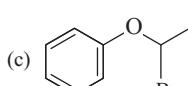
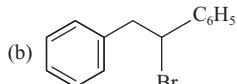
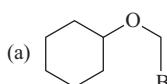
16. The increasing order of reactivity of the following halides for the  $S_N1$  reaction is (2017 Main)



(a) (III) < (II) < (I)      (b) (II) < (I) < (III)

(c) (I) < (III) < (II)      (d) (II) < (III) < (I)

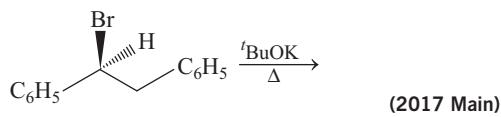
17. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolorise the colour of bromine? (2017 Main)



18. 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is (2017 Main)

(a) six      (b) zero      (c) two      (d) four

19. The major product obtained in the following reaction is



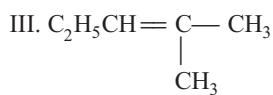
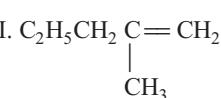
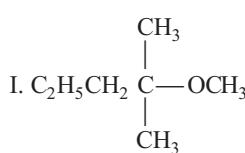
(a)  $(\pm)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$

(b)  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$

(c)  $(+)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$

(d)  $(-)\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$

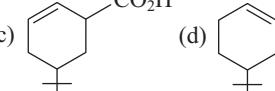
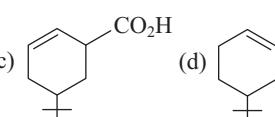
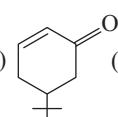
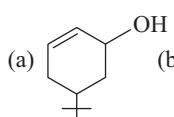
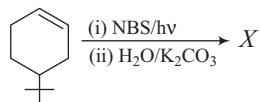
20. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields (2016 Main)



(a) Both I and III

(b) Only III  
(c) Both I and II  
(d) All of these

21. The product of the reaction given below is (2015 Adv.)



22. The synthesis of alkyl fluorides is best accomplished by (2015 Main)

(a) free radical fluorination

(b) Sandmeyer's reaction

(c) Finkelstein reaction

(d) Swarts reaction

23. In  $S_N2$  reactions, the correct order of reactivity for the following compounds  $\text{CH}_3\text{Cl}, \text{CH}_3\text{CH}_2\text{Cl}, (\text{CH}_3)_2\text{CHCl}$  and  $(\text{CH}_3)_3\text{CCl}$  is (2014 Main)

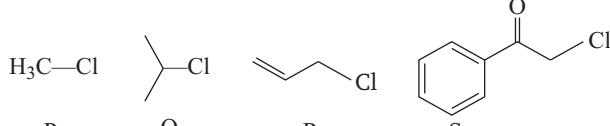
(a)  $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$

(b)  $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

(c)  $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

(d)  $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$

24.  $\text{KI}$  in acetone, undergoes  $S_N2$  reaction with each  $P, Q, R$  and  $S$ . The rates of the reaction vary as (2013 Adv.)



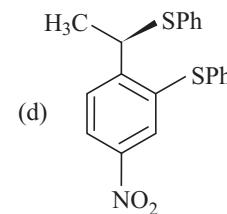
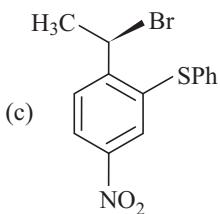
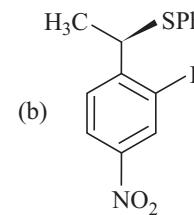
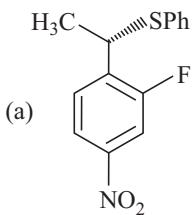
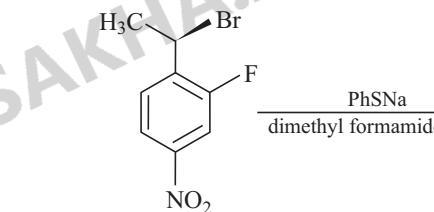
(a)  $P > Q > R > S$

(b)  $S > P > R > Q$

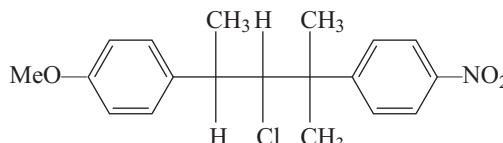
(c)  $P > R > Q > S$

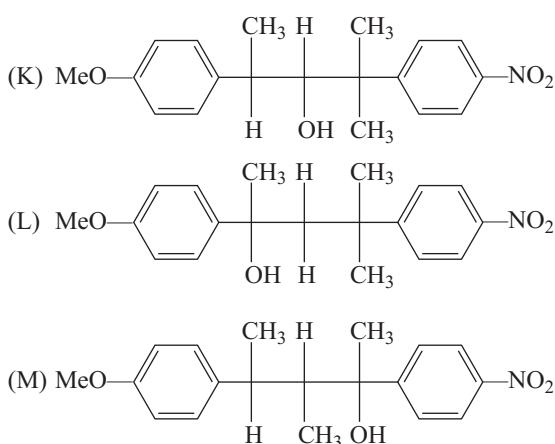
(d)  $R > P > S > Q$

25. The major product of the following reaction is (2008, 3M)



26. The following compound on hydrolysis in aqueous acetone will give (2005, 1M)

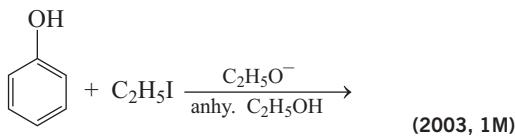




It mainly gives

- (a) K and L    (b) only K    (c) L and M    (d) only M

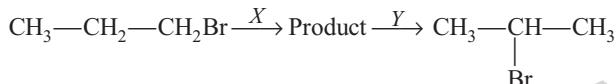
27. The product of following reaction is



- (a)  $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$     (b)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$   
 (c)  $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$     (d)  $\text{C}_6\text{H}_5\text{I}$

28. Identify the set of reagents/reaction conditions  $X$  and  $Y$  in the following set of transformations—

(2002, 3M)



- (a)  $X = \text{dilute aqueous NaOH}, 20^\circ\text{C}$ ,  $Y = \text{HBr}/\text{acetic acid}, 20^\circ\text{C}$   
 (b)  $X = \text{concentrated alcoholic NaOH}, 80^\circ\text{C}$ ,  
        $Y = \text{HBr}/\text{acetic acid}, 20^\circ\text{C}$   
 (c)  $X = \text{dilute aqueous NaOH}, 20^\circ\text{C}$ ,  $Y = \text{Br}_2/\text{CHCl}_3, 0^\circ\text{C}$   
 (d)  $X = \text{concentrated aqueous NaOH}, 80^\circ\text{C}$ ,  
        $Y = \text{Br}_2/\text{CHCl}_3, 0^\circ\text{C}$

29. The compound that will react most readily with NaOH to form methanol is

(2001, 1M)

- (a)  $(\text{CH}_3)_4\text{N}^+\text{I}^-$     (b)  $\text{CH}_3\text{OCH}_3$   
 (c)  $(\text{CH}_3)_3\text{S}^+\text{I}^-$     (d)  $(\text{CH}_3)_3\text{Cl}$

30. An  $S_N2$  reaction at an asymmetric carbon of a compound always gives

(2001)

- (a) an enantiomer of the substrate  
 (b) a product with opposite optical rotation  
 (c) a mixture of diastereomers  
 (d) a single stereoisomer

31. The order of reactivities of the following alkyl halides for a  $S_N2$  reaction is—

(2000, 1M)

- (a)  $\text{RF} > \text{RCI} > \text{RBr} > \text{RI}$     (b)  $\text{RF} > \text{RBr} > \text{RCI} > \text{RI}$   
 (c)  $\text{RCI} > \text{RBr} > \text{RF} > \text{RI}$     (d)  $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$

32. Which of the following has the highest nucleophilicity?

(2000)

- (a)  $\text{F}^-$     (b)  $\text{OH}^-$   
 (c)  $\text{CH}_3^-$     (d)  $\text{NH}_2^-$

33. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of  $\text{SbCl}_5$ , due to the formation of

(1999)

- (a) carbanion    (b) carbene  
 (c) free-radical    (d) carbocation

34. Which of the following is an organometallic compound?

(1997)

- (a) Lithium methoxide  
 (b) Lithium acetate  
 (c) Lithium dimethylamide  
 (d) Methyl lithium

35.  $(\text{CH}_3)_3\text{CMgCl}$  on treatment with  $\text{D}_2\text{O}$  produces

(1997, 1M)

- (a)  $(\text{CH}_3)_3\text{CD}$     (b)  $(\text{CH}_3)_3\text{COD}$   
 (c)  $(\text{CD})_3\text{CD}$     (d)  $(\text{CD})_3\text{COD}$

36. 1-chlorobutane on reaction with alcoholic potash gives

(1991, 1M)

- (a) 1-butene    (b) 1-butanol  
 (c) 2-butene    (d) 2-butanol

37. *n*-propyl bromide on treatment with ethanolic potassium hydroxide produces

(1987, 1M)

- (a) propane    (b) propene  
 (c) propyne    (d) propanol

38. The reaction condition leading to the best yield of  $\text{C}_2\text{H}_5\text{Cl}$  are

(1986, 1M)

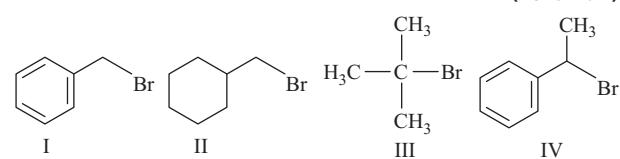
- (a)  $\text{C}_2\text{H}_6(\text{excess}) + \text{Cl}_2 \xrightarrow{\text{UV light}}$   
 (b)  $\text{C}_2\text{H}_6 + \text{Cl}_2(\text{excess}) \xrightarrow[\text{room temp.}]{\text{dark}}$   
 (c)  $\text{C}_2\text{H}_6 + \text{Cl}_2(\text{excess}) \xrightarrow{\text{UV light}}$   
 (d)  $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$

## Objective Questions II

(One or more than one correct option)

39. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are)

(2017 Adv.)



- (a) Compound IV undergoes inversion of configuration  
 (b) The order of reactivity for I, III and IV is : IV > I > III  
 (c) I and III follow  $S_N1$  mechanism  
 (d) I and II follow  $S_N1$  mechanism

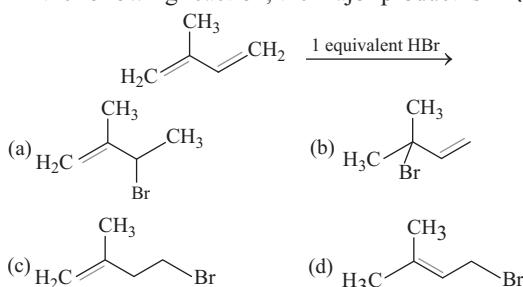
40. Compound(s) that on hydrogenation produce(s) optically inactive compound (s) is/are

(2015 Adv.)

- (a)
- (b)
- (c)
- (d)

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41. In the following reaction, the major product is (2015 Adv.)



42. The compounds used as refrigerant are (1990, 1M)

- (a)  $\text{NH}_3$  (b)  $\text{CCl}_4$  (c)  $\text{CF}_4$  (d)  $\text{CF}_2\text{Cl}_2$   
(e)  $\text{CH}_2\text{F}_2$

### Assertion and Reason

43. An **Assertion** and a **Reason** are given below. Choose the correct answer from the following options.

**Assertion (A)** Vinyl halides do not undergo nucleophilic substitution easily.

**Reason (R)** Even though the intermediate carbocation is stabilised by loosely held  $\pi$ -electrons, the cleavage is difficult because of strong bonding. (2019 Main, 12 April II)

- (a) Both (A) and (R) are wrong statements.  
(b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).  
(c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).  
(d) (A) is a correct statement but (R) is a wrong statement.

### Match the Columns

44. List-I contains reactions and List-II contains major products.

|    | List-I | List-II |
|----|--------|---------|
| P. |        | 1.      |
| Q. |        | 2.      |
| R. |        | 3.      |
| S. |        | 4.      |
|    |        | 5.      |

Match each reaction in List-I with one or more products in List-II and choose the correct option. (2018 Adv.)

- (a) P  $\rightarrow$  1, 5; Q  $\rightarrow$  2; R  $\rightarrow$  3; S  $\rightarrow$  4  
(b) P  $\rightarrow$  1, 4; Q  $\rightarrow$  2; R  $\rightarrow$  4; S  $\rightarrow$  3  
(c) P  $\rightarrow$  1, 4; Q  $\rightarrow$  1, 2; R  $\rightarrow$  3, 4; S  $\rightarrow$  4  
(d) P  $\rightarrow$  4, 5; Q  $\rightarrow$  4; R  $\rightarrow$  4; S  $\rightarrow$  3, 4

45. Match the chemical conversion in Column I with the appropriate reagents in Column II and select the correct answer using the code given below the lists. (2013 Adv.)

|    | Column I | Column II                                                         |
|----|----------|-------------------------------------------------------------------|
| P. |          | 1. (i) $\text{Hg}(\text{OAc})_2$ ;<br>(ii) $\text{NaBH}_4$        |
| Q. |          | 2. $\text{NaOEt}$                                                 |
| R. |          | 3. $\text{Et-Br}$                                                 |
| S. |          | 4. (i) $\text{BH}_3$ ;<br>(ii) $\text{H}_2\text{O}_2/\text{NaOH}$ |

### Codes

|     | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 2 | 3 | 1 | 4 |
| (b) | 3 | 2 | 1 | 4 |
| (c) | 2 | 3 | 4 | 1 |
| (d) | 3 | 2 | 4 | 1 |

46. Match the following : (2006, 3M)

|    | Column I                                                                                                                                                                                 | Column II               |
|----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|
| A. | $\text{CH}_3-\text{CHBr}-\text{CD}_3$ on treatment with alc. KOH gives $\text{CH}_2=\text{CH}-\text{CD}_3$ as a major product.                                                           | p. E1 reaction          |
| B. | Ph-CHBr-CH <sub>3</sub> reacts faster than Ph-CHBr-CD <sub>3</sub>                                                                                                                       | q. E2 reaction          |
| C. | Ph-CH <sub>2</sub> -CH <sub>2</sub> Br on treatment with C <sub>2</sub> H <sub>5</sub> OD/C <sub>2</sub> H <sub>5</sub> O <sup>-</sup> gives Ph-CD=CH <sub>2</sub> as the major product. | r. E1CB reaction        |
| D. | PhCH <sub>2</sub> CH <sub>2</sub> Br and PhCD <sub>2</sub> CH <sub>2</sub> Br react with same rate.                                                                                      | s. First order reaction |

### Fill in the Blanks

47. Vinyl chloride on reaction with the dimethyl copper gives ..... (1997)  
48. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ..... (1983, 1M)  
49. The halogen which is most reactive in the halogenation of alkanes under sunlight is ... (1981, 1M)

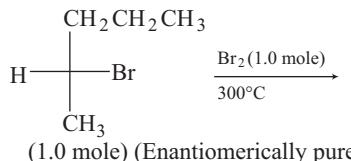
### True/False

50. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1. (1993, 1M)

51. During S<sub>N</sub>1 reactions, the leaving group leaves the molecule before the incoming group is attached to the molecule. (1990, 2M)
52. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule. (1989, 2M)
53. Iodide is better nucleophile than bromide. (1985)
54. Carbon tetrachloride is inflammable. (1985, 1/2M)
55. Carbon tetrachloride burns in air when lighted to give phosgene. (1983, 1M)

### Integer Answer Type Questions

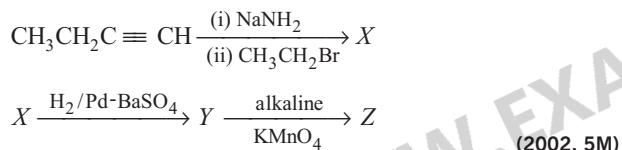
56. In the following monobromination reaction, the number of possible chiral product(s) is (are)... (2014)



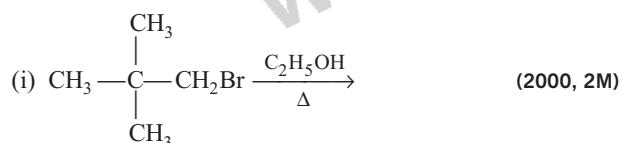
57. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is (2011)

### Subjective Questions

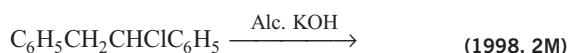
58. Identify X, Y and Z in the following synthetic scheme and write their structures



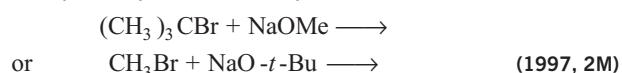
59. What would be the major product in each of the following reactions?



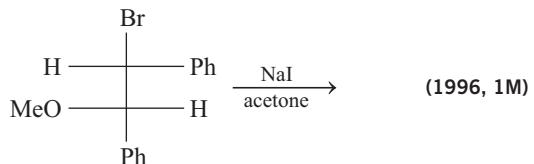
60. Write the structures of the products :



61. Which of the following is the correct method for synthesising methyl-*t*-butyl ether and why?

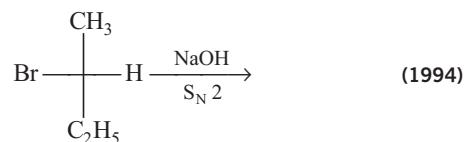


62. Predict the structure of the product in the following reaction



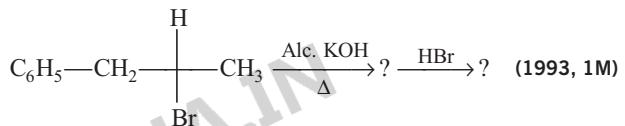
63. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. (1995, 2M)

64. Draw the stereochemical structure of product in the following reaction

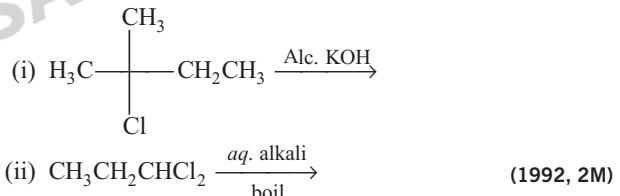


65. Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. (1994, 2M)

66. Identify the major product in the following reaction.



67. Write the structures of the major organic product expected from each of the following reactions :



68. Arrange the following in order of their

- (i) Increasing basicity  
 $\text{H}_2\text{O}, \text{OH}^-, \text{CH}_3\text{OH}, \text{CH}_3\text{O}^-$   
(ii) Increasing reactivity in nucleophilic substitution reactions  
 $\text{CH}_3\text{F}, \text{CH}_3\text{I}, \text{CH}_3\text{Br}, \text{CH}_3\text{Cl}$  (1992, 2M)

69. Chloroform is stored in dark coloured bottles. Explain in not more than two sentences. (1980, 1M)

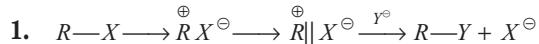
70. Show by chemical equations only, how would you prepare the following from the indicated starting materials? Specify the reagents in each step of the synthesis. (1979, 2M)

- (i) Chloroform from carbon disulphide.  
(ii) Hexachloroethane ( $\text{C}_2\text{Cl}_6$ ) from calcium carbide.

## Answers

- |         |         |         |         |               |                                         |               |                                         |
|---------|---------|---------|---------|---------------|-----------------------------------------|---------------|-----------------------------------------|
| 1. (c)  | 2. (a)  | 3. (c)  | 4. (d)  | 33. (d)       | 34. (d)                                 | 35. (a)       | 36. (a)                                 |
| 5. (b)  | 6. (c)  | 7. (b)  | 8. (b)  | 37. (b)       | 38. (a)                                 | 39. (a, d)    | 40. (b,d)                               |
| 9. (d)  | 10. (d) | 11. (c) | 12. (c) | 41. (d)       | 42. (a,d)                               | 43. (c)       | 44. (b)                                 |
| 13. (d) | 14. (d) | 15. (b) | 16. (b) | 45. (a)       | 46. A → q, B → q, C → r, D → p, s       | 47. (propene) | 48. (ethyne) 49. (chlorine) 50. (False) |
| 17. (a) | 18. (d) | 19. (b) | 20. (d) | 47. (propene) | 48. (ethyne) 49. (chlorine) 50. (False) | 51. (True)    | 52. (True) 53. (True) 54. (False)       |
| 21. (a) | 22. (d) | 23. (b) | 24. (b) | 51. (True)    | 52. (True) 53. (True) 54. (False)       | 55. (False)   | 56. (5) 57. (5)                         |
| 25. (a) | 26. (a) | 27. (a) | 28. (b) | 55. (False)   | 56. (5) 57. (5)                         |               |                                         |
| 29. (a) | 30. (d) | 31. (d) | 32. (c) |               |                                         |               |                                         |

## Hints & Solutions



It indicates  $R^{\oplus}$  (carbocation) formation takes place and  $R^{\oplus}$  got stabilised by electronic factors and polar solvent molecules because solvent separation of  $R^{\oplus}$  is possible.

So, statement (D) is not correct.

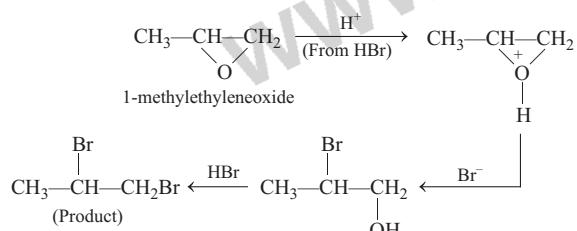
Here,  $X^{\ominus}$  (leaving group) of  $R-X$  is substituted by  $Y^{\ominus}$ , (nucleophile) via the formation of carbocation ( $R^{\oplus}$ ) intermediate. So, it is an  $S_N1$  reaction.

$S_N1$  mechanism supports weaker nucleophiles. So, statement (A) is correct.

$S_N1$  reaction is accompanied by inversion and retention in configuration, i.e. racemisation provided 'R' of  $R-X$  is chiral. So, statement (C) is correct.

Attachment of bulkier substituents or  $3^{\circ}$ -nature of the carbon atom of  $C-X$  bond of  $R-X$  will favour formation of  $R^{\oplus}$  (carbocation). So, statement (D) is also correct.

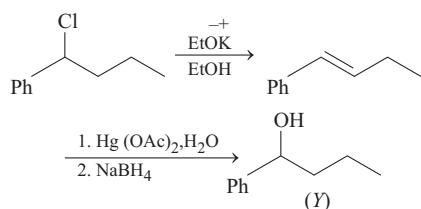
2. The given reaction is completed as follows :



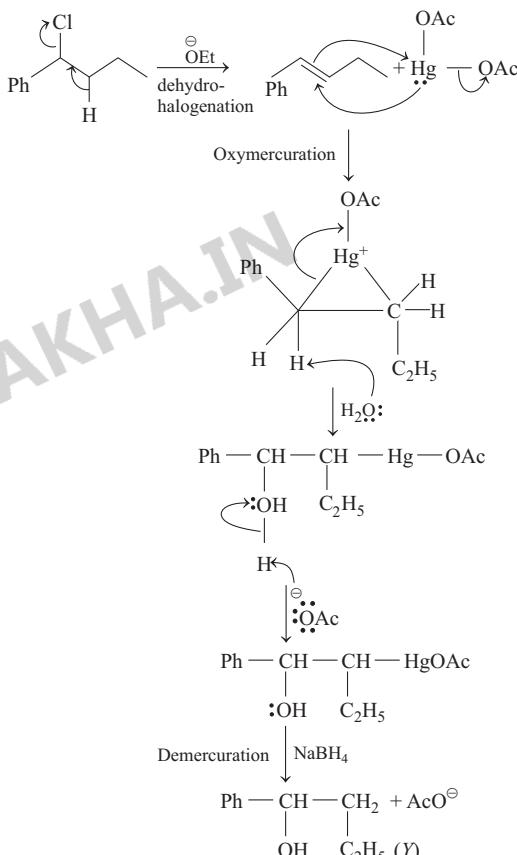
3. Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives 1-phenyl but-1-ene( $X$ ).

Reaction of  $X$  with  $\text{Hg(OAc)}_2 / \text{H}_2\text{O}$  followed by  $\text{NaBH}_4$  gives 1-phenyl butan-1-ol ( $Y$ ).

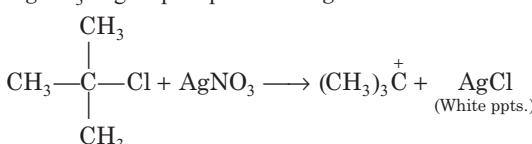
Reaction involved is as follows:



### Mechanism



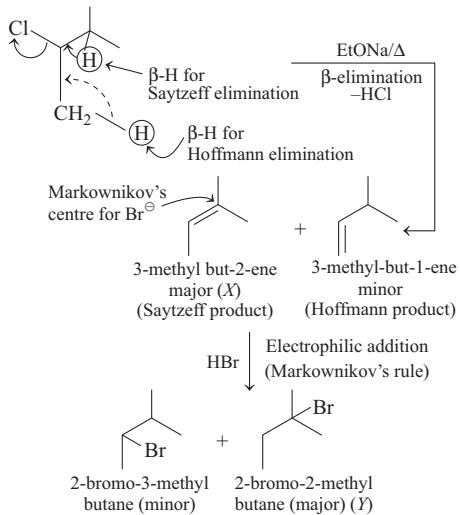
4.  $(\text{CH}_3)_3\text{CCl}$  gives a precipitate with  $\text{AgNO}_3$  solution because it forms stable carbocation. (i.e. tertiary) that readily combines with  $\text{AgNO}_3$  to give precipitates of  $\text{AgCl}$ .



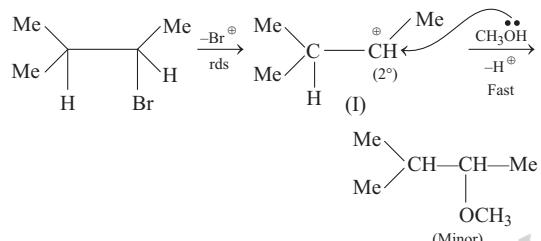
$\text{CH}_2=\text{CH}-\text{Cl}$  forms unstable carbocation.

Hence, it does not readily react with  $\text{AgNO}_3$ .

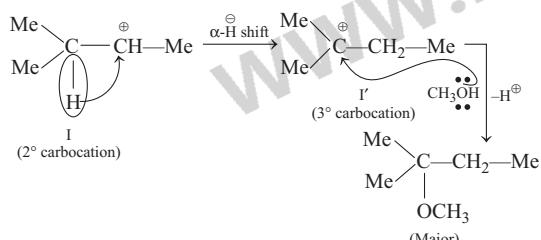
- 5.** The given reaction takes place as follows :



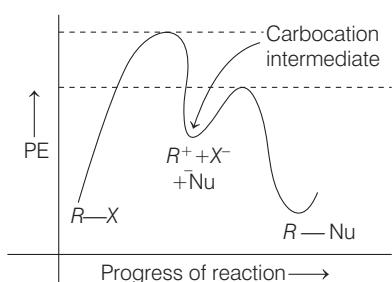
6. In the given question, the substrate is a 2°-halide (bromide) and the medium,  $\text{CH}_3\text{OH}$  (as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly  $\text{S}_{\text{N}}1$  pathways via the formation of a carbocation intermediate (I).



The intermediate, I, can be rearranged into the more stable form I' ( $3^\circ$ ) by  $\alpha$ -hydride shift. I' will give the major product.



7. The potential energy (PE) diagram for S<sub>N</sub>1 reaction is

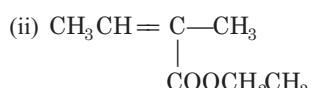
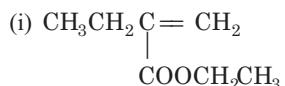


$S_N1$  reaction has two steps. In the first step, the carbon-halogen bond breaks heterolytically, with the halogen retaining the previously shared pair of electrons. In the second step, the

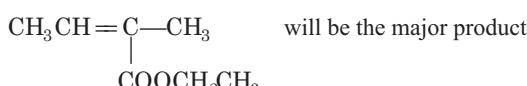
nucleophile reacts rapidly with the carbocation formed in the first step.

In the above graph, the alkyl halide is the only species that participates in the rate limiting step. Here, the rate of reaction depends on the concentration of the alkyl halide and does not depend on the concentration of nucleophile.

8. Presence of strong base ( $\text{EtO}^-$ ) and heat indicates elimination. Thus, the compound undergo dehydrohalogenation and alkene is produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:



In accordance with Saytzeff rule

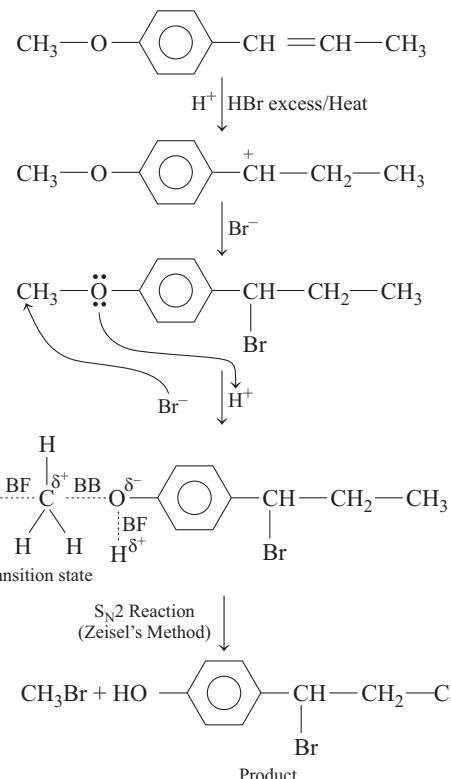


- 9.** **Key Idea** The excess of HBr and high temperature in given reaction serves for dual purpose:

- cation serves for dual purpose.

  - (i) Hydrolysis of ether via  $S_N2$  mechanism, i.e. Zeisel's method.
  - (ii) Markownikoff addition at double bond of the branch.

The road map of complete reaction is as follows:



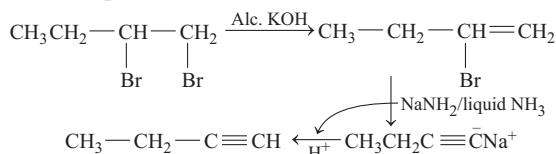
Here, BB = Bond breakage

BF = Bond formation

## 358 Alkyl Halides

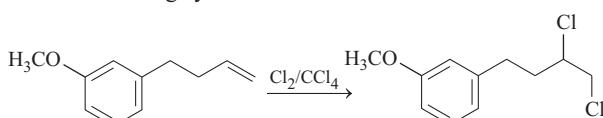
- 10. Key Idea** Both alc. KOH and  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  are dehydrohalogenating reagents. On comparative terms  $\text{NaNH}_2/\text{liquid NH}_3$  is stronger in action.

The reaction proceeds as :

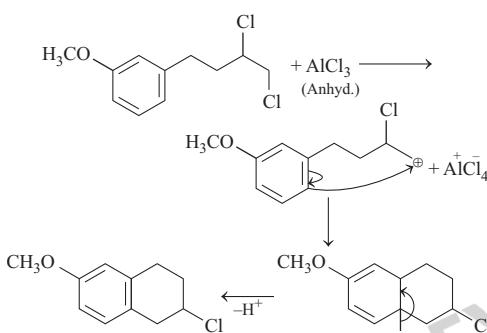


Thus, option (d) is the correct answer.

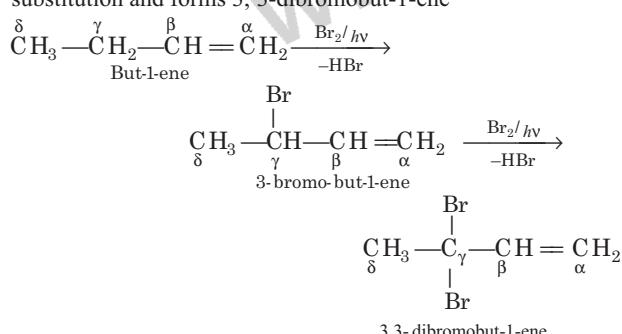
- 11.** The given reactant in presence of  $\text{Cl}_2/\text{CCl}_4$ , given *vicinal* dihalide. Chlorine adds up to alkene via electrophilic addition reaction involving cyclic chlorinium ion formation.



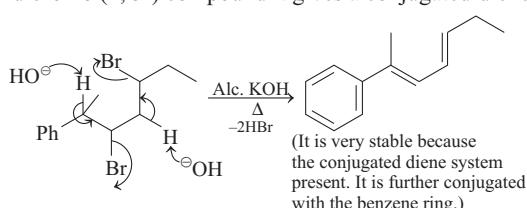
The vicinal dihalide in presence of anhyd.  $\text{AlCl}_3$  results in the formation of carbocation that rearranges itself to form a cyclic compound.



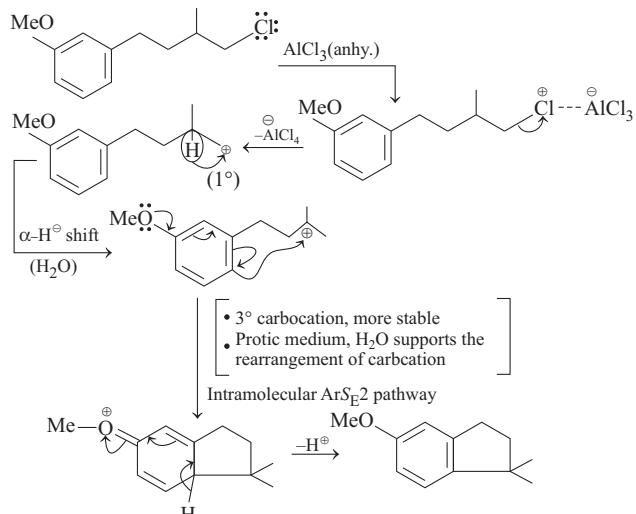
- 12.** The compound (*E*) has two allyl-hydrogen atoms ( $\gamma$ ). When *E* reacts with  $\text{Br}_2/h\nu$ , it readily undergoes allylic free radical substitution and forms 3, 3-dibromobut-1-ene



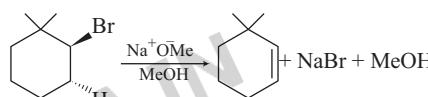
- 13.** The reaction follows  $\alpha, \beta$ -elimination mechanism to give a more substituted stable alkene as a major product. As the substrate is a  $\alpha, \gamma$ -dibromo (1, 3-) compound it gives a conjugated diene.



- 14.** In the given reaction,  $\text{AlCl}_3$  act as Lewis acid and helps in generation of carbocation. The resulting carbocation ( $1^\circ$ ) rearranges itself to stable carbocation ( $3^\circ$ ).

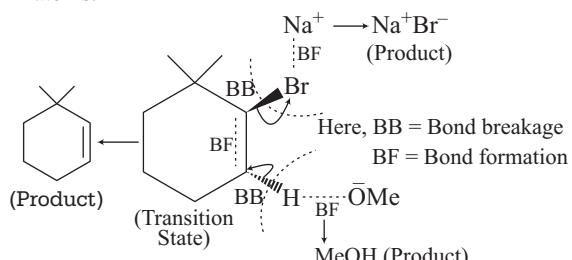


- 15.** Complete reaction can be represented as



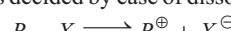
Thus, the given reaction is dehydrohalogenation which is a  $\beta$ -elimination proceeding through  $E_2$  mechanism.

**Mechanism** The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H atoms.



- 16.** (i) The rate of  $S_N1$  reaction depends only upon the concentration of the alkyl halide.

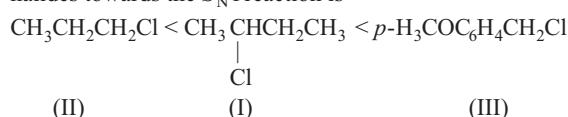
- (ii)  $S_N1$  reaction proceeds through the formation of carbocation. The reactivity is decided by ease of dissociation of alkyl halide.



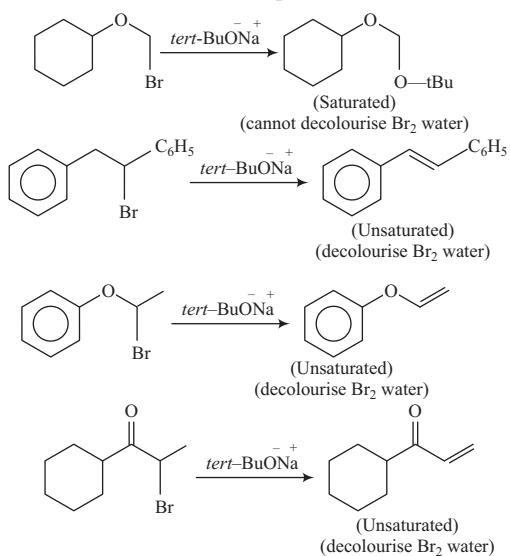
Higher the stability of  $R^{\oplus}$  (carbocation), higher would be the reactivity towards  $S_N1$  reaction.

$p\text{-H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CH}_2^{\oplus}$  is the most stable carbocation due to resonance and then  $\text{CH}_3\text{CHCH}_2\text{CH}_3$  ( $2^\circ$  carbocation) while  $\text{CH}_3\text{CH}_2\text{CH}_2(1^\circ)$  is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the  $S_N1$  reaction is

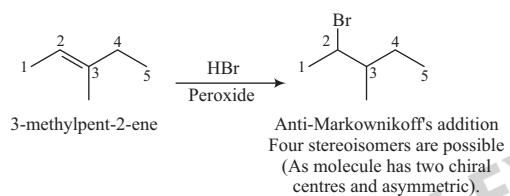


17. To show decolourisation, compound must be unsaturated.

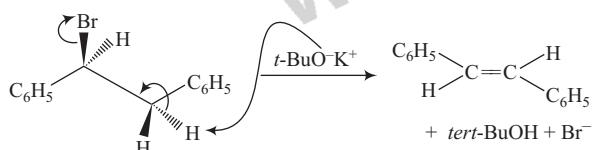


18. The number of stereoisomers in molecules which are not divisible into two equal halves and have  $n$  number of asymmetric C-atoms =  $2^n$ .

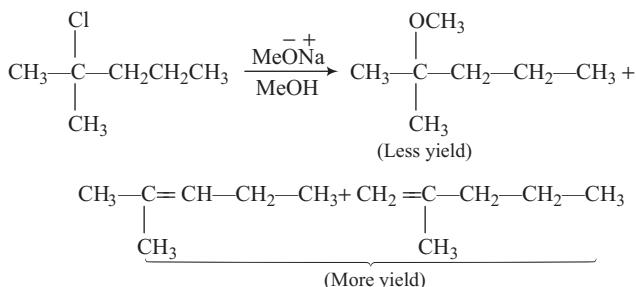
3-methylpent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e. 2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible



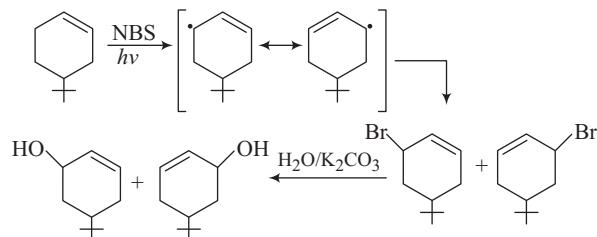
19. An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 ( $\beta$ -elimination reaction).



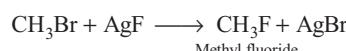
20. **Key Idea** Strong nucleophile ( $\bar{O}Me$ ) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



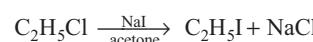
- 21.



22. Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.



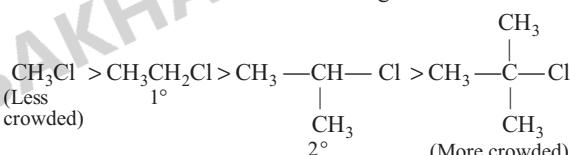
But, when action of NaI/acetone takes place on alkyl chloride or bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'



Free radical fluorination is highly explosive reaction, so not preferred for the preparation of fluoride.

23. Steric hindrance (crowding) is the basis of  $S_N2$  reaction, by using which we can arrange the reactant in correct order of their reactivity towards  $S_N2$  reaction.

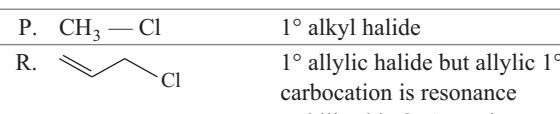
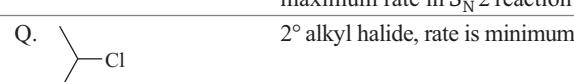
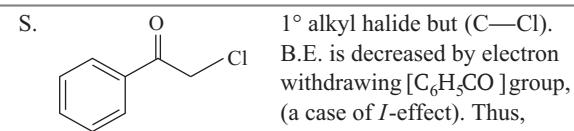
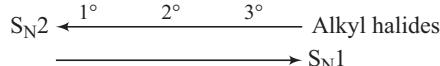
$$\text{Rate of } S_N2 \propto \frac{1}{\text{Steric crowding of 'C'}}$$



As steric hinderance (crowding) increases, rate of  $S_N2$  reaction decreases.

**Note** The order of reactivity towards  $S_N2$  reaction for alkyl halides is  
 Primary halides > Secondary halides > Tertiary halides  
 (1°) (2°) (3°)

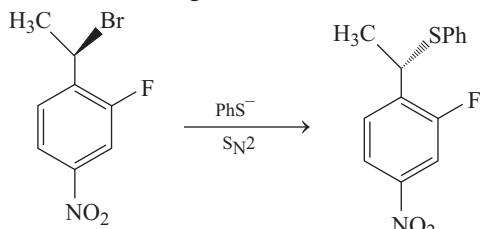
24. **PLAN** Acetone is an aprotic solvent and can dissolve both the nucleophile and the substrate and thus  $S_N2$  reaction is favoured. Also



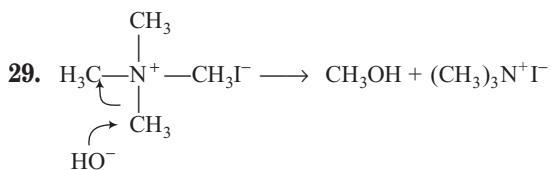
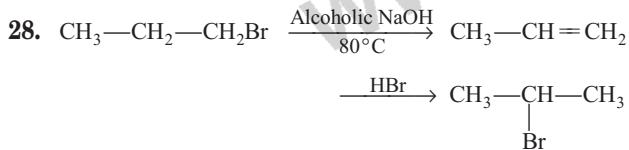
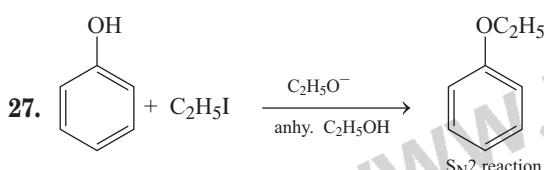
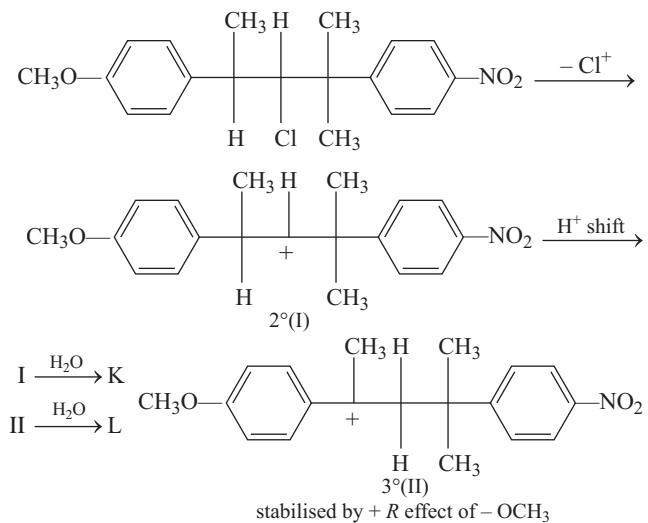
Thus, reactivity order is  $S > P > R > Q$

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25. Nucleophile  $\text{PhS}^-$  substitute the  $\text{Br}^-$  through  $\text{S}_{\text{N}}2$  mechanism with inversion of configuration at  $\alpha$ -C.



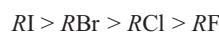
26. Reaction proceed through carbocation intermediate



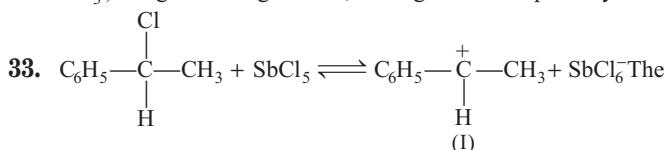
Lack of  $\beta$ -H on quaternary ammonium iodide leads to  $\text{S}_{\text{N}}2$  reaction otherwise E2 elimination usually takes place.

30.  $\text{S}_{\text{N}}2$  reaction at asymmetric carbon occur with inversion of configuration and a single stereoisomer is formed because the reactant and product are not enantiomer. Therefore the sign of optical rotation may or may not change.

31. If alkyl groups are same, the order of leaving ability of halides in  $\text{S}_{\text{N}}2$  reaction is

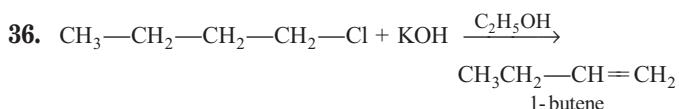
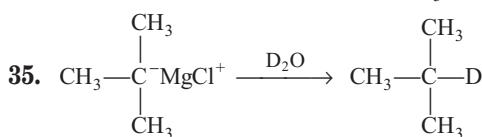


32.  $\text{CH}_3^-$ , being the strongest base, has highest nucleophilicity.



planar carbocation (I), when return back, forms racemic mixture of the starting compounds.

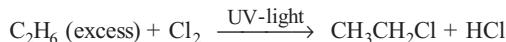
34. Compound in which metal is directly bonded to carbon, is known are organometallic compound, e.g.  $\text{CH}_3\text{Li}$ .



37. An alkyl halide containing at least one  $\beta$ -H, on treatment with ethanolic KOH, undergoes dehydrohalogenation, giving alkene.



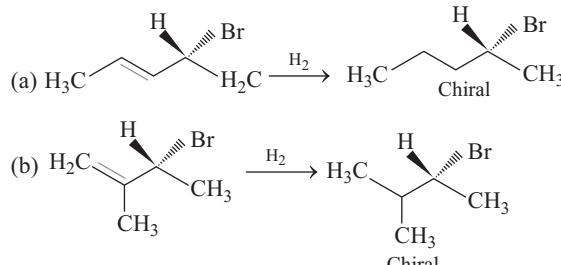
38. During chlorination of alkane, if excess of alkane is treated with  $\text{Cl}_2(g)$  in presence of light or heat, chance of mono-chlorination predominate.



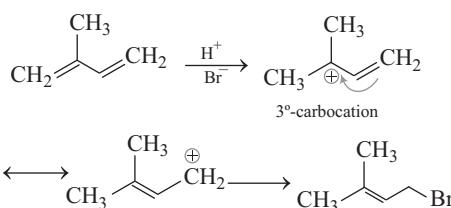
39. (a) Both I and II are  $1^\circ$  halide, undergoes  $\text{S}_{\text{N}}2$  reaction.

(d) III is a tertiary halide, undergoes  $\text{S}_{\text{N}}2$  reaction. I is benzylic bromide, it is very reactive in  $\text{S}_{\text{N}}1$  also as it produces stable benzylic carbonation.

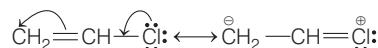
40. In both cases, hydrogenation of olefinic bond will render compound achiral as two identical ethyl group will come at the  $\alpha$ -carbon which was earlier chiral carbon. However, in (a) and (c), chirality will be retained even after hydrogenation.



41. Since, there is no mention of temperature, room temperature will be considered and thermodynamically controlled product would be the major product as:



42. Both  $\text{NH}_3$  and  $\text{CF}_2\text{Cl}_2$  are used as refrigerant.
43. Vinyl halide ( $\text{CH}_2=\text{CH}-\text{Cl}$ ) do not undergo nucleophilic substitution reactions. This is because it forms highly unstable carbocation ( $\text{CH}_2=\overset{\oplus}{\text{C}}\text{H}$ ). It cannot delocalise its  $\pi$ -electron. In vinyl halide C—Cl bond possess double bond character also.



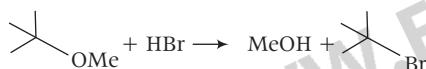
44. For P, i.e.

For this reaction 1 and 4 are probable products.

Product 1 i.e., is formed due to substitution while product 4 i.e., is formed due to elimination. A tertiary carbocation i.e., formed during the reaction. Remember for 3° carbocation ions elimination product predominates.

For Q, i.e.

Correctly matched product for this reaction is 2 i.e., . The reaction proceeds as



For R i.e.,

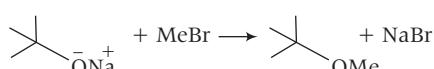
Correctly matched product is 4 i.e., . It is a normal elimination reaction and proceeds as



3° alkyl halide prefers elimination.

For S i.e.,

The correct match is 3 i.e., . The reaction proceeds as



#### 45.

|    | Column I | Column II                                                           | Explanation                                                                                      |
|----|----------|---------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| P. |          | NaOEt(2)                                                            | $\text{O}^-$ Et (strong nucleophile) causes dehydrohalogenation of 3° alkyl halide               |
| Q. |          | EtBr(3)                                                             | 3° butoxide undergoes $\text{S}_\text{N}$ reaction with 1° alkyl halide                          |
| R. |          | (i) $\text{Hg}(\text{OAc})_2$<br>(ii) $\text{NaBH}_4$<br>(1)        | Mercuration-demercuration adds $\text{H}_2\text{O}$ by Markownikoff's rule without rearrangement |
| S. |          | (i) $\text{BH}_3$<br>(ii) $\text{H}_2\text{O}_2/\text{OH}^-$<br>(4) | Hydrobоро-oxidation adds $\text{H}_2\text{O}$ by anti-Markownikoff's rule                        |

Thus, P — (2), Q — (3), R — (1), S — (4)

46. A.  $\text{CH}_3-\text{CHBr}-\text{CD}_3 \xrightarrow[\text{E2}]{\text{Alc. KOH}} \text{CH}_2=\text{CH}-\text{CD}_3$

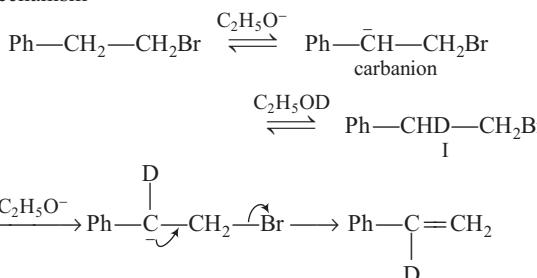
E2 reaction is a single-step reaction in which both deprotonation from  $\beta$ -C and loss of leaving group from  $\alpha$ -C occur simultaneously in the rate-determining step.

C—D bond is stronger than C—H bond, C—H is preferably broken in elimination.

- B.  $\text{Ph}-\text{CHBr}-\text{CH}_3$  reacts faster than  $\text{Ph}-\text{CHBr}-\text{CD}_3$  in E2 reaction because in latter case, stronger C—D bond is to be broken in the rate determining step.

- C.  $\text{Ph}-\text{CH}_2-\text{CH}_2\text{Br} \xrightarrow[\text{C}_2\text{H}_5\text{O}^-]{\text{C}_2\text{H}_5\text{OD}} \text{Ph}-\text{CD}=\text{CH}_2$

Deuterium incorporation in the product indicates E1CB mechanism



- D. Both  $\text{PhCH}_2\text{CH}_2\text{Br}$  and  $\text{PhCD}_2\text{CH}_2\text{Br}$  will react at same rate in E1 reaction because C—H bond is broken in fast non rate determining step. Also E1 reaction follow first order kinetics.

47. Propene is produced



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48. Vinyl chloride is obtained by the reaction of HCl with ethyne.

49. Chlorine is most reactive.

50. 2-bromo-2-methylpropane is formed as major product.

51. In  $S_N1$  reaction, leaving group is detached in the first step forming carbocation intermediate.

52. True

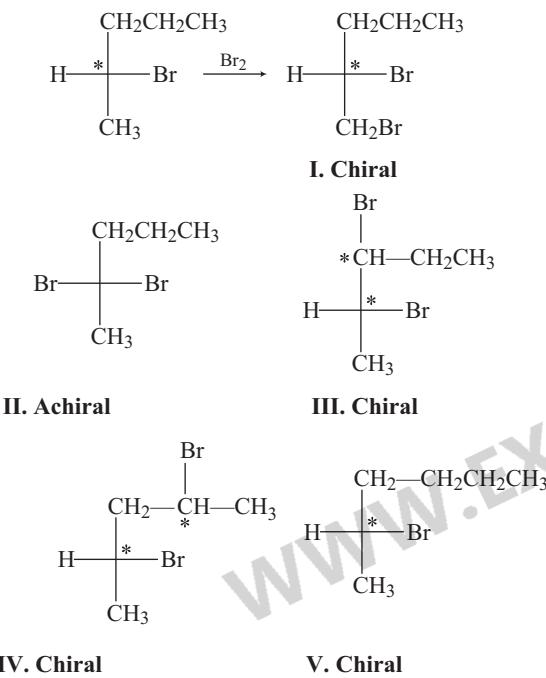
53. Larger the size of donor atom, greater is its polarisability, stronger is the nucleophile.

54. False

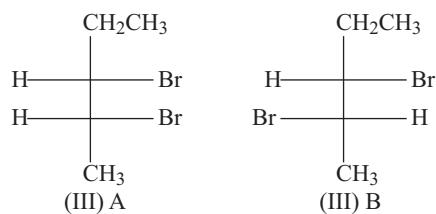
55.  $CCl_4$  is fire retardent, used as fire-extinguisher.

56. Given compound undergoes free-radical bromination under given conditions, replacing H by Br.

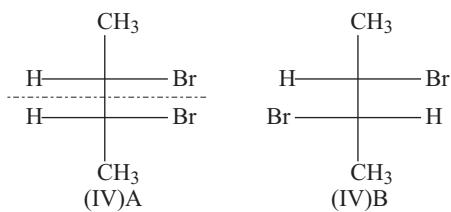
C\* is chiral carbon.



(III) has two chiral centres and can have two structures.



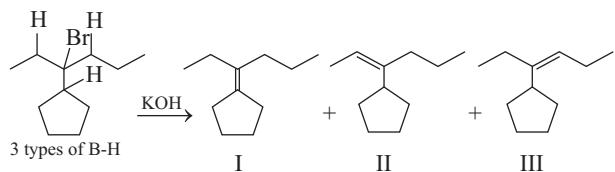
(IV) has also two chiral centres and can have two structures.



It has plane of symmetry thus, achiral.

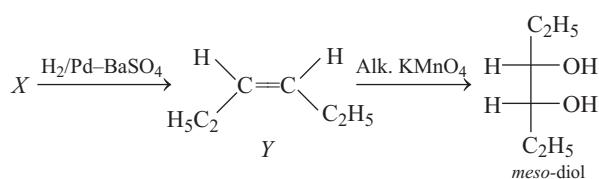
Thus, chiral compounds are five. I, III A, III B, IV B and V.

- 57.** The substrate has three different types of B—H, therefore, first three structural isomers of alkenes are expected as :

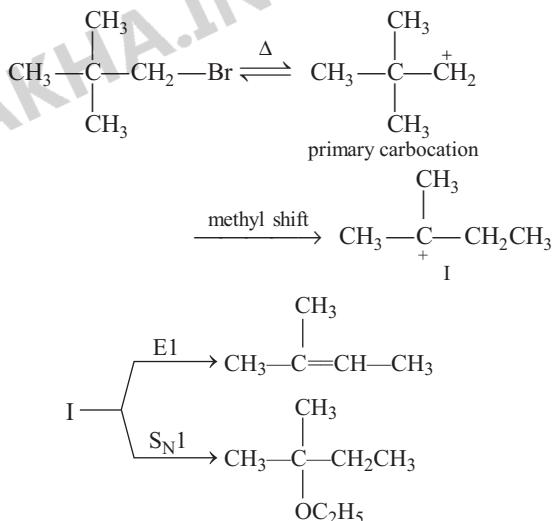


The last two alkenes II and III are also capable of showing geometrical isomerism, hence two geometrical isomers for each of them will be counted giving a total of five isomers.

- 58.**  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH} \xrightarrow[\text{(ii) } \text{CH}_3\text{CH}_2\text{Br}]{\text{(i) } \text{NaNH}_2} \text{CH}_3\text{CH}_2-\underset{\chi}{\text{C}}\equiv\text{C}-\text{CH}_2\text{CH}_3$

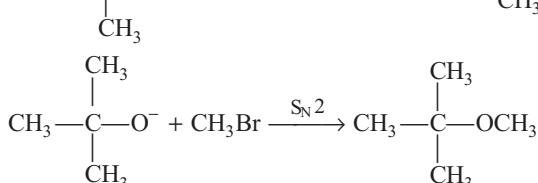


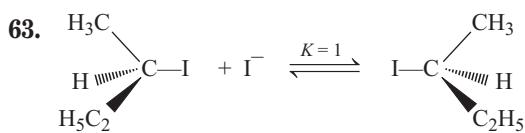
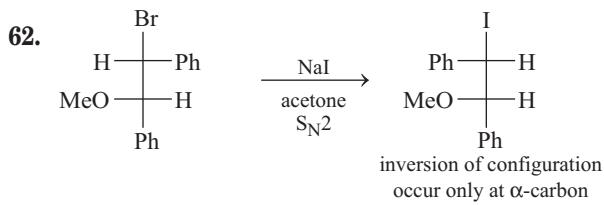
- 59.** Unimolecular reaction occur



- 60.**  $\text{C}_6\text{H}_5\text{CH}_2-\underset{\substack{| \\ \text{Cl}}}{\text{CH}}-\text{C}_6\text{H}_5 \xrightarrow[\text{E2}]{\text{Alc. KOH}} \text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$

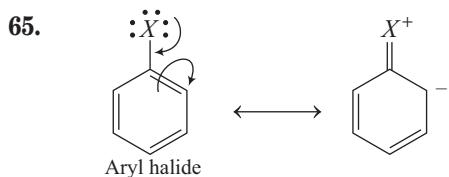
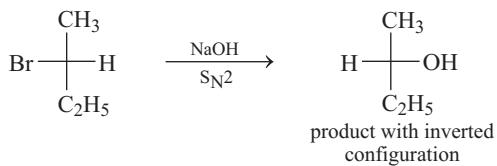
61.  $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{Br} + \text{CH}_3\text{O}^- \xrightarrow{\text{E2}} \text{CH}_2=\text{C}\begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$



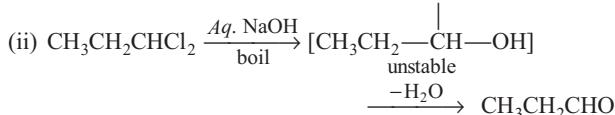
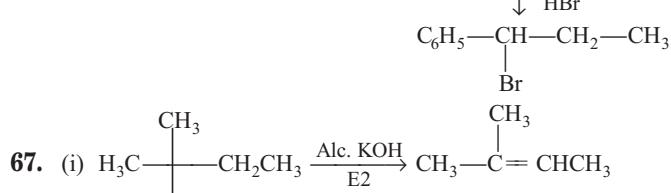
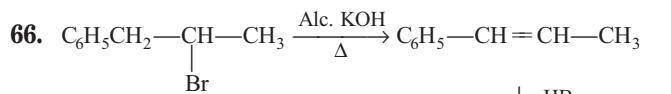


Above equilibrium is established which has equilibrium constant equal to 1. Therefore, equilibrium mixture will have both the enantiomers in equal amount giving racemic mixture.

64.  $S_N2$  reactions leads to inversion of configuration at  $\alpha$ -C

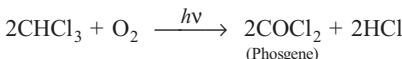


Due to the above resonance phenomena, C—X bond acquire partial double bond character and becomes difficult to break in the rate determining step of  $S_N2$  reaction.



68. (i)  $H_2O < CH_3OH < HO^- < CH_3O^-$   
(ii)  $CH_3F < CH_3Cl < CH_3Br < CH_3I$

69. Chloroform in presence of air and sunlight, oxidises slowly to form a highly poisonous compound called phosgene



To prevent the above oxidation reaction, chloroform is kept in dark bottles.

70. (i)
- $$\begin{aligned} CS_2 + Cl_2 &\longrightarrow CCl_4 + S_2Cl_2 \\ CS_2 + 2S_2Cl_2 &\longrightarrow CCl_4 + 6S \\ CCl_4 + 2[H] &\xrightarrow{Fe/H_2O} CHCl_3 + HCl \\ &\quad \text{(Chloroform)} \end{aligned}$$
- (ii)
- $$\begin{aligned} CaC_2 + H_2O &\longrightarrow C_2H_2 + Ca(OH)_2 \\ C_2H_2 &\xrightarrow{H_2/Ni} C_2H_6 \xrightarrow[h\nu]{Cl_2 \text{ (excess)}} Cl_3C—CCl_3 \\ &\quad \text{(Hexachloroethane)} \end{aligned}$$

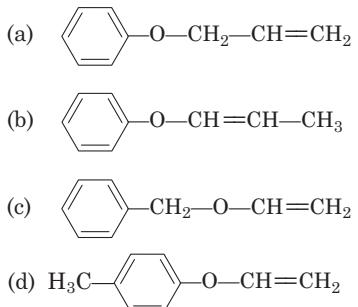
# 24

## Alcohols and Ethers

### Objective Questions I (Only one correct option)

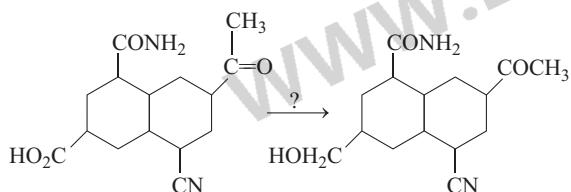
1. An organic compound 'A' ( $C_9H_{10}O$ ) when treated with conc. HI undergoes cleavage to yield compounds 'B' and 'C'. 'B' gives yellow precipitate with  $AgNO_3$  whereas 'C' tautomerises to 'D'. 'D' gives positive iodoform test. 'A' could be

(2020 Main, 2 Sep II)



2. The most suitable reagent for the given conversion is

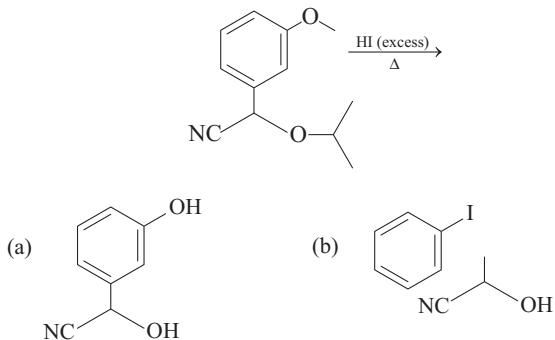
(2020 Main, 8 Jan I)



- (a)  $B_2H_6$   
(c)  $NaBH_4$
- (b)  $LiAlH_4$   
(d)  $H_2 / Pd$

3. The major product of the following reaction is

(2019 Main, 10 April I)



4. The synonym for water gas when used in the production of methanol is

(2019 Main, 10 April I)

- (a) natural gas  
(c) *syn* gas
- (b) laughing gas  
(d) fuel gas

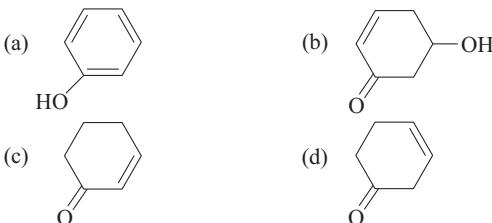
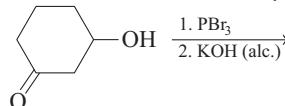
5. The major product of the following reaction is



- (a)  $CH_3CH = CHCH_2OH$   
(c)  $CH_3CH_2CH_2CO_2CH_3$
- (b)  $CH_3CH_2CH_2CH_2OH$   
(d)  $CH_3CH_2CH_2CHO$

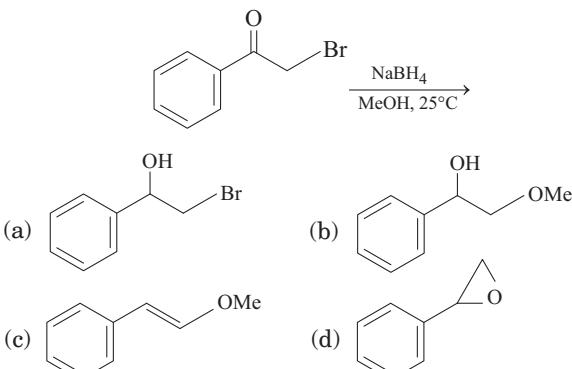
6. The major product of the following reaction is

(2019 Main, 9 April I)

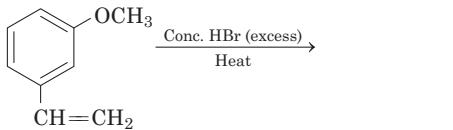


7. The major product of the following reaction is

(2019 Main, 8 April I)



8. The major product of the following reaction is  
(2019 Main, 8 April I)

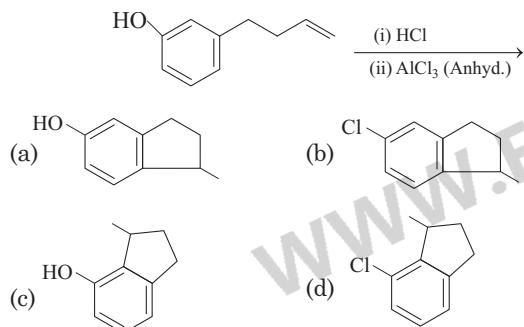


- (a) (b)   
 (c) (d)

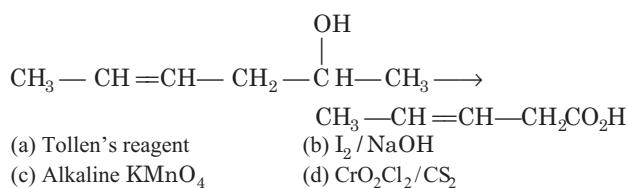
9. cannot be prepared by  
(2019 Main, 12 Jan I)

- (a)  $\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{PhMgX}$   
 (b)  $\text{PhCOCH}_3 + \text{CH}_3\text{CH}_2\text{MgX}$   
 (c)  $\text{PhCOCH}_2\text{CH}_3 + \text{CH}_3\text{MgX}$   
 (d)  $\text{HCHO} + \text{PhCH}(\text{CH}_3)\text{CH}_2\text{MgX}$

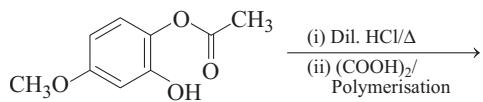
10. The major product of the following reaction is  
(2019 Main, 11 Jan II)



11. Which is the most suitable reagent for the following transformation?  
(2019 Main, 10 Jan II)

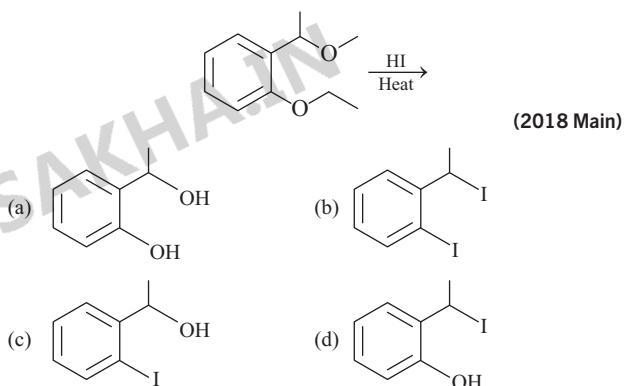


12. The major product of the following reaction is  
(2019 Main, 10 Jan II)

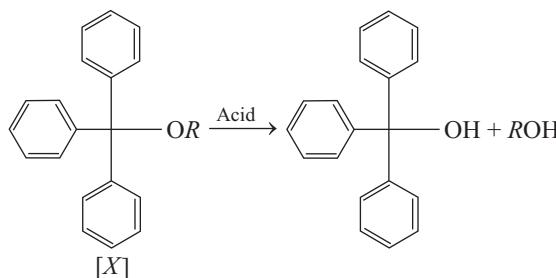


- (a) (b)   
 (c) (d)

13. The major product formed in the following reaction is  
(2018 Main)



14. The acidic hydrolysis of ether (X) shown below is fastest when  
(2014 Adv.)



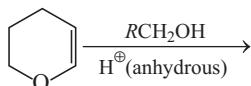
- (a) one phenyl group is replaced by a methyl group  
 (b) one phenyl group is replaced by a para-methoxyphenyl group  
 (c) two phenyl groups are replaced by two para-methoxyphenyl groups  
 (d) no structural change is made to X

## 366 Alcohols and Ethers

15. An unknown alcohol is treated with the “Lucas reagent” to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism? (2013 Main)

(a) Secondary alcohol by  $S_N1$  (b) Tertiary alcohol by  $S_N1$   
 (c) Secondary alcohol by  $S_N2$  (d) Tertiary alcohol by  $S_N2$

16. The major product of the following reaction is



(a) a hemiacetal (b) an acetal  
 (c) an ether (d) an ester

17. (I) 1, 2-dihydroxy benzene (II) 1, 3-dihydroxy benzene  
 (III) 1, 4-dihydroxy benzene (IV) Hydroxy benzene

The increasing order of boiling points of above mentioned alcohols is (2006, 3M)

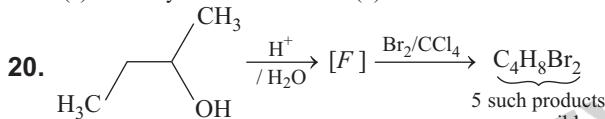
(a) I < II < III < IV (b) I < II < IV < III  
 (c) IV < I < II < III (d) IV < II < I < III

18. The best method to prepare cyclohexene from cyclohexanol is by using (2005, 1M)

(a) conc. HCl + ZnCl<sub>2</sub> (b) conc. H<sub>3</sub>PO<sub>4</sub>  
 (c) HBr (d) conc. HCl

19. When phenyl magnesium bromide reacts with *tert* butanol, which of the following is formed? (2005, 1M)

(a) *Tert* butyl methyl ether (b) Benzene  
 (c) *Tert* butyl benzene (d) Phenol

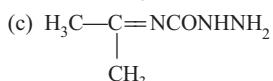
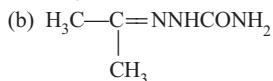


How many structures of F is possible? (2003, 1M)

(a) 2 (b) 5  
 (c) 6 (d) 3

21. Compound ‘A’ (molecular formula C<sub>3</sub>H<sub>8</sub>O) is treated with acidified potassium dichromate to form a product ‘B’ (molecular formula C<sub>3</sub>H<sub>6</sub>O) ‘B’ forms a shining silver mirror on warming with ammoniacal silver nitrate. ‘B’ when treated with an aqueous solution of H<sub>2</sub>NCONHNH<sub>2</sub> and sodium acetate gives a product ‘C’. Identify the structure of ‘C’.

(a) CH<sub>3</sub>CH<sub>2</sub>CH=NNHCONH<sub>2</sub> (2002, 3M)



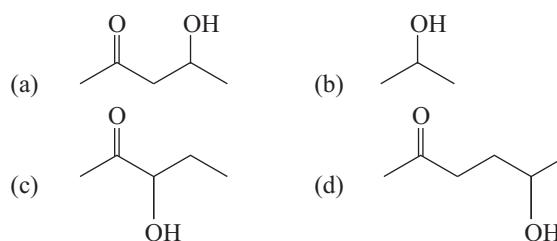
(d) CH<sub>3</sub>CH<sub>2</sub>OH + NCONHNH<sub>2</sub>

22. 1-propanol and 2-propanol can be best distinguished by

(a) oxidation with alkaline KMnO<sub>4</sub> followed by reaction with Fehling solution (2001, 1M)  
 (b) oxidation with acidic dichromate followed by reaction with Fehling solution

- (c) oxidation by heating with copper followed by reaction with Fehling solution  
 (d) oxidation with concentrated H<sub>2</sub>SO<sub>4</sub> followed by reaction with Fehling solution

23. Which one of the following will most readily be dehydrated in acidic condition? (2000, 1M)



24. The products of combustion of an aliphatic thiol (RSH) at 298 K are (1992)

(a) CO<sub>2</sub>(g), H<sub>2</sub>O(g) and SO<sub>2</sub>(g)  
 (b) CO<sub>2</sub>(g), H<sub>2</sub>O(l), and SO<sub>2</sub>(g)  
 (c) CO<sub>2</sub>(l), H<sub>2</sub>O(g) and SO<sub>2</sub>(g)  
 (d) CO<sub>2</sub>(g), H<sub>2</sub>O(l) and SO<sub>2</sub>(l)

25. In CH<sub>3</sub>CH<sub>2</sub>OH, the bond that undergoes heterolytic cleavage most readily is (1988, 1M)

(a) C—C (b) C—O  
 (c) C—H (d) O—H

26. Hydrogen bonding is maximum in (1987, 1M)

(a) ethanol (b) diethyl ether  
 (c) ethyl chloride (d) triethyl amine

27. HBr reacts fastest with (1986, 1M)

(a) 2-methyl propan-2-ol (b) propan-1-ol  
 (c) propan-2-ol (d) 2-methyl propan-1-ol

28. An industrial method of preparation of methanol is (1984, 1M)

(a) catalytic reduction of carbon monoxide in presence of ZnO-Cr<sub>2</sub>O<sub>3</sub>  
 (b) by reacting methane with steam at 900°C with nickel catalyst  
 (c) by reducing formaldehyde with LiAlH<sub>4</sub>  
 (d) by reacting formaldehyde with aqueous sodium hydroxide solution

29. Diethyl ether on heating with conc. HI gives two moles of (1983, 1M)

(a) ethanol (b) iodoform  
 (c) ethyl iodide (d) methyl iodide

30. The compound which reacts fastest with Lucas reagent at room temperature is (1981, 1M)

(a) butan-2-ol (b) butan-1-ol  
 (c) 2-methyl propan-1-ol (d) 2-methyl propan-2-ol

31. Ethyl alcohol is heated with conc. H<sub>2</sub>SO<sub>4</sub>. The product formed is

(a) CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> (b) C<sub>2</sub>H<sub>2</sub>  
 (c) C<sub>2</sub>H<sub>4</sub> (d) C<sub>2</sub>H<sub>6</sub> (1980, 1M)

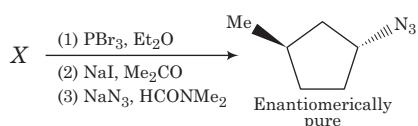
32. Which of the following is soluble in water? (1980, 1M)

(a) CS<sub>2</sub> (b) C<sub>2</sub>H<sub>5</sub>OH  
 (c) CCl<sub>4</sub> (d) CHCl<sub>3</sub>

## Objective Questions II

(One or more than one correct option)

- 33.** In the following reaction sequence, the correct structure (s) of  $X$  is (are) (2018 Adv.)



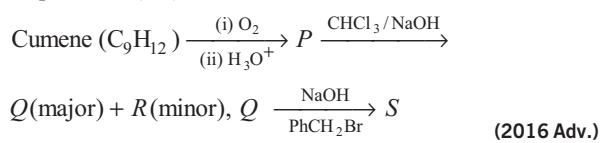
- (a) Me  


(b) Me  


(c) Me  

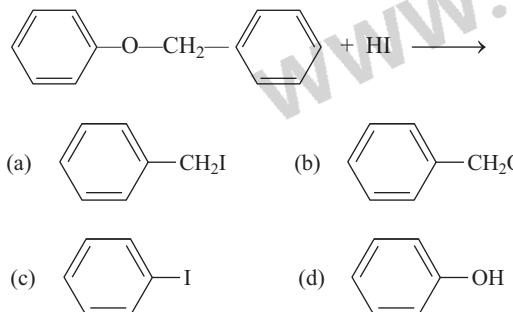

(d) Me  


- 34.** The correct statement(s) about the following reaction sequence is (are)



- (a)  $R$  is steam volatile
  - (b)  $Q$  gives dark violet colouration with 1% aqueous  $\text{FeCl}_3$  solution
  - (c)  $S$  gives yellow precipitate with 2, 4-dinitrophenylhydrazine
  - (d)  $S$  gives dark violet colouration with 1% aqueous  $\text{FeCl}_3$  solution

- 35.** The following ether, when treated with HI produces  
(1999, 3M)



- 36.** The products of reaction of alcoholic silver nitrate with ethyl bromide are (1991, 1M)

  - (a) ethane
  - (b) ethene
  - (c) nitroethane
  - (d) ethyl alcohol
  - (e) ethyl nitrite

## Assertion and Reason

*Read the following question and answer as per the direction given below :*

- (a) Statement I is correct; Statement II is correct; Statement II is a correct explanation of Statement I.

- (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
  - (c) Statement I is correct; Statement II is incorrect.
  - (d) Statement I is incorrect; Statement II is correct.

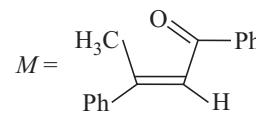
- 37. Statement I** Solubility of *n*-alcohol in water decreases with increase in molecular weight.

**Statement II** The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permit enhanced hydrogen bonding with water. (1988, 2M)

## Passage Based Questions

## Passage 1

A tertiary alcohol *H* upon acid catalysed dehydration gives a product *I*. Ozonolysis of *I* leads to compounds *J* and *K*. Compound *J* upon reaction with KOH gives benzyl alcohol and a compound *L*, whereas *K* on reaction with KOH gives only *M*.



- 38.** The structures of compounds *J*, *K* and *L* respectively, are

- (a) PhCOCH<sub>3</sub>, PhCH<sub>2</sub>COCH<sub>3</sub> and PhCH<sub>2</sub>COO<sup>-</sup>K<sup>+</sup>  
 (b) PhCHO, PhCH<sub>2</sub>CHO and PhCOO<sup>-</sup>K<sup>+</sup>  
 (c) PhCOCH<sub>3</sub>, PhCH<sub>2</sub>CHO and CH<sub>3</sub>COO<sup>-</sup>K<sup>+</sup>  
 (d) PhCHO, PhCOCH<sub>3</sub> and PhCOO<sup>-</sup>K<sup>+</sup>

- 39.** The structure of compound I is

- |     |  |     |  |
|-----|--|-----|--|
| (a) |  | (b) |  |
| (c) |  | (d) |  |

- 40.** Compound *H* is formed by the reaction of

- (a)  ; PhMgBr

(b)  ; PhCH<sub>2</sub>MgBr

(c)  ; PhCH<sub>2</sub>MgBr

(d)  ; 

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### Numerical Answer Type Question

41. Total number of isomers considering both structural and stereoisomers of cyclic ethers with the molecular formula  $C_4H_8O$  is ..... (2019 Adv.)

### Fill in the Blanks

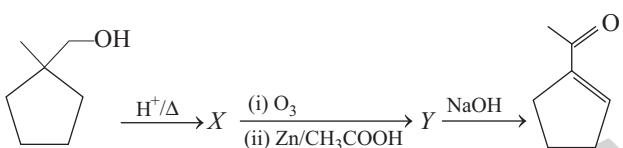
42. Glycerine contains one ..... hydroxyl group. (1997, 1M)  
 43. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove ..... which are formed on prolonged standing in contact with water. (1992, 1M)  
 44. A ..... diol has two hydroxyl groups on ..... carbon atoms. (1986, 1M)  
 45. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ..... (1983, 1M)

### True or False

46. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. (1985, 1M)  
 47. The yield of a ketone when a secondary alcohol is oxidised is more than the yield of aldehyde when a primary alcohol is oxidised. (1983, 1M)

### Subjective Questions

48.

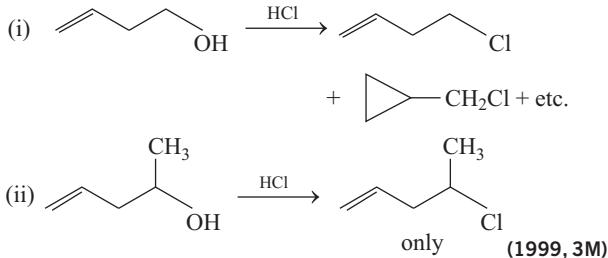


Identify  $X$  and  $Y$ . (2005, 2M)

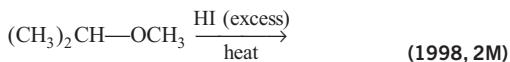
49. An organic compound  $P$  having the molecular formula  $C_5H_{10}O$  when treated with dil  $H_2SO_4$  gives two compounds,  $Q$  and  $R$  both gives positive iodoform test. The reaction of  $C_5H_{10}O$  with dil.  $H_2SO_4$  gives reaction  $10^{15}$  times faster than ethylene. Identify organic compound of  $Q$  and  $R$ . Give the reason for the extra stability of  $P$ . (2004)

50. Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic compound ( $A$ ). The organometallic reacts with ethanal to give an alcohol ( $B$ ) after mild acidification. Prolonged treatment of alcohol ( $B$ ) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane ( $C$ ). Write the structures of ( $A$ ), ( $B$ ) and explain how ( $C$ ) is obtained from ( $B$ ). (2001, 5M)

51. Explain briefly the formation of products giving the structures of the intermediates.



52. Write the structures of the products :



53. Give reasons for the following in one or two sentences.  
 "Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. (1998, 2M)

54. 2, 2-dimethyloxirane can be cleaved by acid ( $H^+$ ). Write mechanism. (1997, 2M)

55. A compound  $D(C_8H_{10}O)$  upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid  $E(C_7H_6O_2)$ . Write the structures of  $D$ ,  $E$  and explain the formation of  $E$ . (1996, 2M)

56. 3, 3-dimethylbutan-2-ol losses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. (1996, 2M)

57. When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute  $KMnO_4$  in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? (1994, 2M)

58. Compound  $X$  (molecular formula,  $C_5H_8O$ ) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate with excess of  $MeMgBr$ . 0.42 g of  $X$  gives 224 mL of  $CH_4$  at STP. Treatment of  $X$  with  $H_2$  in presence of Pt catalyst followed by boiling with excess HI, gives *n*-pentane. Suggest structure for  $X$  and write the equation involved. (1992, 5M)

59. Arrange the following in increasing order of boiling point : *n*-butane, *n*-butanol, *n*-butylchloride, *iso*-butane. (1988, 1M)

60. How may be the following transformation be carried out (in not more than six steps)?

"Ethyl alcohol to vinyl acetate." (1986, 3M)

61. Write down the main product of the following reaction :



62. Give a chemical test to distinguish between methanol and ethanol. (1985, 1M)

63. Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water. (1985, 2M)

64. An alcohol  $A$ , when heated with conc.  $H_2SO_4$  gives an alkene  $B$ . When  $B$  is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound  $C$  is obtained. The compound  $C$  gives  $D$  when treated with warm dilute  $H_2SO_4$  in presence of  $HgSO_4$ .  $D$  can also be obtained either by oxidising  $A$  with  $KMnO_4$  or from acetic acid through its calcium salt. Identify  $A$ ,  $B$ ,  $C$  and  $D$ . (1983, 4M)

65. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.

- (i) Ethanol from acetylene
- (ii) Lead tetraethyl from sodium-lead alloy
- (iii) Methyl chloride from aluminium carbide

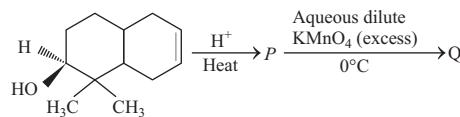
(1983, 3M)

66. A compound 'X' containing C, H and O is unreactive towards sodium. It does not add with bromine. It also does not react with Schiff's reagent. On refluxing with an excess of HI, 'X' yields only one organic product 'Y'. 'Y' on hydrolysis yields a new compound 'Z' which can be converted into 'Y' by reaction with red phosphorus and iodine. The compound 'Z' on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of acid is 60. What are the compounds 'X', 'Y' and 'Z'? Write chemical equations leading to the conversion of 'X' to 'Y'. (1981, 3M)

67. An organic liquid 'A' containing C, H and O with boiling point 78°C, possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product 'B' with the empirical formula, CH<sub>2</sub>. 'B' decolourises bromine water as well as alkaline permanganate solution and takes up one mole of H<sub>2</sub> (per mole of B) in presence of finely divided nickel at high temperature. Identify the substances A and B. (1979, 2M)

### Integer Answer Type Question

68. The number of hydroxyl group(s) in Q is (2015 Adv.)



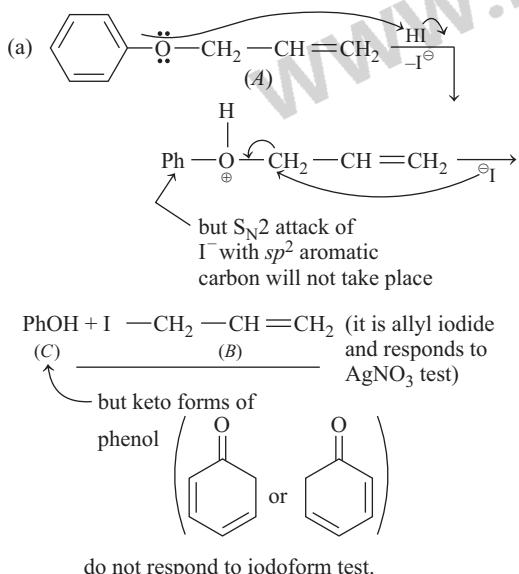
### Answers

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (c)  | 2. (a)  | 3. (d)  | 4. (c)  |
| 5. (a)  | 6. (c)  | 7. (d)  | 8. (b)  |
| 9. (d)  | 10. (a) | 11. (b) | 12. (c) |
| 13. (d) | 14. (c) | 15. (b) | 16. (b) |
| 17. (c) | 18. (b) | 19. (b) | 20. (d) |
| 21. (a) | 22. (c) | 23. (a) | 24. (b) |
| 25. (d) | 26. (a) | 27. (a) | 28. (a) |

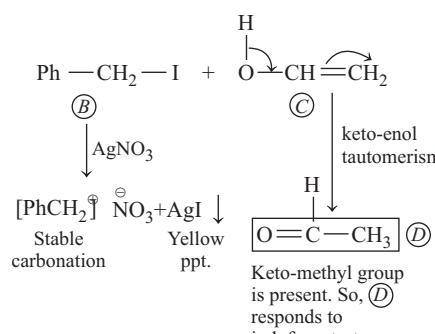
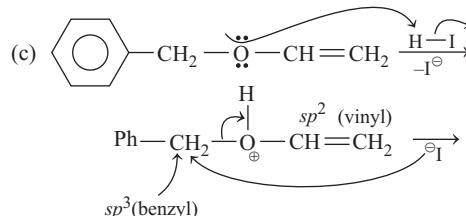
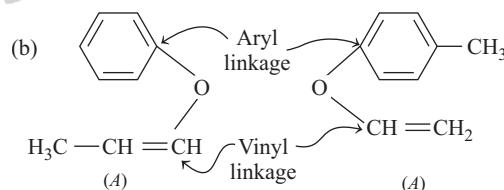
- |                     |                 |                 |           |
|---------------------|-----------------|-----------------|-----------|
| 29. (c)             | 30. (d)         | 31. (c)         | 32. (b)   |
| 33. (b)             | 34. (b,c)       | 35. (a,d)       | 36. (c,e) |
| 37. (c)             | 38. (d)         | 39. (a)         | 40. (b)   |
| 41. (10.0)          | 42. (secondary) | 43. (peroxides) |           |
| 44. (vicinal; same) | 45. (aldol)     | 46. (False)     |           |
| 47. (False)         | 68. (4)         |                 |           |

### Hints & Solutions

1. A (C<sub>9</sub>H<sub>10</sub>O) has four isomeric ethers (options (a), (b), (c) and (d)), of each of which gets treated with conc. HI.

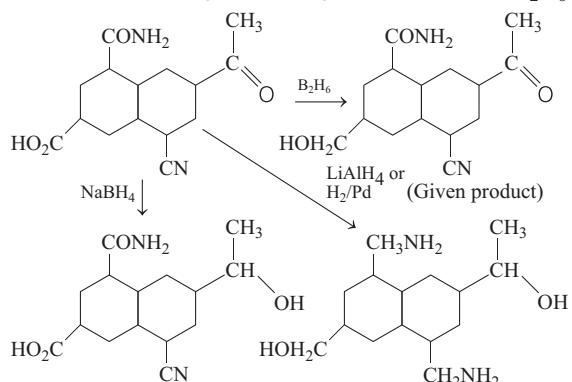


(b) and (d) will not respond to HI solvolysis, because in both of the ethers, the ether linkage (—O—) is attached with sp<sup>2</sup> carbon, one is phenyl (aryl), while the other is vinyl.

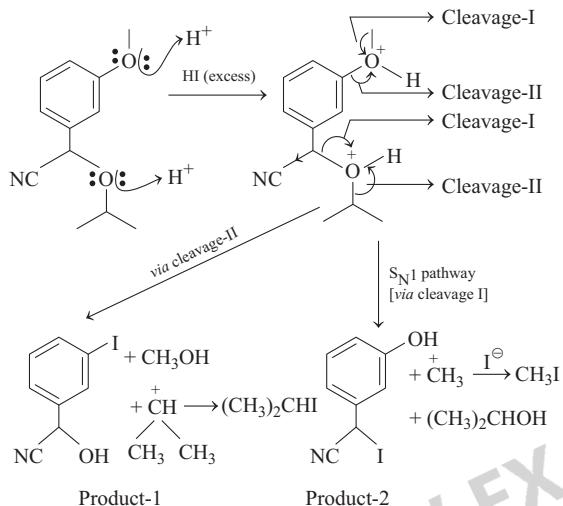


## 370 Alcohols and Ethers

- 2.** The most suitable reagent for the given conversion is  $\text{B}_2\text{H}_6$ .



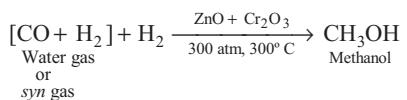
3. The given reaction takes place as follows:



Product-2 is formed because

- (i) Cleavage-I will give more stable aryl carbocation.
  - (ii) Cleavage- I will give intermediate which is in conjugation with ring.

4. The production of methanol from water gas is as follows:

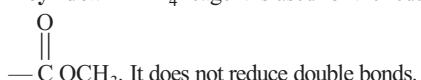


It is an industrial process used for the production of methanol where volume ratio of the reactant gases is maintained as:

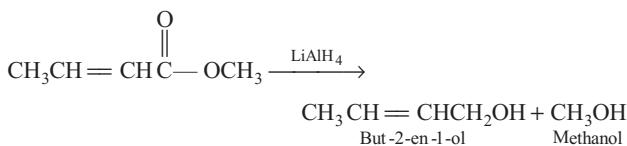
*syn* gas : H<sub>2</sub> = 2 : 1 and ZnO-Cr<sub>2</sub>O<sub>3</sub> act as catalysts

Thus, water gas is also called *syn* gas because it is used for synthesis of methanol.

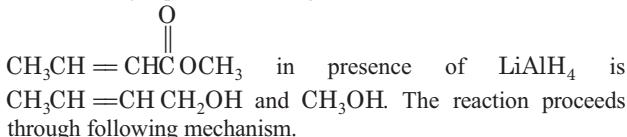
- 5 Key Idea**  $\text{LiAlH}_4$  reagent is used for the reduction of  $-\text{CHO}$ .



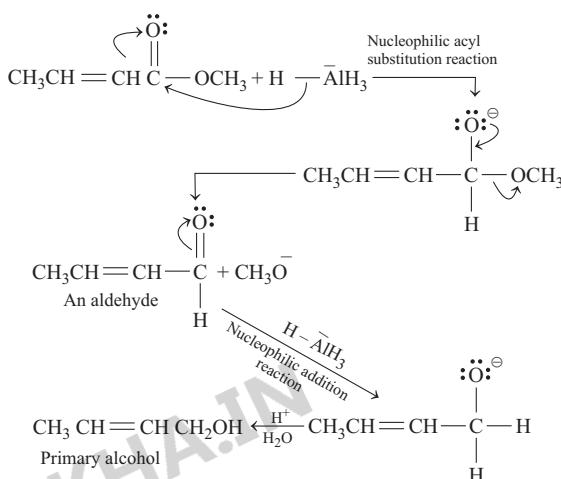
The reaction of an ester with  $\text{LiAlH}_4$  produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.



Thus, the major product of the given reactant



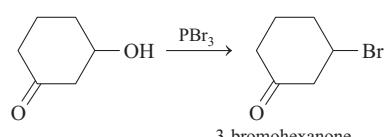
## Mechanism



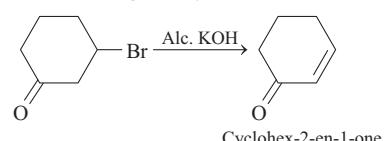
- 6. Key Idea**  $\text{PBr}_3$  reagent is used for the substitution of —Br group while alc. KOH reagent is used to carry out elimination reaction.

The given reaction proceed in following manner:

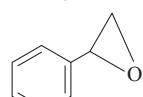
**Step I** In presence of  $\text{PBr}_3$ , alcohols undergo substitution reactions to give halides. Reagent  $\text{PBr}_3$  is usually generated *in situ* by the reaction of red phosphorus with bromine.



**Step II** 3-bromohexanone in presence of alc. KOH undergoes elimination reaction and gives cyclohex-2-en-1-one

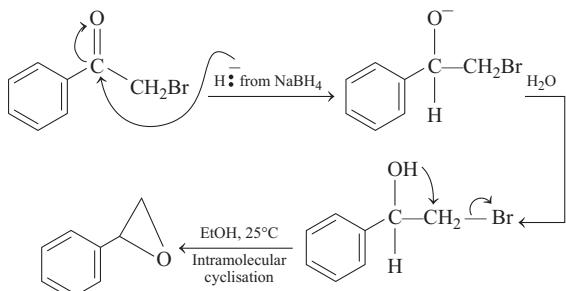


7. Major product obtained in the given reaction is



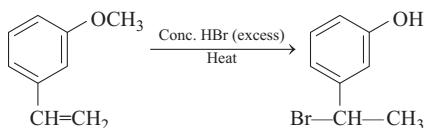
$\text{NaBH}_4$  in the reaction is used for the reduction by addition of a hydride ion and a proton. Carbon-oxygen double bonds are easily reduced by sodium borohydride. The actual reducing agent in

these reductions is hydride ion ( $H^-$ ). Hydride ion adds to the carbonyl carbon and the alkoxide ion that is formed is subsequently protonated by water. In other words, the carbonyl group is reduced by adding an  $H^-$  followed by an  $H^+$ . The mechanism of the given reaction is as follows :



- 8. Key Idea** Ethers are least reactive functional groups. The cleavage of C—O bond in ethers take place under drastic conditions with excess of  $HX$ .

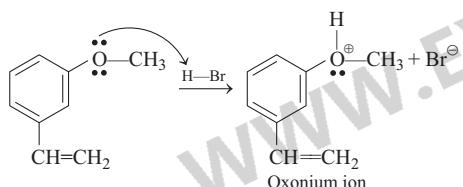
The major product obtained in the reaction is as follows :



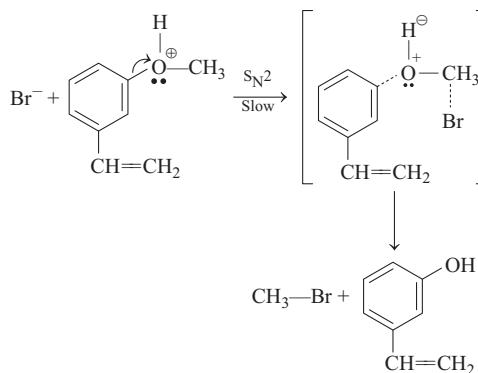
As conc.  $\text{HBr}$  is in excess. So, reaction will take place at both the substituents.

#### Mechanism

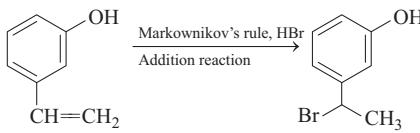
**Step 1** Protonation of ether to form oxonium ion.



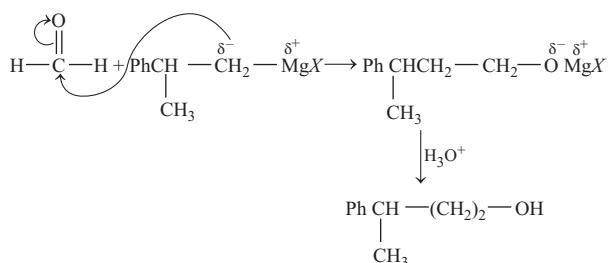
**Step 2** Attack of nucleophile at the protonated ether.



**Step 3** As  $\text{HBr}$  is in excess, so, reaction will also take place at alkene.

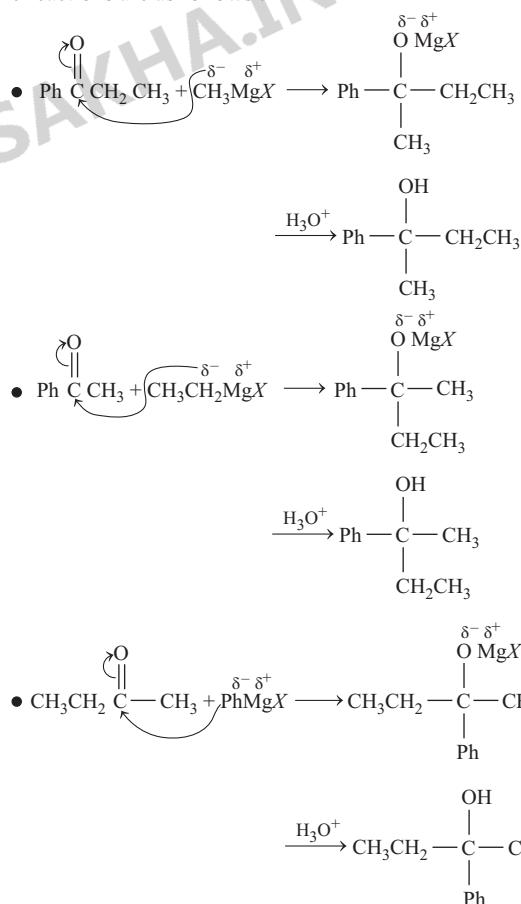


- 9.**  $\text{CH}_3\text{CH}_2-\underset{\text{Ph}}{\overset{\text{OH}}{\underset{\text{C}}{\text{---}}}}-\text{CH}_3$  cannot be prepared by  $\text{HCHO}$  and  $\text{PhCH}(\text{CH}_3)\text{CH}_2\text{MgX}$ . This can be easily illustrated by following reaction.



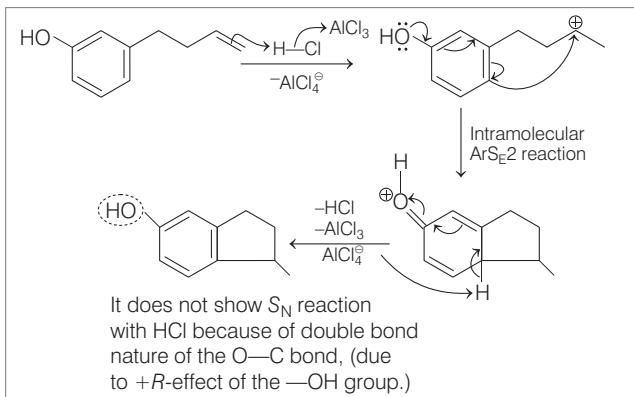
The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance.

The reactions are as follows :

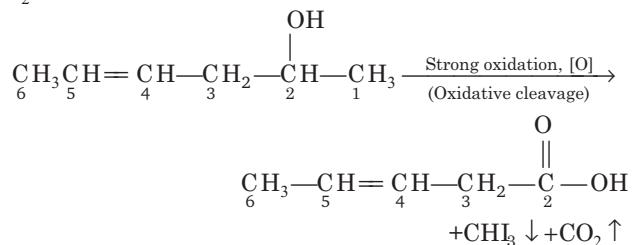


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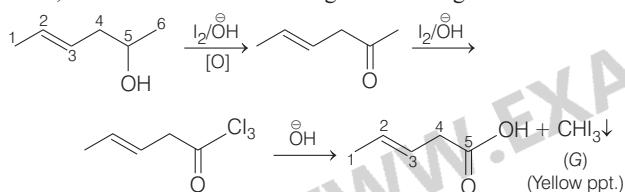
10. In the given reaction,  $\text{AlCl}_3$  helps in the generation of electrophile that further undergoes  $\text{ArS}_{\text{E}}2$  reaction to give the required product.



11. The most suitable reagent to carry out given transformation is  $\text{I}_2/\text{NaOH}$

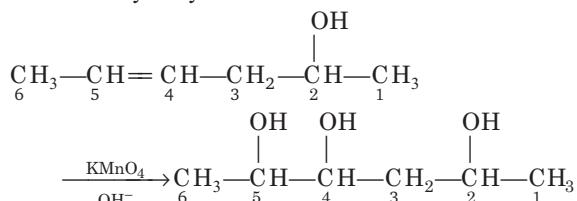


Here, the haloform reaction will give following reaction:



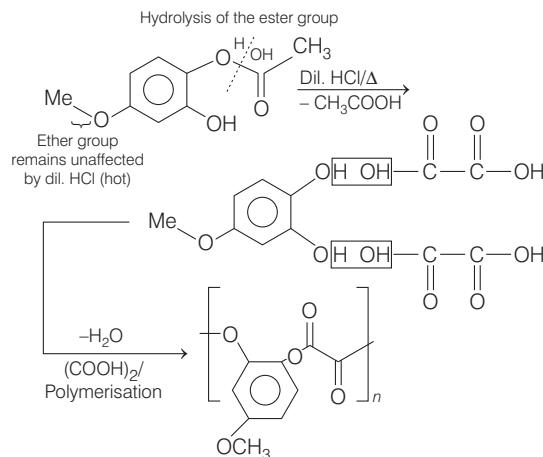
- (i) Tollen's reagent ( $\text{AgNO}_3 + \text{NH}_4\text{OH}$ ) is a mild oxidising agent. It does not react with  $\text{CH}(\text{OH})\text{—CH}_3$  group (2°-alcohol).

- (ii) Alkaline  $\text{KMnO}_4$  cannot perform the oxidative cleavage, rather it will hydroxylate the  $\text{C}=\text{C}$ .

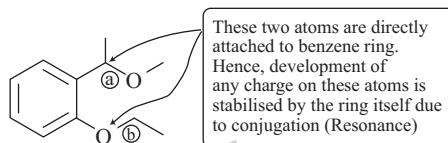


- (iv)  $\text{CrO}_2\text{Cl}_2/\text{CS}_2$  will not react here.

12. In the given reaction, ester get cleaved in presence of dil.  $\text{HCl}$  and readily forms alcohol. This alcohol on reaction with oxalic acid undergoes polymerisation reaction.

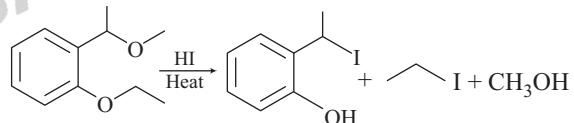


13. Key idea The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.



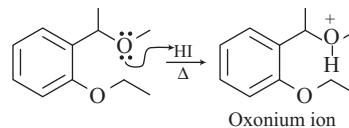
If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

The reaction can be represented as

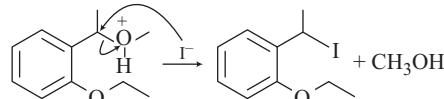


### Mechanism

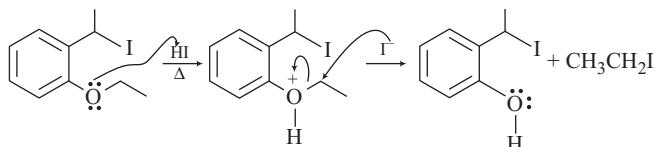
**Step I** The reaction begins with the attack of  $\text{H}^+$  of  $\text{HI}$  on oxygen to form oxonium ion as



**Step II** This oxonium ion undergoes lysis and addition of  $\text{I}^-$  to form two products as



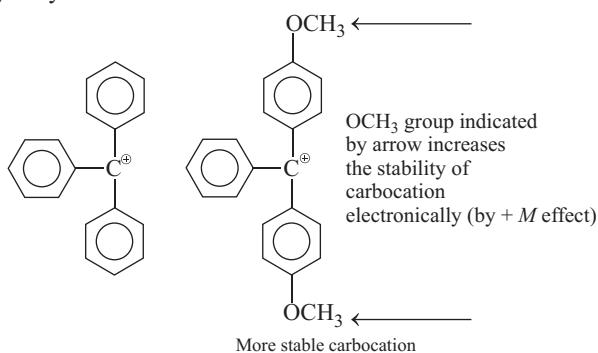
**Step III** Similar pathway is followed at the other oxygen atom, which can be visualised as



**Note** Mechanism of a reaction is always a logical sequencing of events which may occur simultaneously as well.

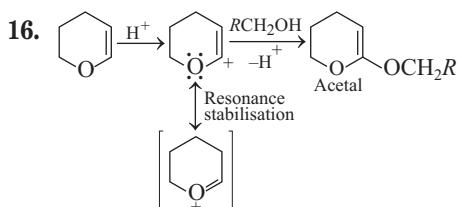
- 14. PLAN** This problem can be solved by using the concept of stability of carbocation and  $S_N1$  reaction.

When two phenyl groups are replaced by two *para* methoxy group, carbocation formed will be more stable. As the stability of carbocation formed increases, rate of acidic hydrolysis increases.

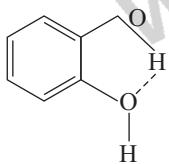


Hence, (c) is the correct choice.

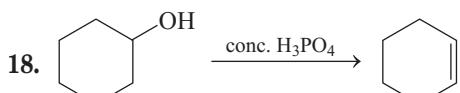
- 15.** The reaction of alcohol with Lucas reagent is mostly an  $S_N1$  reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since  $3^\circ R-OH$  forms  $3^\circ$  carbocation (most stable), hence it will react fastest.



- 17.** All dihydroxy benzene will have higher boiling points than monohydroxy benzene. Also, among dihydroxy benzenes, 1, 2-di-hydroxy benzene has lowest boiling point due to intramolecular H-bonding.

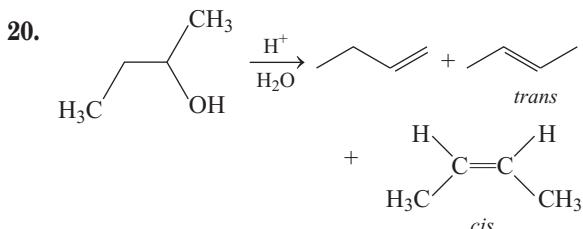


(intramolecular H-bonding in 1,2-dihydroxy benzene)

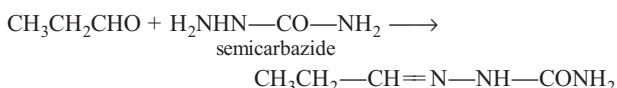


Concentrated  $H_3PO_4$  solution does not involve any substitution product while with others, substitution products are also formed.

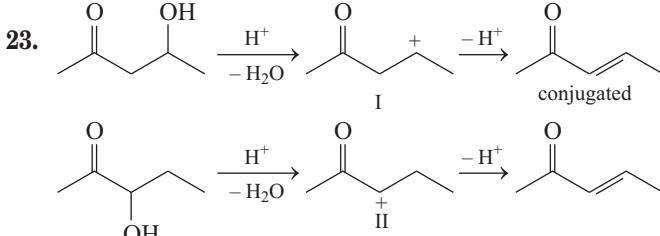
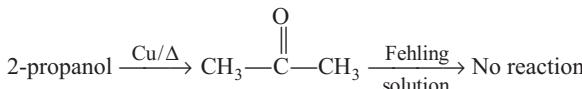
- 19.**  $C_6H_5MgBr + (CH_3)_3COH \rightarrow C_6H_6 + Mg[(CH_3)_3CO]Br$



- 21.** *A* is an alcohol and its oxidation product gives Tollen's test, i.e. *B* must be an aldehyde ( $CH_3CH_2CHO$ ).



- 22.** 1-propanol  $\xrightarrow{Cu/\Delta} CH_3-CH_2-CHO \xrightarrow[\text{solution}]{\text{Fehling}} Cu_2O \downarrow \text{red}$

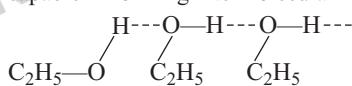


Although both reactions are giving the same product, carbocation I is more stable than II.

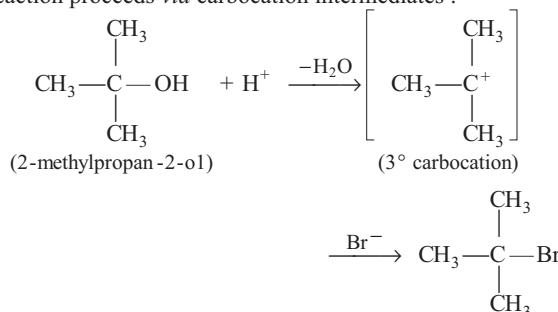
- 24.** Thiol, ( $RSH$ ), on combustion produces  $CO_2(g)$ ,  $SO_2(g)$  and  $H_2O(l)$ . At 298 K,  $H_2O$  will be in liquid phase.

- 25.**  $OH \longrightarrow O^- + H^+$  (has maximum electronegativity difference)

- 26.** Ethanol is capable in forming intermolecular H-bonds :



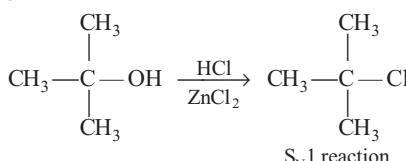
- 27.** Reaction proceeds via carbocation intermediates :



- 28.**  $CO + H_2 \xrightarrow[\text{heat}]{ZnO-Cr_2O_3} CH_3OH$

- 29.**  $CH_3-CH_2-O-CH_2-CH_3 + HI \longrightarrow 2C_2H_5I$

- 30.** 2-methyl propan-2-ol is a tertiary alcohol, will react fastest with Lucas reagent :



- 31.** On heating with concentrated  $H_2SO_4$ , ethanol would undergo dehydration to produce ethene.

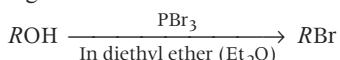
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32. Ethanol is soluble in water due to its ability to form intermolecular H-bonds with water :

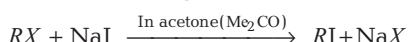
33. **Key idea** All the reactions involved in the problem are Nucleophilic substitution of second order i.e.,  $S_N2$  which have the speciality of inversion of configuration at the carbon atom involved.

Of the reactions given

**Reaction 1** in its generalised format is seen as



**Reaction 2** is simple halogen exchange reaction called **Finkelstein reaction**. Its generalised format is



where  $X = Cl$  or  $Br$

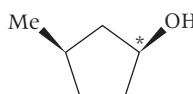
**Reaction 3** in its generalised format seen as



Now if the given product is

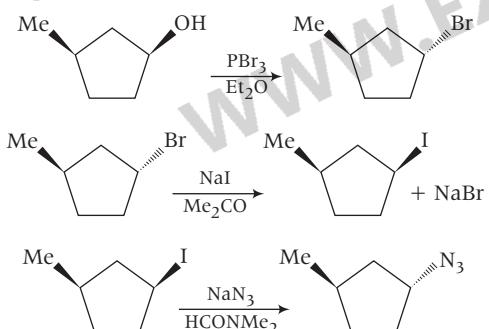


and which is too enantiomerically pure i.e. 100% either dextrorotatory or levorotatory form, then the 'X' must be

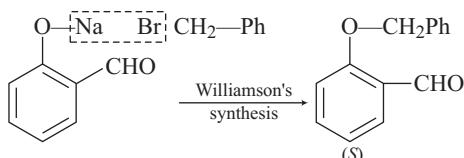
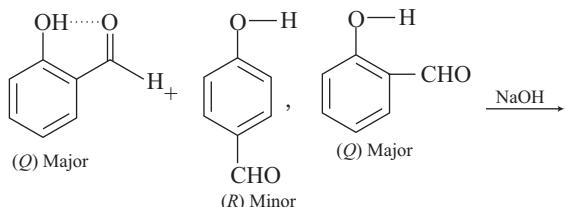
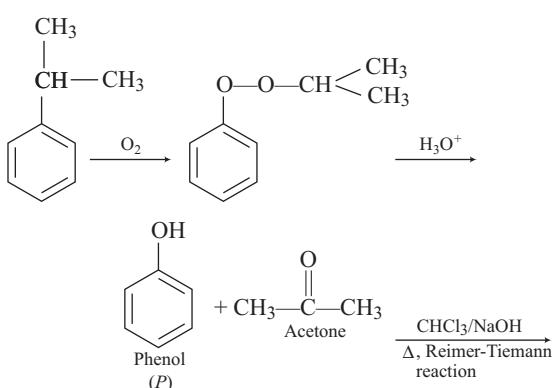


**Note** The configuration at carbon \* atom in 'X' becomes inverted due to  $S_N2$  mechanism which is visible in the product as well.

Thus, the probable reactions will be

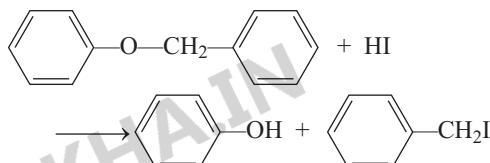


34.



- (a)  $R$  is not steam volatile, but  $Q$  is steam volatile thus, incorrect.
- (b)  $Q$  has enolic group thus, gives violet colour with 1% aqueous  $FeCl_3$  solution thus, correct.
- (c)  $S$  has carbonyl group hence, gives yellow precipitate with 2, 4-DNP thus, correct.
- (d)  $S$  does not give colour with  $FeCl_3$  thus, incorrect.

35.



Phenol does not react further with HI.

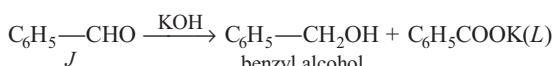
36.  $CH_3CH_2Br + O=\overset{\bullet\bullet}{N}-O^- \xrightarrow[\text{ambient nucleophile}]{\text{nitroethane}} CH_3CH_2NO_2 + CH_3CH_2ONO$

37.  $R-OH \leftarrow \begin{matrix} \text{Hydrophilic} \\ \text{Hydrophobic} \end{matrix}$

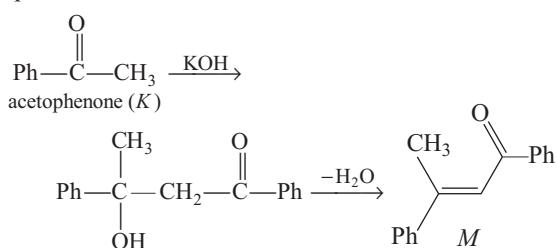
Increasing molecular weight increases hydrocarbon ( $R$ ) proportion that lowers the solubility in water.

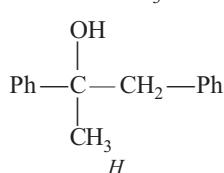
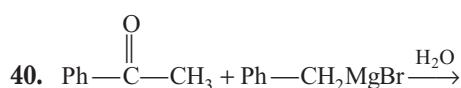
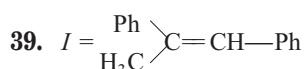
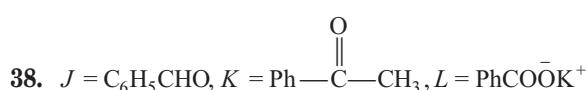
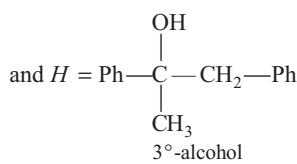
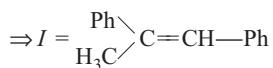
### Passage 1

Compound  $J$  must be benzaldehyde because it on treatment with KOH undergoing Cannizzaro's reaction producing benzyl alcohol and pot-benzoate ( $L$ ).

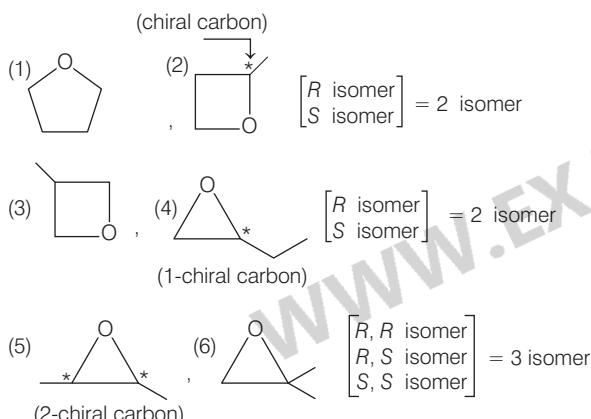


Also  $M$  is aldol condensation product formed from acetophenone

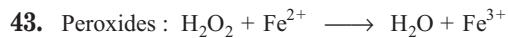
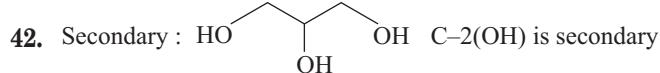




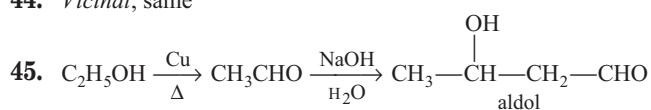
41. The structure of cyclic ether with molecular formula,  $\text{C}_4\text{H}_8\text{O}$  are as follows:



Total number of isomers of cyclic ether with molecular formula,  $\text{C}_4\text{H}_8\text{O}$  are 10.

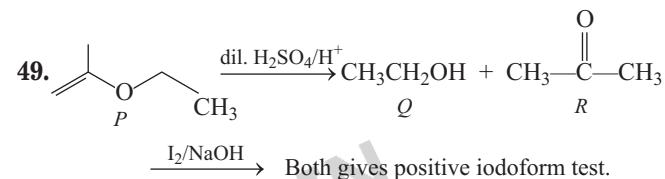
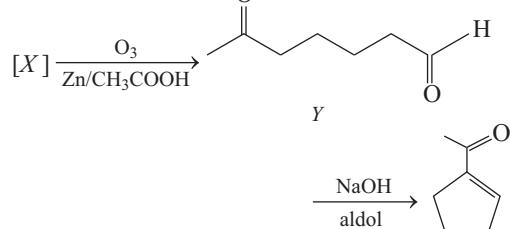
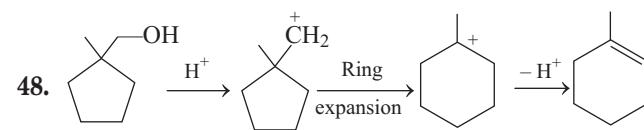


44. Vicinal, same

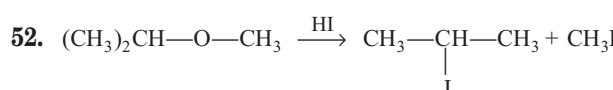
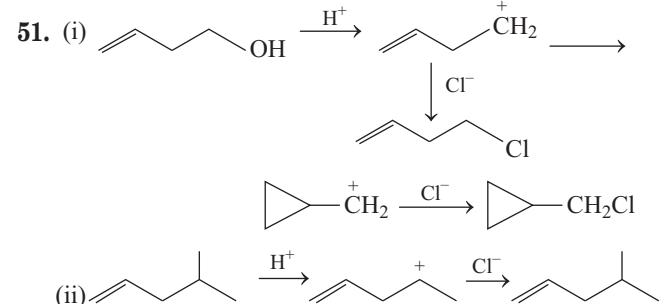
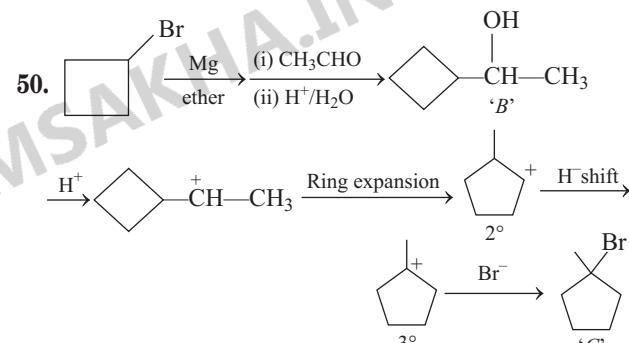


46. Ethanol is weaker acid than water, not neutralised with NaOH.

47. 2°-alcohol on oxidation yields ketone while 1°alcohol on oxidation produces aldehyde which can further be oxidised to acid.

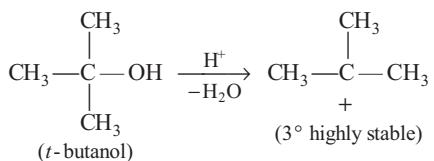


$\xrightarrow{\text{I}_2/\text{NaOH}}$  Both gives positive iodoform test.

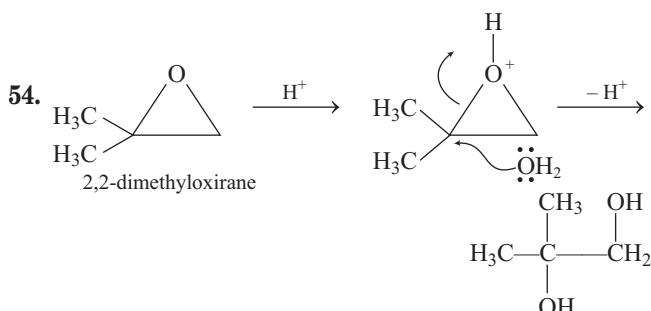


## 376 Alcohols and Ethers

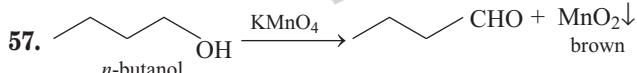
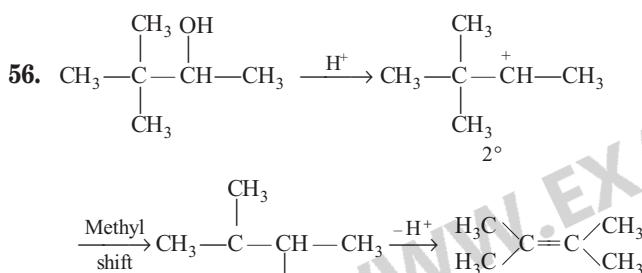
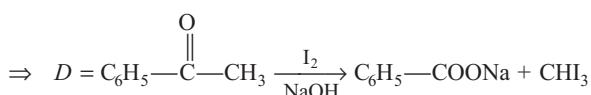
53. Acid catalysed dehydration proceeds via carbocation intermediate. Also, greater the stability of reactive intermediate, faster the reaction :



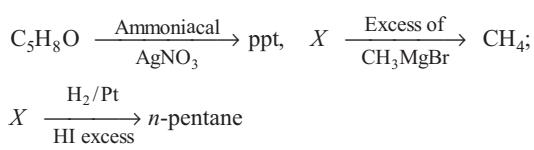
*n*-butanol forms less stable ( $1^\circ$ ) carbocation.



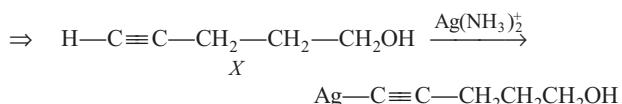
55.  $E = \text{C}_6\text{H}_5\text{COOH}$  (benzoic acid)



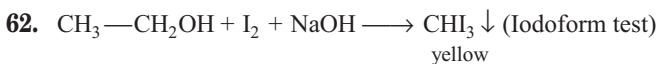
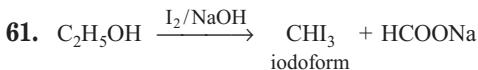
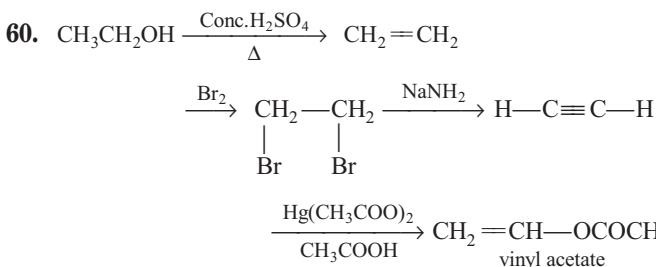
58. Compound 'X'  $\xrightarrow{\text{Lucas reagent}}$  No reaction at room temperature.



Above information suggest that X has a terminal triple bond and it contain primary —OH group.

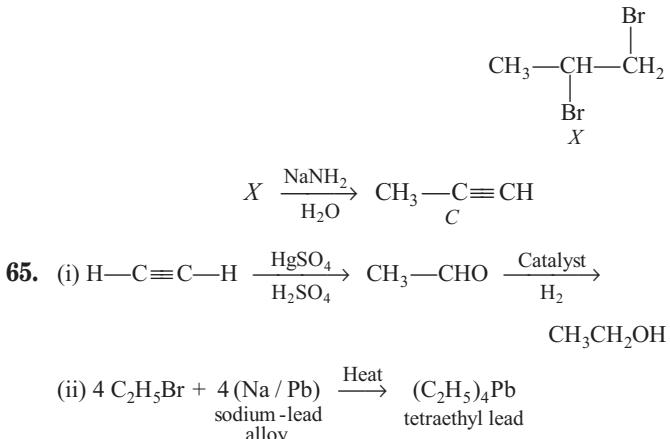
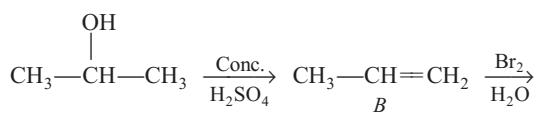
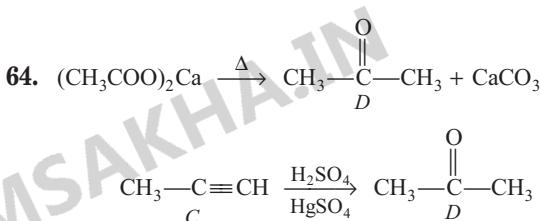


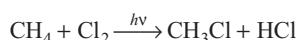
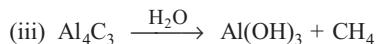
59. Isobutane < *n*-butane < *n*-butylchloride < *n*-butanol



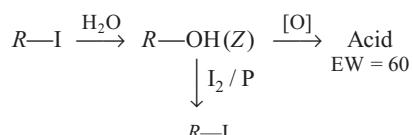
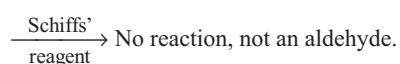
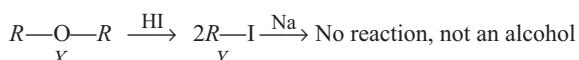
Iodoform test is not given by methanol.

63. Butanol forms intermolecular H-bonds, has higher boiling point than butanal.



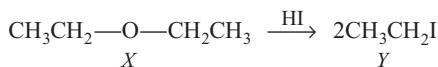


66. Compound *X* must be a symmetrical ether :

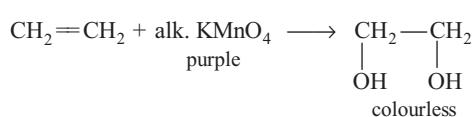
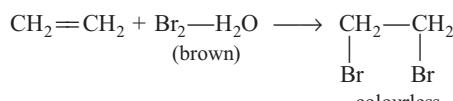
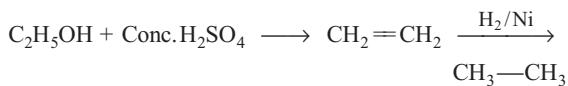


$\Rightarrow$  Acid is  $\text{CH}_3\text{COOH}$  and  $Z = \text{CH}_3\text{CH}_2\text{OH}$

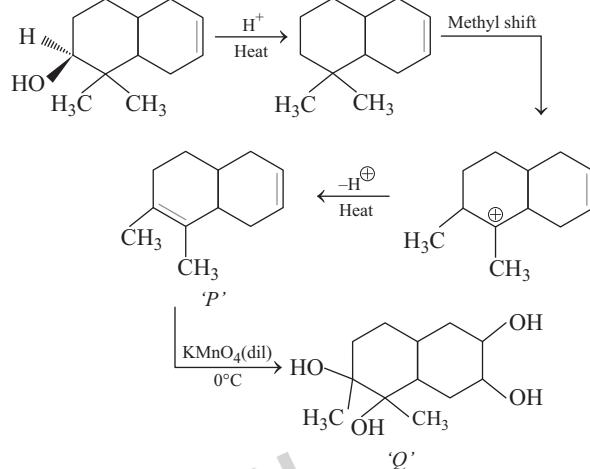
$\Rightarrow X = \text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5, Y = \text{CH}_3-\text{CH}_2-\text{I}$



67. *A* is ethanol because *B* is an alkene (ethene).



68.

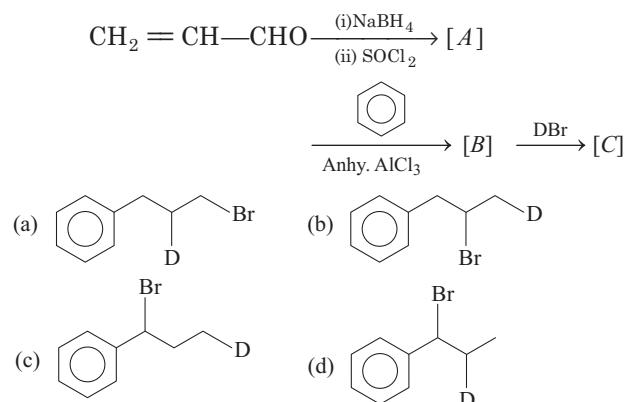


# 25

## Aldehydes and Ketones

### Objective Questions I (Only one correct option)

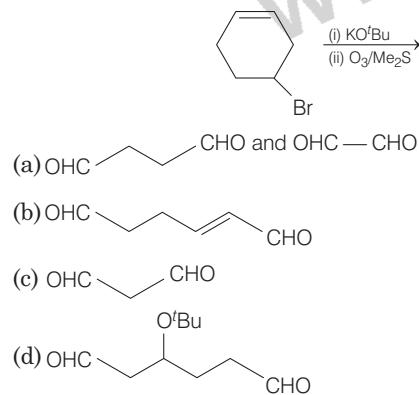
1. The major product [C] of the following reaction sequence will be  
 (2020 Main, 4 Sep II)



2. Which one of the following polymers is not obtained by condensation polymerisation?  
 (2020 Main, 5 Sep II)

(a) Nylon 6,6 (b) Buna-N (c) Bakelite (d) Nylon 6

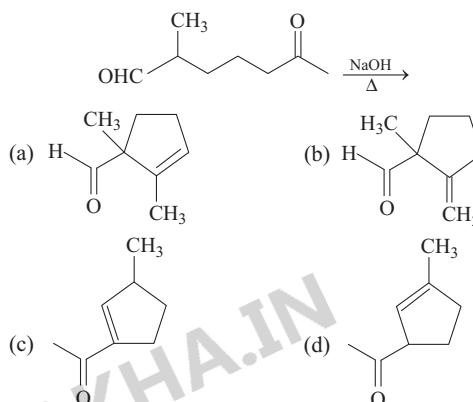
3. The major product(s) obtained in the following reaction is/are  
 (2019 Main, 12 April I)



4. In the following reaction,  
 Carbonyl compound + MeOH  $\xrightleftharpoons{\text{HCl}}$  acetal  
 Rate of the reaction is the highest for:  
 (2019 Main, 9 April II)

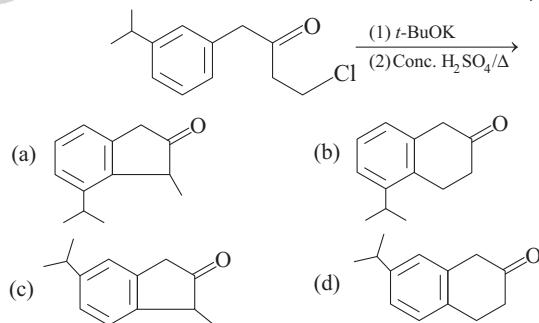
(a) Acetone as substrate and methanol in excess  
 (b) Propanal as substrate and methanol in stoichiometric amount  
 (c) Acetone as substrate and methanol in stoichiometric amount  
 (d) Propanal as substrate and methanol in excess

5. The major product obtained in the following reaction is  
 (2019 Main, 8 April II)

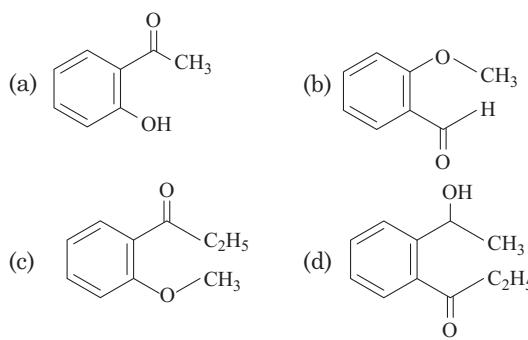


6. The major product of the following reaction is

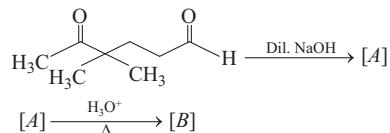
(2019 Main, 8 April II)



7. An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is  
 (2019 Main, 8 April I)



8. In the following reactions, products A and B are  
(2019 Main, 12 Jan I)



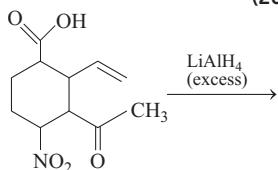
- (a)  $A = \text{HO}-\text{C}_6\text{H}_9-\text{CH}_3$ ;  $B = \text{C}_6\text{H}_9-\text{CH}_3$

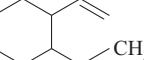
(b)  $A = \text{HO}-\text{C}_6\text{H}_9-\text{CH}_3$ ;  $B = \text{C}_6\text{H}_9-\text{CH}_3$

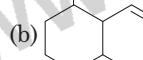
(c)  $A = \text{H}_3\text{C}-\text{C}_4\text{H}_7-\text{CH}_3$ ;  $B = \text{H}_3\text{C}-\text{C}_4\text{H}_7-\text{CH}_3$

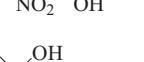
(d)  $A = \text{H}_3\text{C}-\text{C}_4\text{H}_7-\text{CH}_3$ ;  $B = \text{H}_2\text{C}=\text{C}_4\text{H}_7-\text{CH}_3$

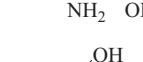
9. The major product obtained in the following reaction is  
(2019 Main, 11 Jan II)



- (a)  O=C1C=CC2=C1C(O)=C(C(=O)N)C=C2

(b)  O=C1C=CC2=C1C(O)=C(N)C=C2

(c)  O=C1C=CC2=C1C(O)=C(C(=O)N)C(=O)C=C2

(d)  O=C1C=CC2=C1C(O)=C(N)C(=O)C=C2

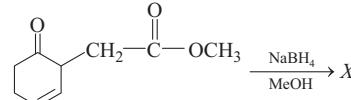
- 10.** The correct match between item 'I' and item 'II' is

| Item 'I'<br>(Compound) |                | Item 'II'<br>(Reagent) |                        |
|------------------------|----------------|------------------------|------------------------|
| (A)                    | Lysine         | (P)                    | 1-naphthol             |
| (B)                    | Furfural       | (Q)                    | Ninhydrin              |
| (C)                    | Benzyl alcohol | (R)                    | KMnO <sub>4</sub>      |
| (D)                    | Styrene        | (S)                    | Ceric ammonium nitrate |

(2019 Main, 10 Jan II)

| <b>Codes</b> | A | B | C | D |
|--------------|---|---|---|---|
| (a)          | Q | R | S | P |
| (b)          | R | P | Q | S |
| (c)          | Q | P | S | R |
| (d)          | Q | P | R | S |

- 11.** The major product 'X' formed in the following reaction is  
**(2019 Main, 10 Jan I)**



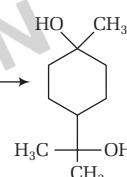
- (a) 

(b) 

(c) 

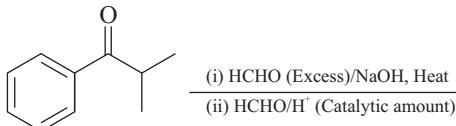
(d) 

- 12.** The correct sequence of reagents for the following conversion will be **(2017 Main)**



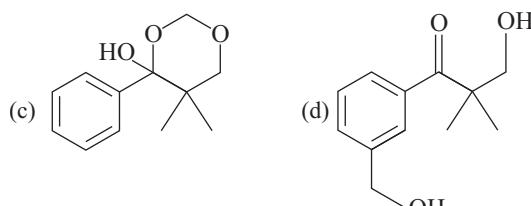
- (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  OH<sup>-</sup>, H<sup>+</sup> / CH<sub>3</sub>OH, CH<sub>3</sub>MgBr  
 (b) CH<sub>3</sub>MgBr, H<sup>+</sup> / CH<sub>3</sub>OH,  $[\text{Ag}(\text{NH}_3)_2]^+$  OH<sup>-</sup>  
 (c) CH<sub>3</sub>MgBr,  $[\text{Ag}(\text{NH}_3)_2]^+$  OH<sup>-</sup>, H<sup>+</sup> / CH<sub>3</sub>OH  
 (d)  $[\text{Ag}(\text{NH}_3)_2]^+$  OH<sup>-</sup>, CH<sub>3</sub>MgBr, H<sup>+</sup> / CH<sub>3</sub>OH

- 13.** The major product of the following reaction sequence is  
(2016 Adv.)



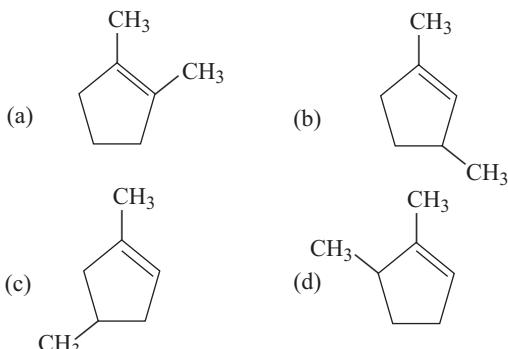
- (a) 

(b) 

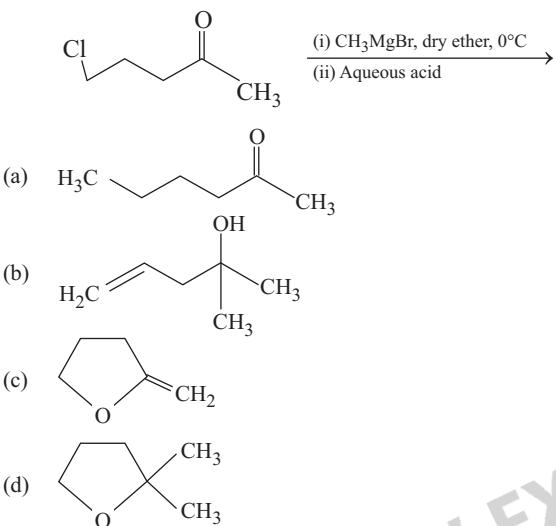


## **380** Aldehydes and Ketones

- 14.** Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? (2015 Main)



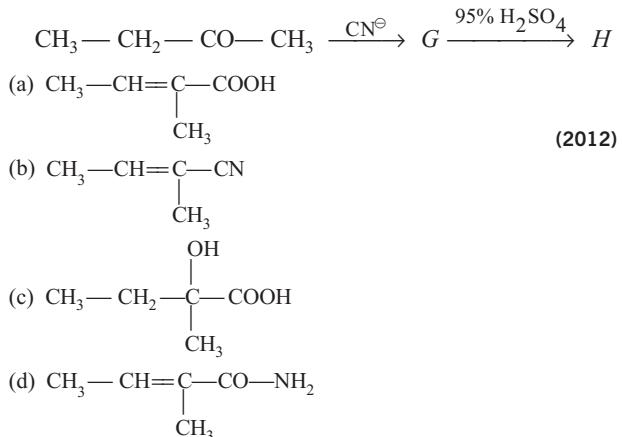
- 15.** The major product in the following reaction is (2014 Adv.)



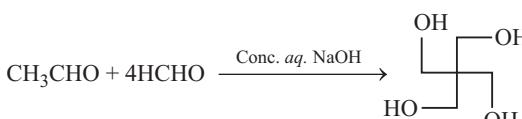
- 16.** The most suitable reagent for the conversion of  $R-\text{CH}_2-\text{OH} \rightarrow R-\text{CHO}$  is (2014 Main)

- (a)  $\text{KMnO}_4$   
 (b)  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (c)  $\text{CrO}_3$   
 (d) PCC (pyridinium chlorochromate)

- 17.** The major product H in the given reaction sequence is

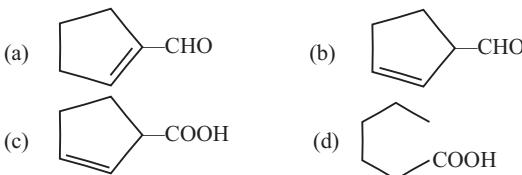


- 18.** The number of aldol reaction(s) that occurs in the given transformation is **(2012)**





19. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound *E*. Compound *E* on further treatment with aqueous KOH yields compound *F*. Compound *F* is (2007, 3M)

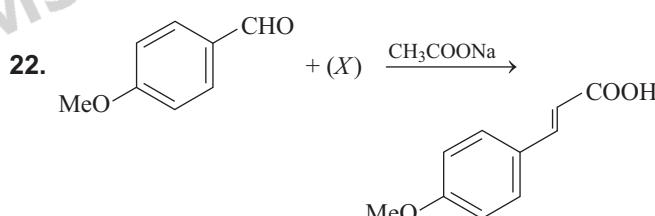


- 20.** The smallest ketone and its next homologue are reacted with  $\text{NH}_2\text{OH}$  to form oxime (2006)

- (a) two different oximes are formed
  - (b) three different oximes are formed
  - (c) two oximes are optically active
  - (d) all oximes are optically active

- 21.** Butan-2-one can be converted to propanoic acid by which of the following ? (2006)

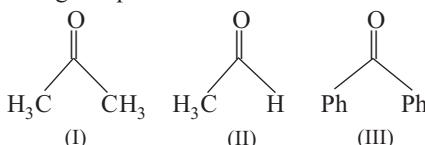
- (a) NaOH, NaI/H<sup>+</sup>      (b) Fehling's solution  
 (c) NaOH, I<sub>2</sub>/H<sup>+</sup>      (d) Tollen's reagent



What is  $X$ ?

- (a)  $\text{CH}_3\text{COOH}$       (b)  $\text{BrCH}_2\text{COOH}$   
 (c)  $(\text{CH}_3\text{CO})_2\text{O}$       (d)  $\text{HOC}-\text{COOH}$

- 23.** The order of reactivity of phenyl magnesium bromide with the following compounds is (2004, 1M)

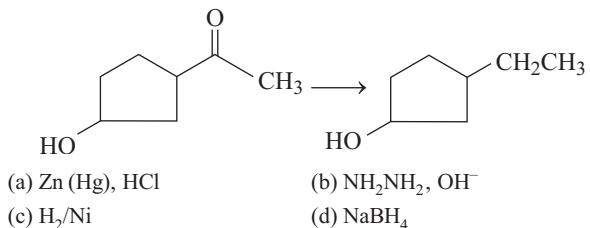


- (a) (II) > (III) > (I)      (b) (I) > (III) > (II)  
 (c) (II) > (I) > (III)      (d) All of the above

- 24.** A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives (2001, 1M)

- (a) benzyl alcohol and sodium formate
  - (b) sodium benzoate and methyl alcohol
  - (c) sodium benzoate and sodium formate
  - (d) benzyl alcohol and methyl alcohol

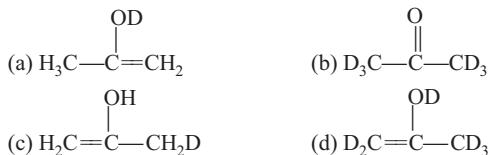
25. The appropriate reagent for the following transformation:



26. Which of the following has the most acidic hydrogen? (2000, 1M)

- (a) 3-hexanone  
 (b) 2, 4-hexanedione  
 (c) 2, 5-hexanedione  
 (d) 2, 3-hexanedione

27. The enol form of acetone, after treatment with D<sub>2</sub>O, gives (1999, 2M)



28. Which of the following will react with water? (1998, 2M)

- (a) CHCl<sub>3</sub>  
 (b) Cl<sub>3</sub>CCHO  
 (c) CCl<sub>4</sub>  
 (d) ClCH<sub>2</sub>CH<sub>2</sub>Cl

29. Which of the following compounds is oxidised to prepare methyl ethyl ketone? (1987, 1M)

- (a) 2-propanol  
 (b) 1-butanol  
 (c) 2-butanol  
 (d) *t*-butyl alcohol

30. The compound that will not give iodoform on treatment with alkali and iodine is (1985, 1M)

- (a) acetone  
 (b) ethanol  
 (c) diethyl ketone  
 (d) isopropyl alcohol

31. The Cannizzaro's reaction is not given by (1983, 1M)

- (a) trimethyl acetaldehyde  
 (b) acetaldehyde  
 (c) benzaldehyde  
 (d) formaldehyde

32. When acetaldehyde is treated with Fehling's solution, it gives a precipitate of (1983, 1M)

- (a) Cu  
 (b) CuO  
 (c) Cu<sub>2</sub>O  
 (d) Cu + Cu<sub>2</sub>O + CuO

33. A compound that gives a positive iodoform test is (1982, 1M)

- (a) 1-pentanol  
 (b) 3-pentanone  
 (c) 2-pentanone  
 (d) pentanal

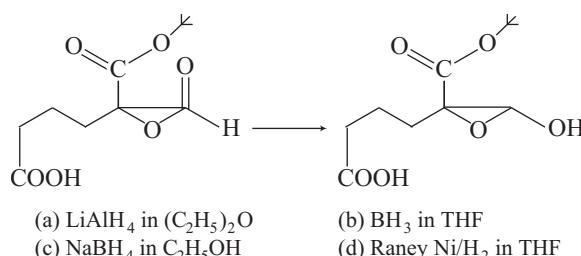
34. The reagent with which both acetaldehyde and acetone react easily is (1981, 1M)

- (a) Tollen's reagent  
 (b) Schiff's reagent  
 (c) Grignard's reagent  
 (d) Fehling's reagent

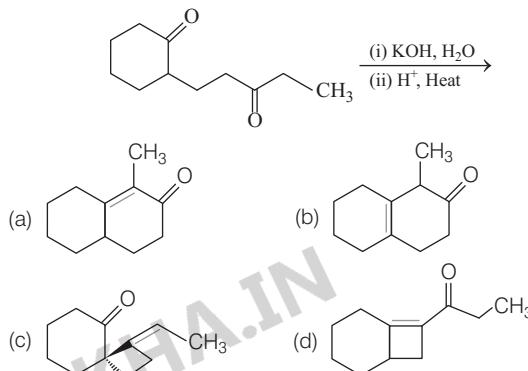
### Objective Questions II

(One or more than one correct option)

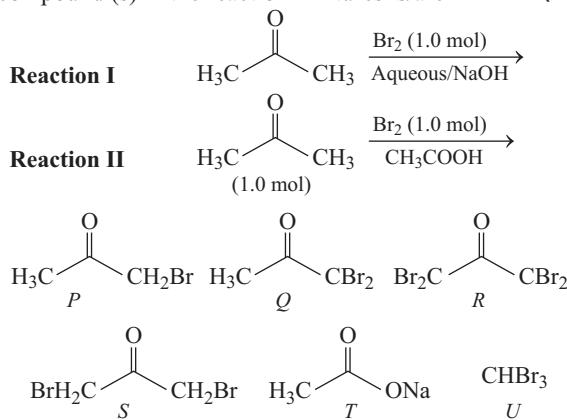
35. Reagent(s) which can be used to bring about the following transformation is (are) (2016 Adv.)



36. The major product of the following reaction is (2015 Adv.)

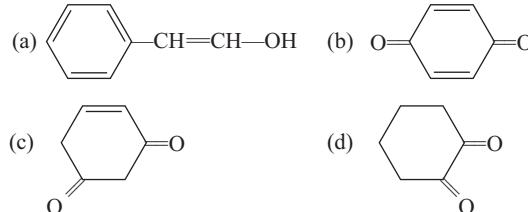


37. After completion of the reactions (I and II), the organic compound (s) in the reaction mixtures is/are (2013)



- (a) reaction I : P and reaction II : P  
 (b) reaction I : U, acetone and reaction II : Q, acetone  
 (c) reaction I : T, U, acetone and reaction II : P  
 (d) reaction I : R, acetone and reaction II : S, acetone

38. Tautomerism is exhibited by (1998)



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39. A new carbon–carbon bond formation is possible in  
(1998, 2M)

(a) Cannizzaro's reaction      (b) Friedel-Crafts' reaction  
 (c) Clemmensen's reduction    (d) Reimer-Tiemann reaction

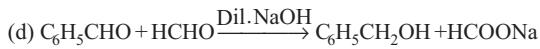
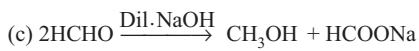
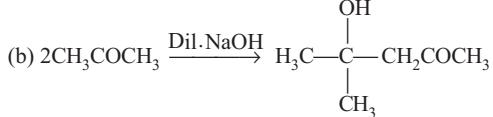
40. Which of the following will undergo aldol condensation?  
(1998, 2M)

(a) Acetaldehyde      (b) Propanaldehyde  
 (c) Benzaldehyde      (d) Trideutero acetaldehyde

41. Among the following compounds, which will react with acetone to give a product containing  $\text{C}=\text{N}-$ ?  
(1998, 2M)

(a)  $\text{C}_6\text{H}_5\text{NH}_2$       (b)  $(\text{CH}_3)_3\text{N}$   
 (c)  $\text{C}_6\text{H}_5\text{NHCO}_2\text{H}_5$     (d)  $\text{C}_6\text{H}_5\text{NHNH}_2$

42. Which of the following is an example of aldol condensation?



43. Which of the following compounds will react with ethanolic KCN?  
(1984, 1M)

(a) Ethyl chloride      (b) Acetyl chloride  
 (c) Chlorobenzene      (d) Benzaldehyde

44. Which of the following compounds will give a yellow precipitate with iodine and alkali?  
(1984, 1M)

(a) 2-hydroxy propane      (b) Acetophenone  
 (c) Methyl acetate      (d) Acetamide

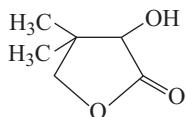
45. Base catalysed aldol condensation occurs with  
(1984, 1M)

(a) propionaldehyde      (b) benzaldehyde  
 (c) 2-methyl propionaldehyde    (d) 2, 2-dimethyl propionaldehyde

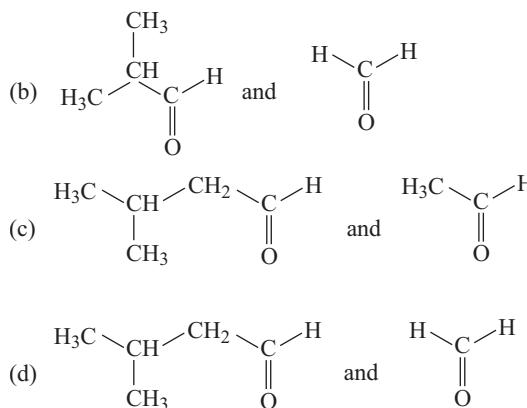
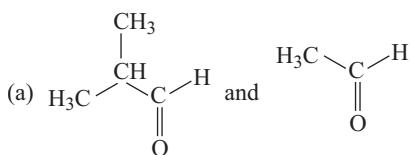
### Passage Based Questions

#### Passage 1

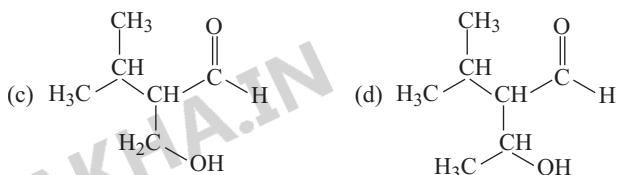
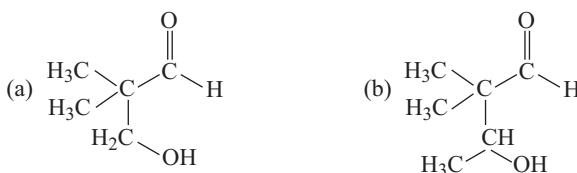
Two aliphatic aldehydes  $P$  and  $Q$  react in the presence of aqueous  $\text{K}_2\text{CO}_3$  to give compound  $R$ , which upon treatment with HCN provides compound  $S$ . On acidification and heating,  $S$  gives the product shown below :  
(2010)



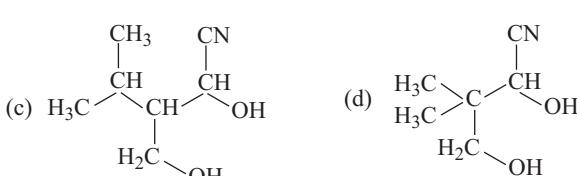
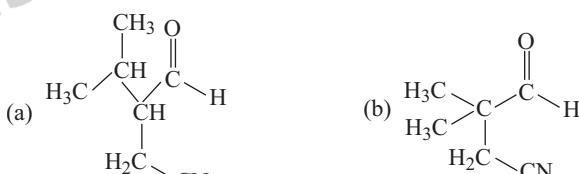
46. The compounds  $P$  and  $Q$  respectively are



47. The compound  $R$  is

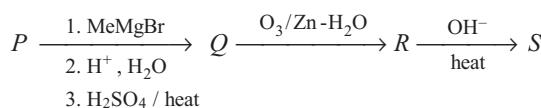


48. The compound  $S$  is

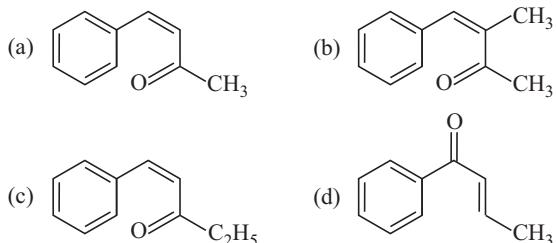


#### Passage 2

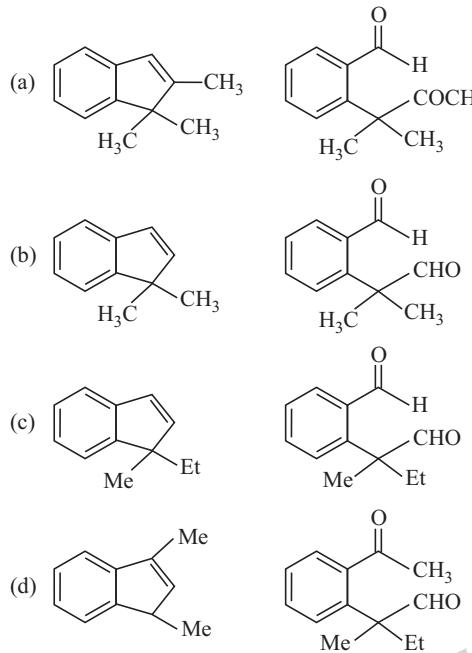
A carbonyl compound  $P$ , which gives positive iodoform test, undergoes reaction with  $\text{MeMgBr}$  followed by dehydration to give an olefin  $Q$ . Ozonolysis of  $Q$  leads to a dicarbonyl compound  $R$ , which undergoes intramolecular aldol reaction to give predominantly  $S$ .  
(2009)



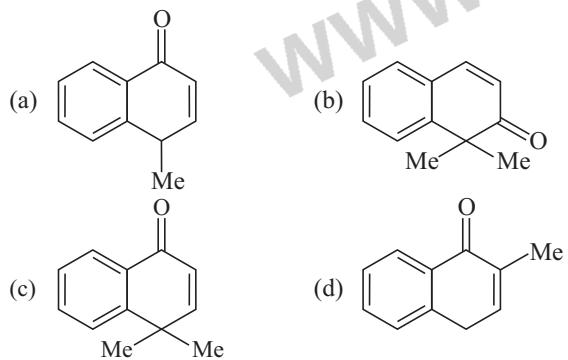
49. The structure of the carbonyl compound *P*, is



50. The structures of the products *Q* and *R*, respectively, are

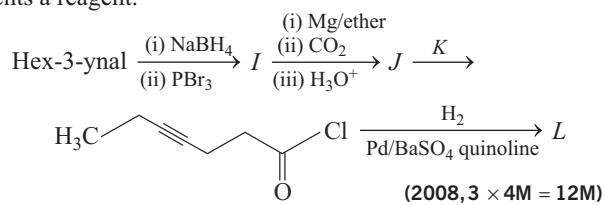


51. The structure of the product *S*, is

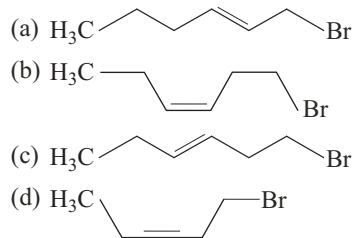


### Passage 3

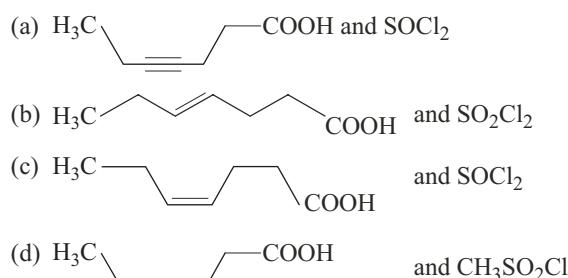
In the following sequence, product *I*, *J* and *L* are formed. *K* represents a reagent.



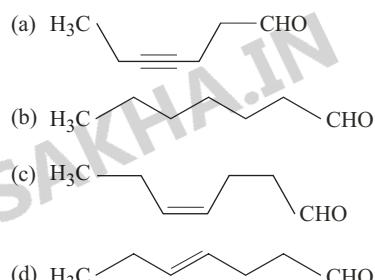
52. The structure of the product *I* is



53. The structures of compounds *J* and *K*, respectively, are



54. The structure of product *L* is



### Match the Columns

55. Match each of the compounds given in Column I with the reaction(s) that they can undergo, given in Column II.

| Column I |    | Column II                            |
|----------|----|--------------------------------------|
| A.       | p. | Nucleophilic substitution            |
| B.       | q. | Elimination                          |
| C.       | r. | Nucleophilic addition                |
| D.       | s. | Esterification with acetic anhydride |
|          | t. | Dehydrogenation                      |

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56. Match the compounds/ions in Column I with their properties/reactions in Column II. (2007, 6M)

| Column I                                | Column II                                             |
|-----------------------------------------|-------------------------------------------------------|
| A. $\text{C}_6\text{H}_5\text{CHO}$     | p. gives precipitate with 2, 4-dinitrophenylhydrazine |
| B. $\text{CH}_3\text{C}\equiv\text{CH}$ | q. gives precipitate with $\text{AgNO}_3$             |
| C. $\text{CN}^-$                        | r. is a nucleophile                                   |
| D. $\Gamma^-$                           | s. is involved in cyanohydrin formation               |

### Fill in the Blank

57. Fehling's solution A consists of an aqueous solution of copper sulphate, while Fehling's solution B consists of an alkaline solution ..... (1990, 1M)

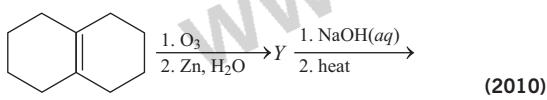
### True or False

58. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. (1987, 1M)  
 59. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982, 1M)

### Integer Answer Type Questions

60. Consider all possible isomeric ketones including stereoisomers of MW = 100. All these isomers are independently reacted with  $\text{NaBH}_4$ . The total number of ketones that gives a racemic product(s) is/are  
**NOTE** (Stereoisomers are also reacted separately). (2014 Adv.)

61. In the scheme given below, the total number of intramolecular aldol condensation products formed from Y is



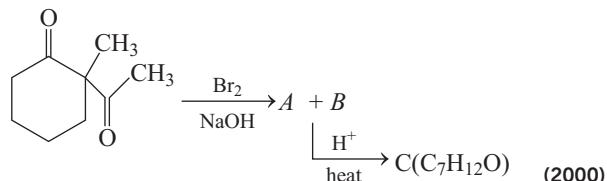
### Subjective Questions

62. (A),  $\text{C}_6\text{H}_{12} \xrightarrow{\text{HCl}} (\text{B}), \text{C}_6\text{H}_{13}\text{Cl} + (\text{C}), \text{C}_6\text{H}_{13}\text{Cl}$   
 $(\text{B}) \xrightarrow{\text{Alcoholic KOH}} (\text{D}),$  (an isomer of (A))  
 $(\text{D}) \xrightarrow{\text{Ozonolysis}} (\text{E}),$  (positive iodoform and negative Fehling's solution test)  
 $(\text{A}) \xrightarrow{\text{Ozonolysis}} (\text{F}) + (\text{G}),$  (positive Tollen's test for both)  
 $(\text{F}) + (\text{G}) \xrightarrow{\text{Conc. NaOH}} \text{HCOONa} + \text{A primary alcohol}$   
 Identify the compounds (A) to (D). (2003)

63. A compound  $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$  exists predominantly in enol form (A) and also in keto form (B). On oxidation with  $\text{KMnO}_4$  it gives m-chlorobenzoic acid as one of the products. Identify the compounds (A) and (B). (2003)

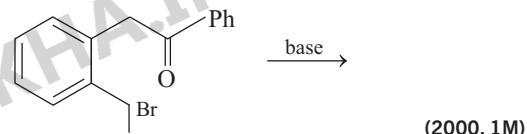
64. An alkene (A)  $\text{C}_{16}\text{H}_{16}$  on ozonolysis gives only one product (B)  $\text{C}_8\text{H}_8\text{O}$ . Compound (B) on reaction with  $\text{NaOH}/\text{I}_2$  yields sodium benzoate. Compound (B) reacts with  $\text{KOH}/\text{NH}_2\text{NH}_2$  yielding a hydrocarbon (C)  $\text{C}_8\text{H}_{10}$ . Write the structures of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation ( $\text{H}_2/\text{Pd-C}$ ) gives a racemic mixture. (2001, 5M)

65. Identify A, B and C, and give their structures.

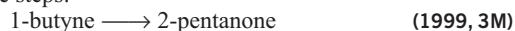


66. An organic compound A,  $\text{C}_6\text{H}_{10}\text{O}$ , on reaction with  $\text{CH}_3\text{MgBr}$  followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetyl cyclopentane D. The compound B on reaction with  $\text{HBr}$  gives compound E. Write the structures of A, B, C and E. Show, how D is formed from C. (2000, 5M)

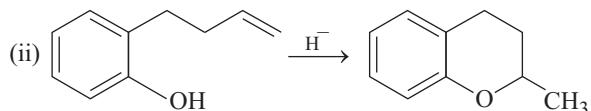
67. What would be the major product in the following reaction?



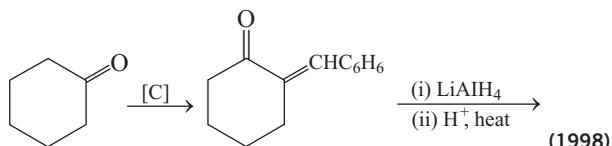
68. (a) Compound A ( $\text{C}_8\text{H}_8\text{O}$ ) on treatment with  $\text{NH}_2\text{OH}, \text{HCl}$  given B and C. B and C rearrange to give D and E, respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula ( $\text{C}_8\text{H}_9\text{NO}$ ). When D is boiled with alcoholic KOH, an oil F ( $\text{C}_6\text{H}_7\text{N}$ ) separates out. F reacts rapidly with  $\text{CH}_3\text{COCl}$  to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G ( $\text{C}_7\text{H}_6\text{O}_2$ ). Identify A-G.  
 (b) Carry out the following transformation in not more than three steps.



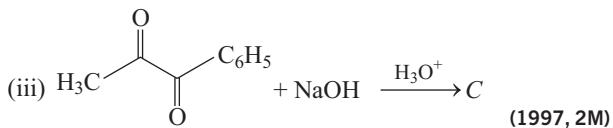
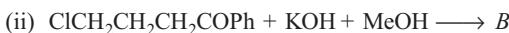
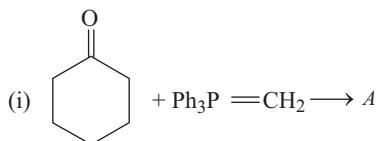
69. Write the intermediate steps for each of the following reactions



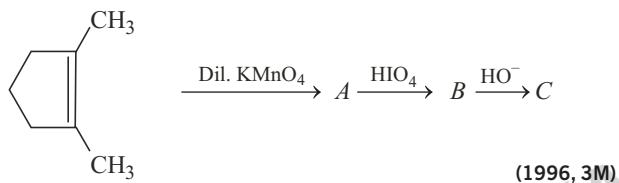
70. Complete the following reactions with appropriate structures of products/reagents.



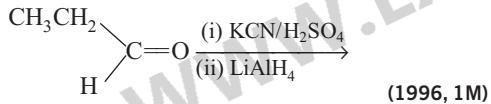
- 71.** An aldehyde *A* ( $C_{11}H_8O$ ), which does not undergo self aldol condensation, gives benzaldehyde and two moles of *B* on ozonolysis. Compound *B*, on oxidation with silver ion gives oxalic acid. Identify the compounds *A* and *B*. (1998, 2M)
- 72.** Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oxime. (1997, 2M)
- 73.** Complete the following, giving the structures of the principal organic products,



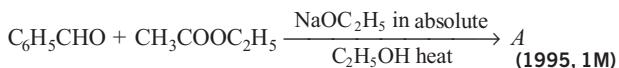
- 74.** Suggest appropriate structures for the missing compounds. (the number of carbon atoms remains the same throughout the reaction)



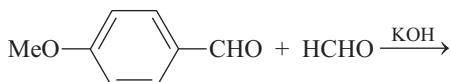
- 75.** Complete the following reaction with appropriate structure :



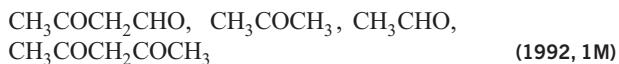
- 76.** Complete the following reaction with appropriate structure.



- 77.** Write the structure of the major organic product expected from the following reaction. (1992, 1M)



- 78.** Arrange the following in the increasing order of expected enol content.



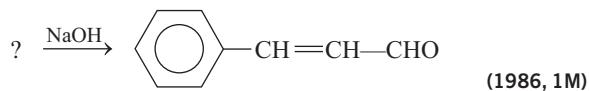
- 79.** Give reason in one or two sentences : "Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide". (1991)

- 80.** A ketone *A*, which undergoes haloform reaction, gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms mono-ozonide *D*. *D* on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify *A*, *B* and *C*. Write down the reactions involved. (1989, 4M)

- 81.** Answer the followings with suitable equations wherever necessary

- (i) suggest a reagent to distinguish acetaldehyde from acetone.  
(ii) what happens when excess chlorine is passed through boiling toluene in the presence of sunlight? (1987, 2M)

- 82.** Complete the following with appropriate structures



- 83.** How may the following transformation be carried out (in not more than six steps) "benzaldehyde to cyanobenzene"? (1986, 2M)

- 84.** Give reason in one or two sentences for the following: "Hydrazone of aldehydes and ketones are not prepared in highly acidic medium". (1986, 1M)

- 85.** Write down product of the following reaction



- 86.** Arrange the following in order of their increasing reactivity towards HCN :



- 87.** Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis: "Acetoxime from acetaldehyde." [K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> / H<sup>+</sup>, Ca(OH)<sub>2</sub> and NH<sub>2</sub>OH, HCl] (1984, 2M)

- 88.** Show with balanced equation, what happens, when the following are mixed :

"Chloral is heated with aqueous hydroxide" (1984, 2M)

- 89.** An alkene *A* on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid *B*. When *B* is treated with bromine in presence of phosphorus yields a compound *C* which on hydrolysis gives a hydroxyl acid *D*. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds *A*, *B*, *C* and *D*. (1982, 2M)

- 90.** Outline the reaction sequence for the conversion of methanal to ethanol (the number of steps should not be more than three). (1981, 2M)

- 91.** Write the structural formula of the main organic product formed when methanal reacts with ammonia. (1981, 1/2M)

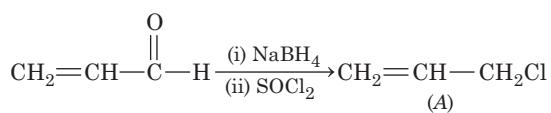
## 386 Aldehydes and Ketones

## Answers

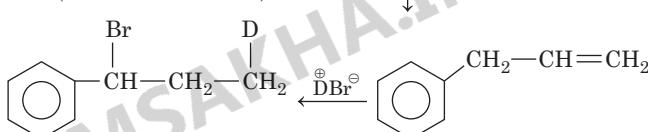
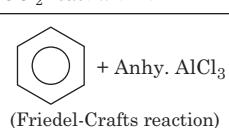
- |         |         |         |         |                                                          |             |             |             |
|---------|---------|---------|---------|----------------------------------------------------------|-------------|-------------|-------------|
| 1. (c)  | 2. (b)  | 3. (a)  | 4. (d)  | 37. (c)                                                  | 38. (a,c,d) | 39. (b,d)   | 40. (a,b,d) |
| 5. (c)  | 6. (d)  | 7. (d)  | 8. (b)  | 41. (a,d)                                                | 42. (a,b)   | 43. (a,b,d) | 44. (a,b)   |
| 9. (b)  | 10. (c) | 11. (b) | 12. (a) | 45. (a,c)                                                | 46. (b)     | 47. (a)     | 48. (d)     |
| 13. (a) | 14. (b) | 15. (d) | 16. (d) | 49. (b)                                                  | 50. (a)     | 51. (b)     | 52. (d)     |
| 17. (a) | 18. (c) | 19. (a) | 20. (b) | 53. (a)                                                  | 54. (c)     |             |             |
| 21. (c) | 22. (c) | 23. (c) | 24. (a) | 55. (A → p, q, t    B → p, s, t    C → r, s    D → p)    |             |             |             |
| 25. (b) | 26. (b) | 27. (b) | 28. (b) | 56. (A → p, q, s    B → q, r    C → q, r, s    D → q, r) |             |             |             |
| 29. (c) | 30. (c) | 31. (b) | 32. (c) | 57. (Sodium potassium tartarate)                         |             |             |             |
| 33. (c) | 34. (c) | 35. (c) | 36. (a) | 58. (False)                                              | 59. (False) | 60. (5)     | 61. (1)     |

## Hints & Solutions

1.



(i)  $\text{NaBH}_4$  reduce  $\overset{\text{O}}{\underset{\parallel}{\text{C}}}$  group in  $-\text{OH}$  and then  
(ii)  $\text{SOCl}_2$  react with it

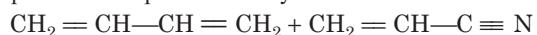


Step I  $\text{NaBH}_4$  reduce  $\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$  group into alcohol.  
Step II  $\text{SOCl}_2$  react with this alcohol and form  $R-X$ .

Step III This  $R-X$  react with benzene in the presence of anhydrous  $\text{AlCl}_3$  via Friedel-Crafts reaction and form product.

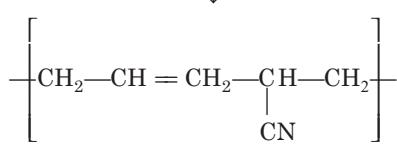
Step IV  $\text{DBr}$  react with this product and form rearranged product.

2. Buna-N is an addition polymer. It is obtained by copolymerisation of 1, 3-butadiene and acrylonitrile in the presence of a peroxide catalyst.



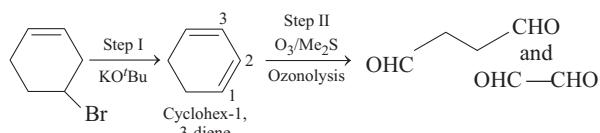
Buta-1, 3-diene

Acrylonitrile

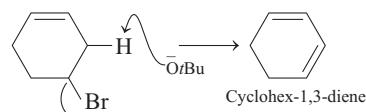


Nitrile rubber (Buna-N)

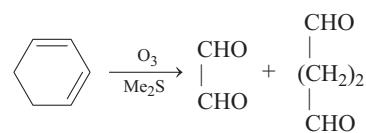
3.



In step-1 dehydrohalogenation reaction takes place. Here, hydrogen is eliminated from  $\beta$ -carbon and the halogen is lost from  $\alpha$ -carbon atom. As a result diene is formed.

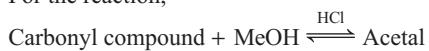


Cyclohex-1, 3-diene on ozonolysis gives butane-1, 4- dial and ethane- 1, 2- dial.

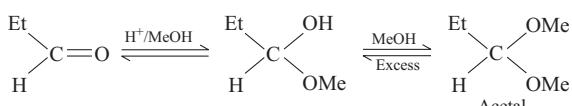


4. **Key Idea** Aldehydes are more reactive than ketones in nucleophilic addition reactions.

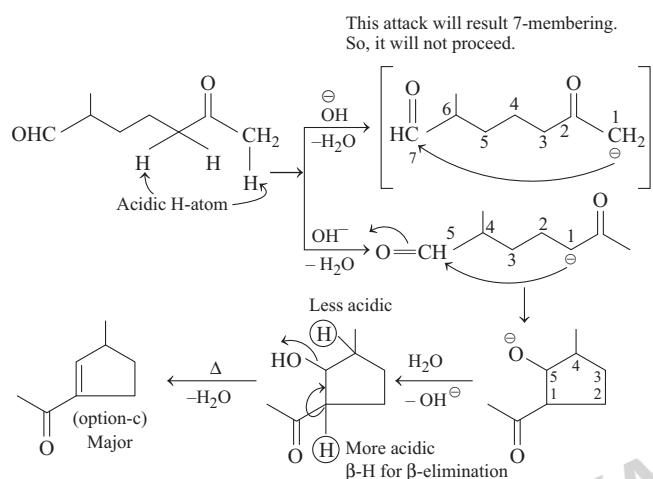
For the reaction,



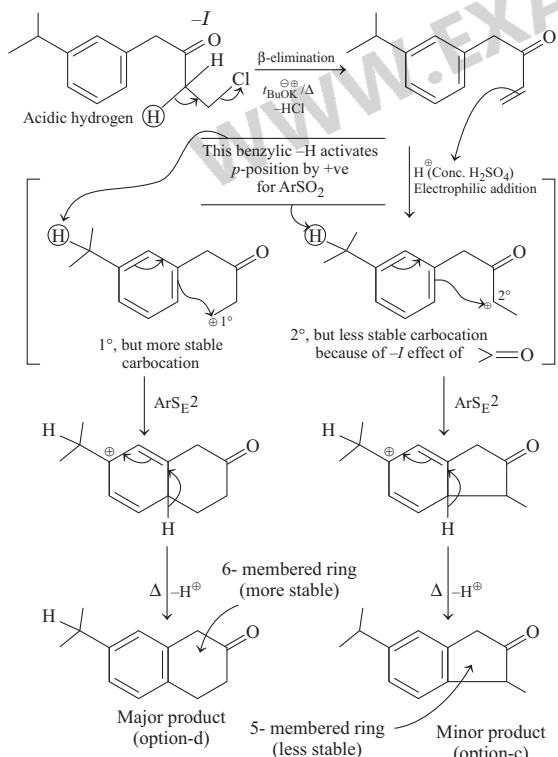
Rate of reaction is the highest for propanal as substrate and methanol in excess. Propanal is an aldehyde and more reactive than ketones. When MeOH is taken in excess then reaction moves in the forward direction that results in the formation of acetal. Reaction involved is as follows :



5. It is an intramolecular aldol condensation reaction.

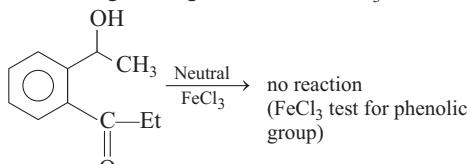


- 6.

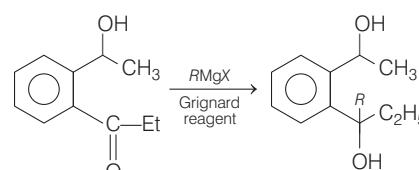


7. According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test.

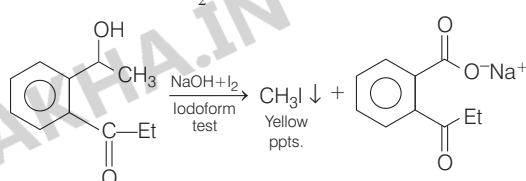
- As the compound does not contain any phenolic —OH group. Hence, it gives negative neutral  $\text{FeCl}_3$  test.



- Compound gives reaction with  $\text{RMgX}$  as it contains  $\text{—C—Et}$ .

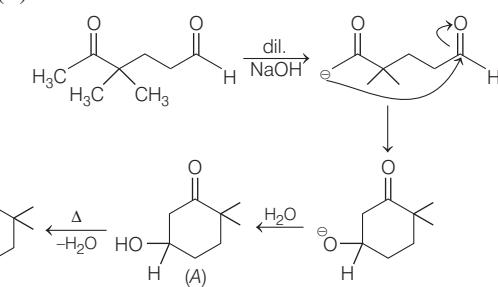


Compound with  $\text{CH}_3\text{CH}_2$  — group undergoes iodoform test in presence of  $\text{NaOH}$  and  $\text{I}_2$ .

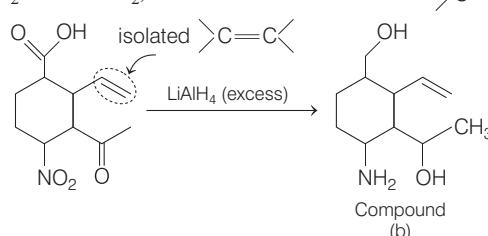


8. The reactant in presence of dil.  $\text{NaOH}$  undergoes intramolecular aldol condensation reaction.

As a result of this,  $\beta$ -hydroxyketone (*A*) is obtained which on hydrolysis followed by heating produces  $\alpha,\beta$ -unsaturated ketone (*B*).



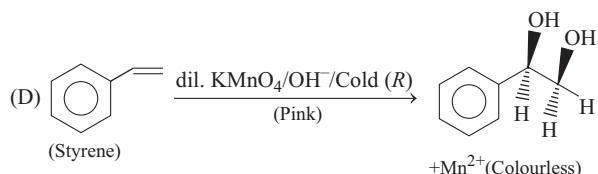
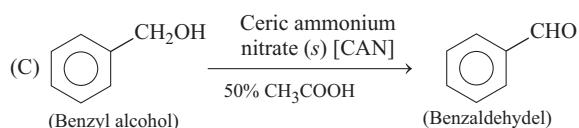
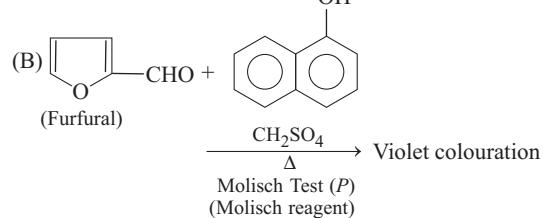
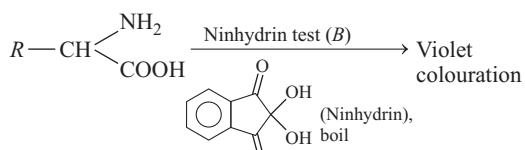
9.  $\text{LiAlH}_4$  acts as a nucleophilic reducing agent that can reduce  $—\text{COOH}$  to  $—\text{CH}_2\text{OH}$ ,  $—\text{C=O}$  into  $—\text{CH(OH)}\text{—}$  and  $—\text{NO}_2$  into  $—\text{NH}_2$ , but it cannot reduce isolated  $>\text{C=C}<$



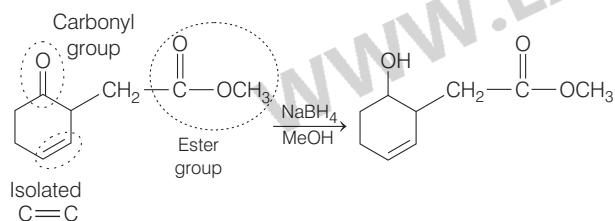
## 388 Aldehydes and Ketones

10. (A)  $\rightarrow$  Q; B  $\rightarrow$  (P); C  $\rightarrow$  (S), D  $\rightarrow$  (R)

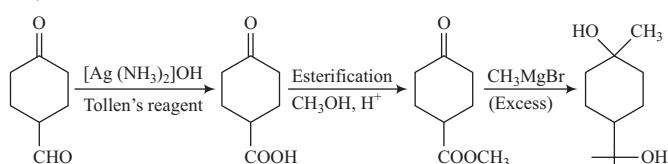
(A) Lysine ( $R=-(CH_2)_4-NH_2$ )



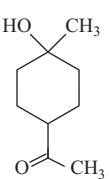
11.  $NaBH_4$  is a selective reducing agent. It reduces carbonyl ( $>C=O$ ) group into an alcohol but cannot reduce an isolated  $C=C$  and an ester group too.



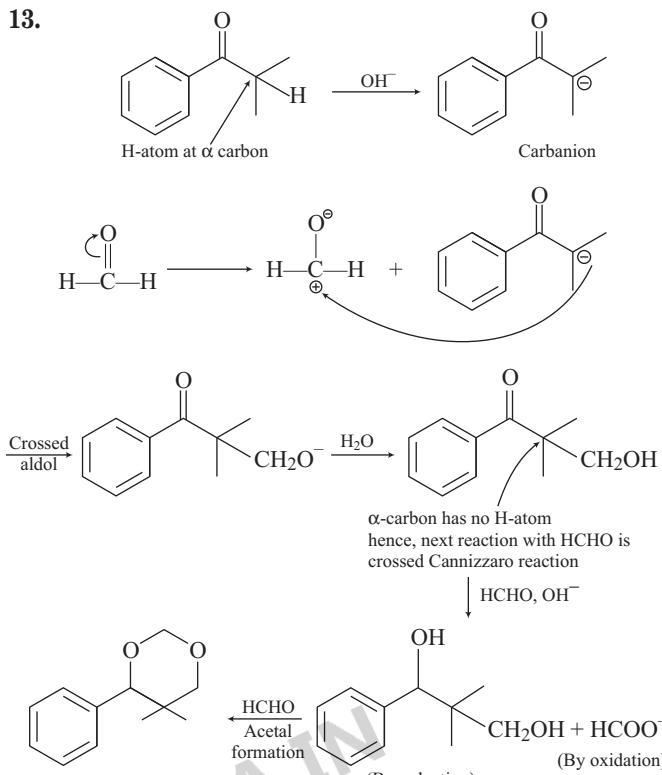
12.



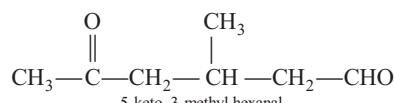
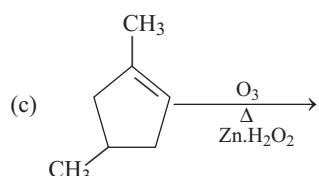
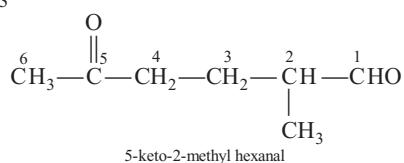
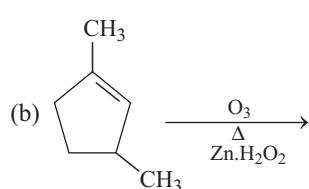
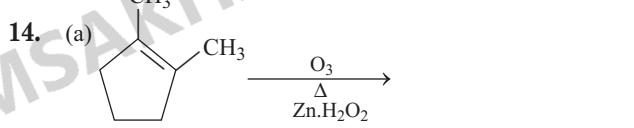
Before final product is formed, intermediate is

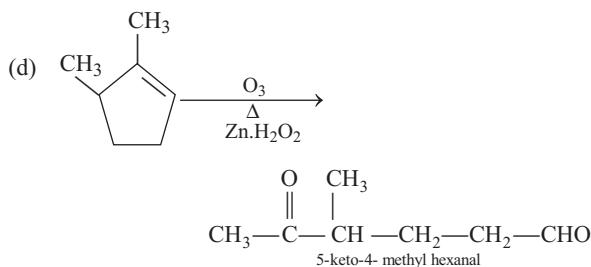


13.



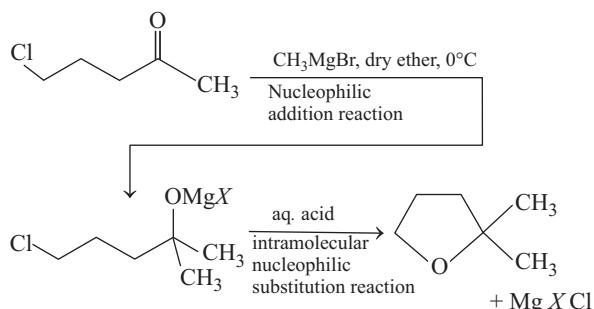
14.





- 15. PLAN** This problem includes concept of nucleophilic addition reaction to carbonyl compound (ketone here) and intramolecular nucleophilic substitution reaction.

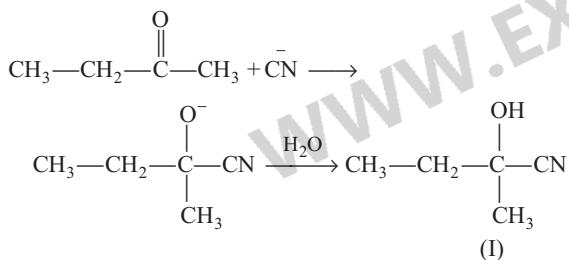
Complete reaction sequence is as shown below:



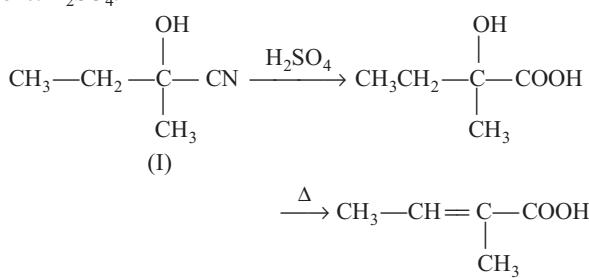
- 16.**  $\text{R---CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{R---CH=O}$

Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

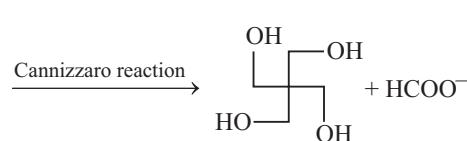
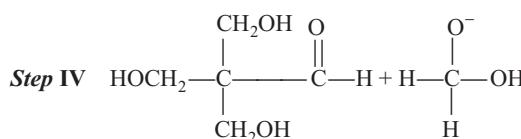
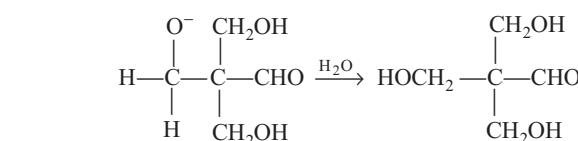
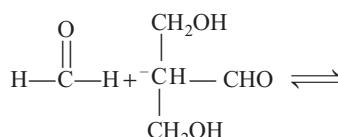
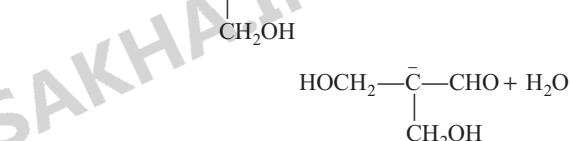
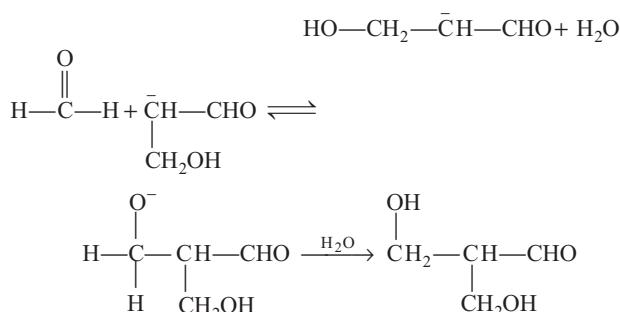
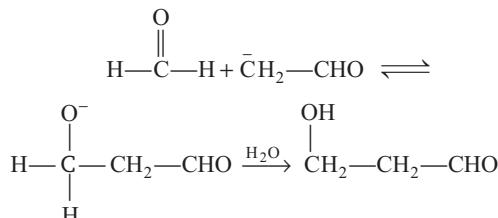
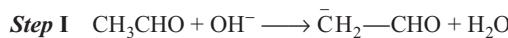
- 17.** The first step is cyanohydrin reaction



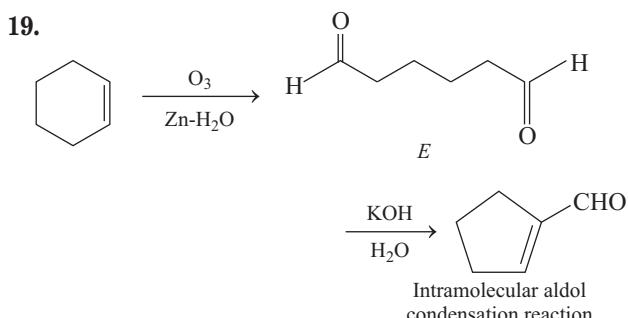
In the second step the —CN of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc.  $\text{H}_2\text{SO}_4$ .



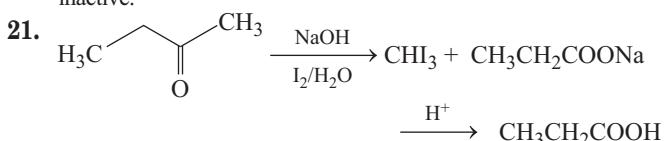
- 18.** The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.



## 390 Aldehydes and Ketones

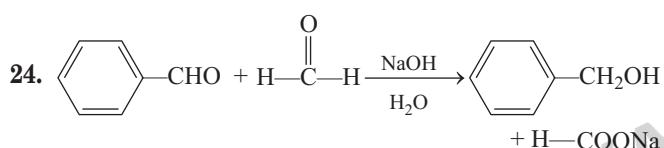
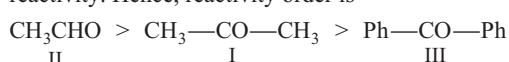


20. Three different oximes are formed out of which two are optically active i.e. exists as a pair of enantiomers while other is optically inactive.

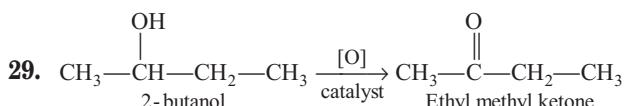
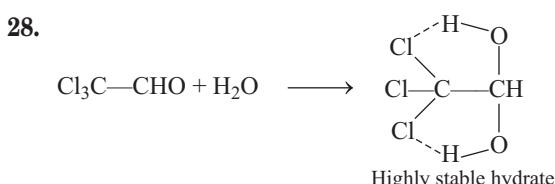
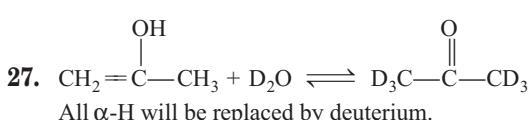
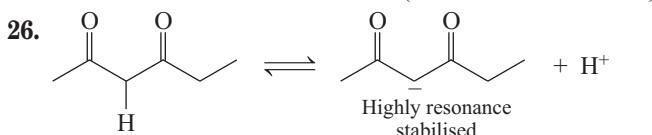
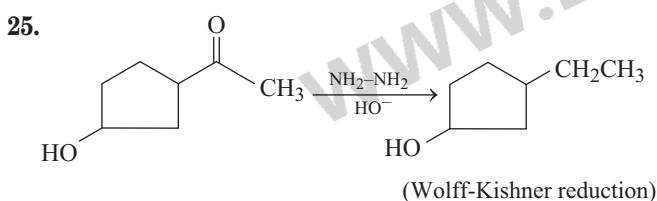


22. X is  $(\text{CH}_3\text{CO})_2\text{O}$  and it is an example of Perkin's reaction.

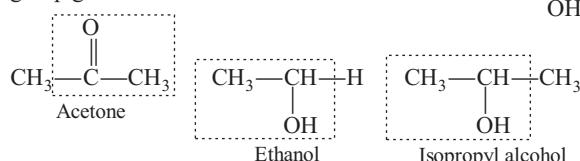
23. The reactivity of carbonyl compound towards nucleophilic addition of Grignard's reagent depends on extent of steric hindrance at  $\alpha$ -carbon. Greater the steric hindrance smaller the reactivity. Hence, reactivity order is



This is an example of cross Cannizzaro reaction in which formaldehyde is always oxidised.

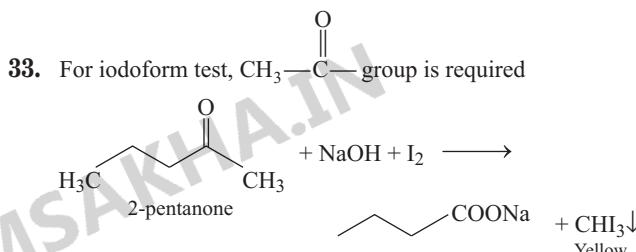


30. Compounds that contain either  $\text{CH}_3-\text{CO}$  or  $\text{CH}_3-\overset{\text{OH}}{\underset{\text{OH}}{|}\text{CH}-}$  group gives iodoform test :



Above three compounds has the desired group for iodoform test. Diethyl ketone does not has the required group for iodoform test.

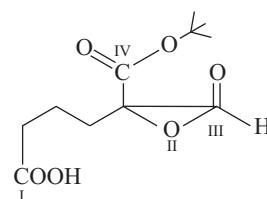
31. Aldehydes lacking presence of  $\alpha$ -H undergo Cannizzaro reaction. When treated with aqueous base  $\text{CH}_3\text{CHO}$  does not undergo Cannizzaro reaction because it has  $\alpha$ -H and in the presence of aqueous base it undergoes aldol condensation.



34. Grignard's reagent reacts with both aldehydes and ketones while other three reagents reacts only with aldehydes, not with ketones.

35. Only  $-\text{CHO}$  group is to be reduced to  $-\text{CH}_2\text{OH}$ .

It can be done using  $\text{NaBH}_4$  in  $\text{C}_2\text{H}_5\text{OH}$ .



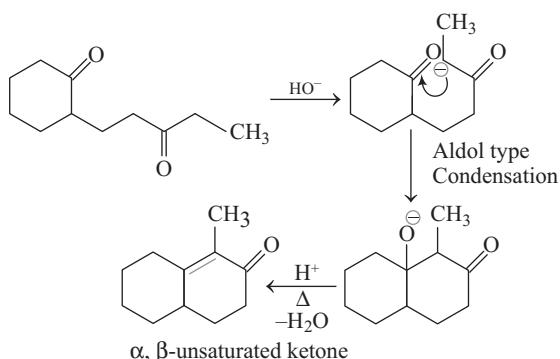
- (a)  $\text{LiAlH}_4 / (\text{C}_2\text{H}_5)_2\text{O}$  reduces I, II and III into  $-\text{CH}_2\text{OH}$ , and IV into diol.

- (b)  $\text{BH}_3 / \text{THF}$  show same properties as (a).

- (c)  $\text{NaBH}_4 / \text{C}_2\text{H}_5\text{OH}$  reduces III into  $-\text{CH}_2\text{OH}$ .

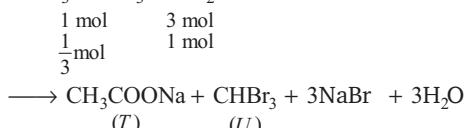
- (d) Raney nickel, same as (a) and (b), thus (c) is correct reagent.

36.



37. **Plan** When acetone reacts with  $\text{Br}_2$  in basic medium, bromoform is formed.

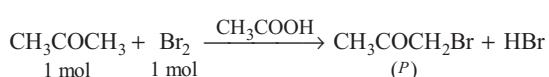
**Reaction I**  $\text{CH}_3\text{COCH}_3 + 3\text{Br}_2 + 4\text{NaOH}$



When  $\text{CH}_3\text{COCH}_3$  and  $\text{Br}_2$  are in equimolar quantity, all the  $\text{Br}_2$  (limiting reactant) is converted into desired products and  $2/3$  mole of  $\text{CH}_3\text{COCH}_3$  remains unreacted, being in excess.

When acetone reacts with  $\text{Br}_2$  in acidic medium, there is monobromination of acetone.

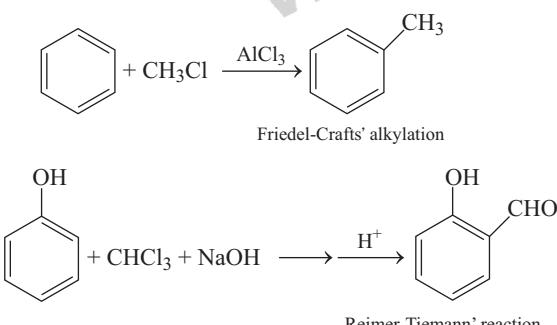
**Reactions II**



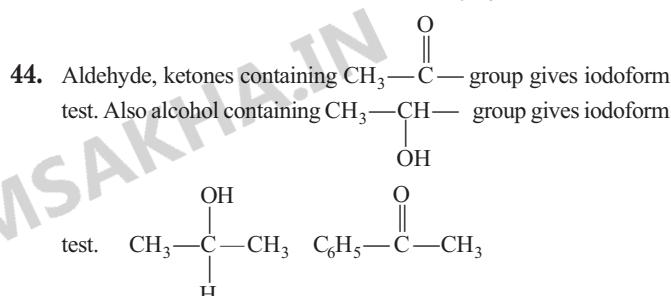
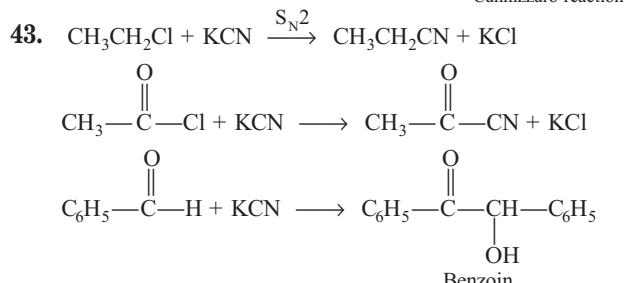
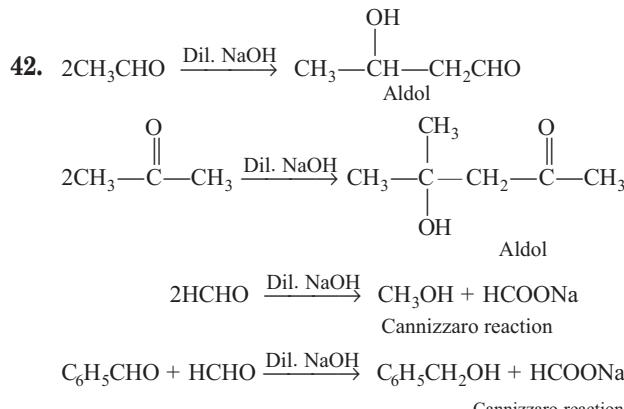
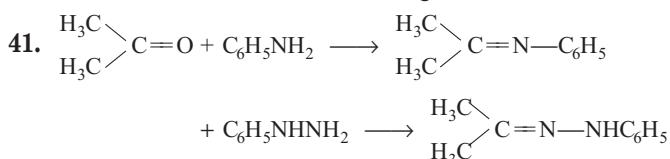
$\text{CH}_3\text{COCH}_3$  and  $\text{Br}_2$  react in  $1 : 1$  mole ratio and (P) is formed. In reaction I, (U) and (T) are formed and acetone (reactant) remains unreacted. In reaction II, (P) is formed.

38. All those carbonyl compounds containing  $\alpha\text{-H}$  to  $sp^2$  carbon show keto-enol tautomerism.

39. In both Friedel-Craft's reaction and Reimer-Tiemann reaction new carbon-carbon bond is formed.

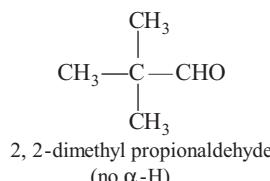
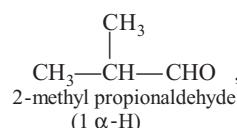
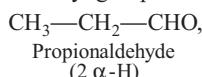


40. All carbonyl compounds containing  $\alpha\text{-H}$  or  $\alpha\text{-D}$  undergo aldol condensation. In given example, benzaldehyde does not contain  $\alpha\text{-H}$  to  $\text{CHO}$ , hence does not undergo aldol condensation.



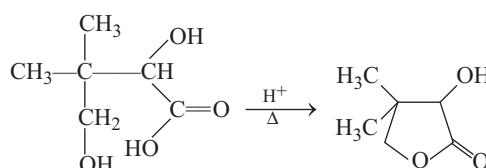
Both gives positive iodoform test  
Esters and amides do not give iodoform test.

45. For base catalysed aldol condensation, there must be at least one  $\alpha\text{-H}$  to carbonyl group.



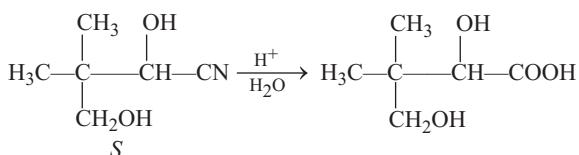
#### Passage 1 (For Q. Nos. 46-48)

The given product is an ester, obtained by condensation of a hydroxy acid obtained through hydrolysis of a cyanohydrin :

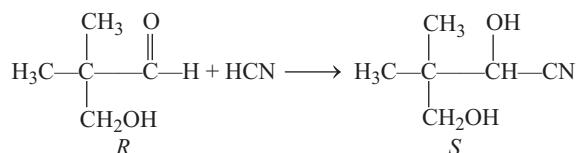


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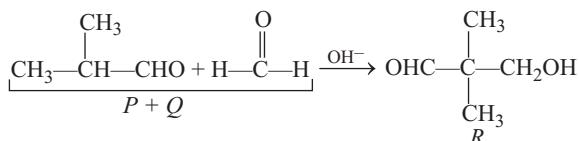
Acid above is obtained by acid hydrolysis of cyanohydrin *S* as



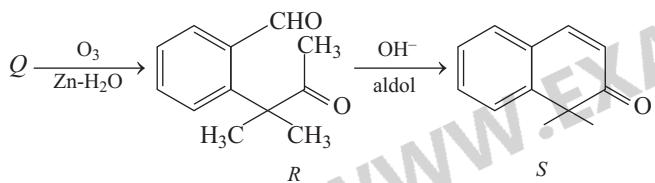
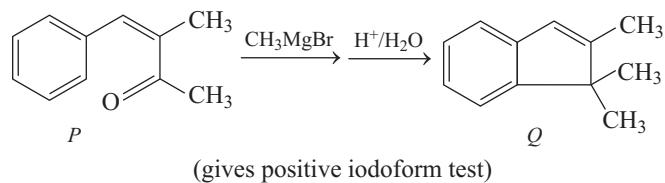
*S* is obtained by nucleophile addition of HCN on *R*, hence *R* is



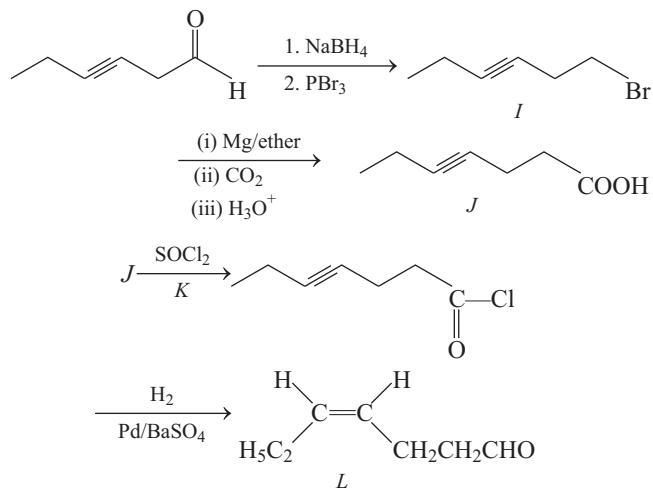
*R* is obtained by treatment of *P* and *Q* with aqueous  $\text{K}_2\text{CO}_3$  through aldol condensation reaction as



### Passage 2 (For Q. Nos. 49-51)



### Passage 3 (For Q. Nos. 52-54)

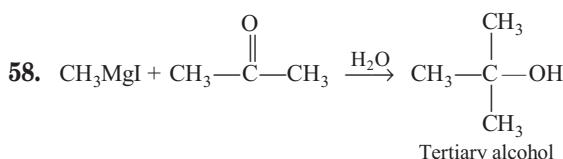


|    | Column I | Column II                                                                                                                                                                                                                                                        |
|----|----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A. |          | Undergo nucleophilic substitution of $\text{Br}^-$ . Undergo elimination of $\text{HBr}$ . Does not undergo nucleophilic addition. Does not esterify with acetic anhydride, can be dehydrogenated.                                                               |
| B. |          | Undergo nucleophilic substitution with $\text{SOCl}_2, \text{PCl}_5$ etc. Does not undergo elimination. Does not undergo nucleophilic addition. Undergo esterification with acetic anhydride. Undergo dehydrogenation to give $\text{C}_6\text{H}_5\text{CHO}$ . |
| C. |          | Does not undergo nucleophilic substitution, there is no leaving group. Does not undergo elimination. Undergo nucleophilic addition at carbonyl carbon of $-\text{CHO}$ . Undergo esterification with acetic anhydride. Does not undergo dehydrogenation.         |
| D. |          | Undergo aromatic nucleophilic substitution ( $\text{S}_{\text{N}}\text{Ar}$ ). Does not undergo elimination, nucleophilic addition, esterification or dehydrogenation.                                                                                           |

### 56.

|    | Column I                                | Column II                                                                                                                              |
|----|-----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| A. | $\text{C}_6\text{H}_5\text{CHO}$        | Gives phenyl hydrazone with 2, 4-dinitrophenyl hydrazine.<br>Gives precipitate with $\text{AgNO}_3$ , Tollen's test forms cyanohydrin. |
| B. | $\text{CH}_3 - \text{C}\equiv\text{CH}$ | Gives precipitate $(\text{CH}_3 - \text{C}\equiv\text{CAg})$ with $\text{AgNO}_3$ .<br>A nucleophile, undergo electrophilic attack.    |
| C. | $\text{CN}^-$                           | Forms $\text{AgCN}$ with $\text{AgNO}_3$ .<br>A nucleophile is involved in cyanohydrin formation.                                      |
| D. | $\text{I}^-$                            | Gives $\text{AgI}$ precipitate with $\text{AgNO}_3$ and it is a nucleophile.                                                           |

### 57. Sodium potassium tartarate



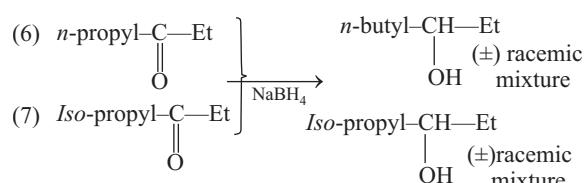
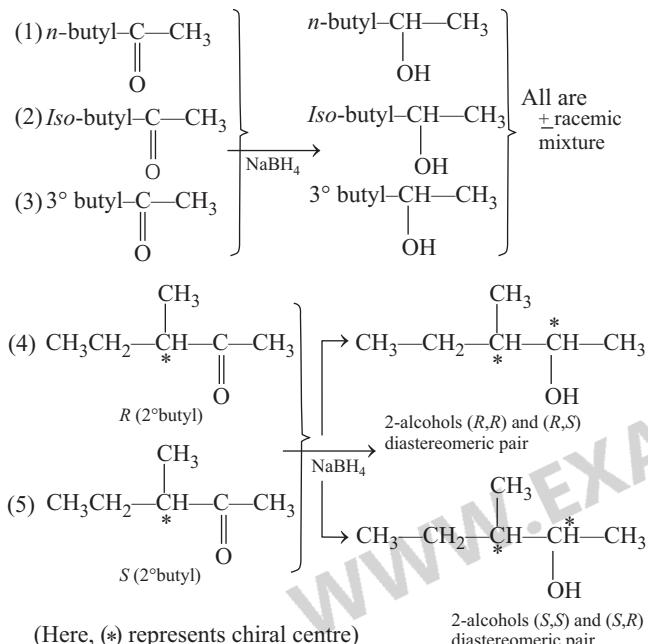
59. Benzaldehyde, lacking  $\alpha$ -H does not undergo aldol condensation, rather it undergoes Cannizzaro reaction.

60. Molecular weight of the ketone is 100

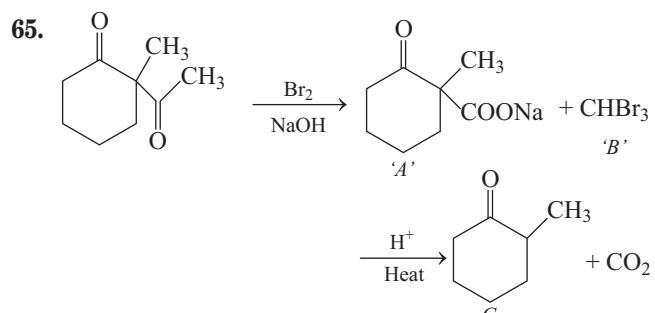
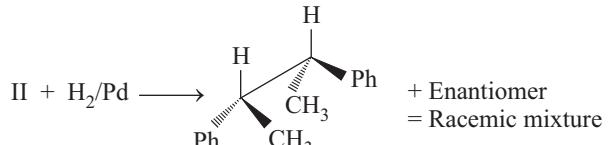
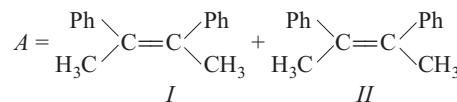
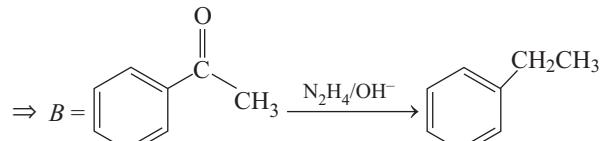
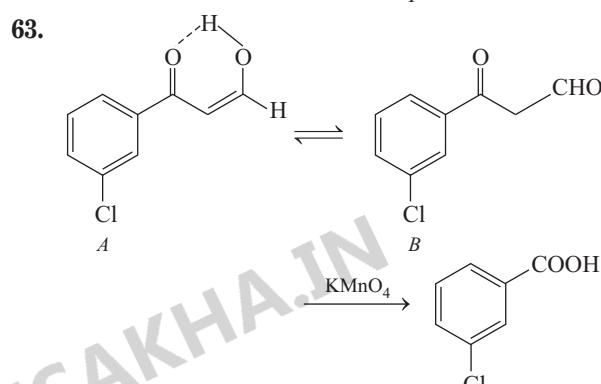
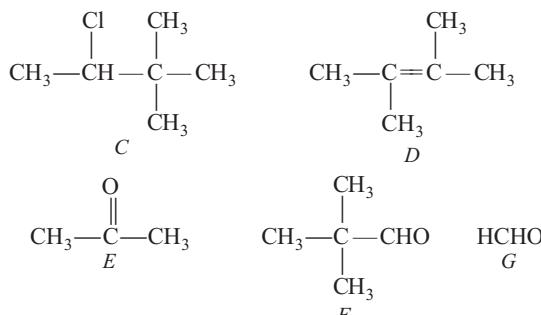
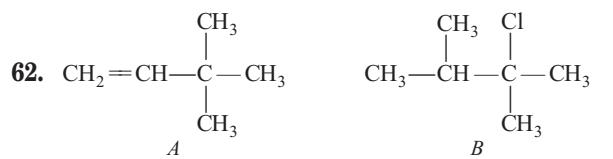
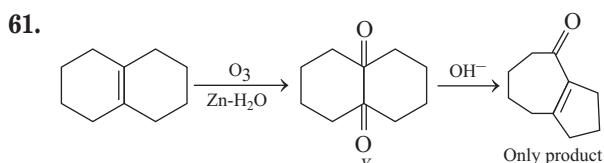
So, molecular formula =  $\text{C}_6\text{H}_{12}\text{O}$

$$\text{Degree of unsaturation} = (6 + 1) - \frac{12}{2} = 1$$

According to question, compound contains ketone group. Since, the compound which contain chiral centre lead to the formation of diastereomer while other produces enantiomers. Various isomers and their possible reduced product are as shown below.

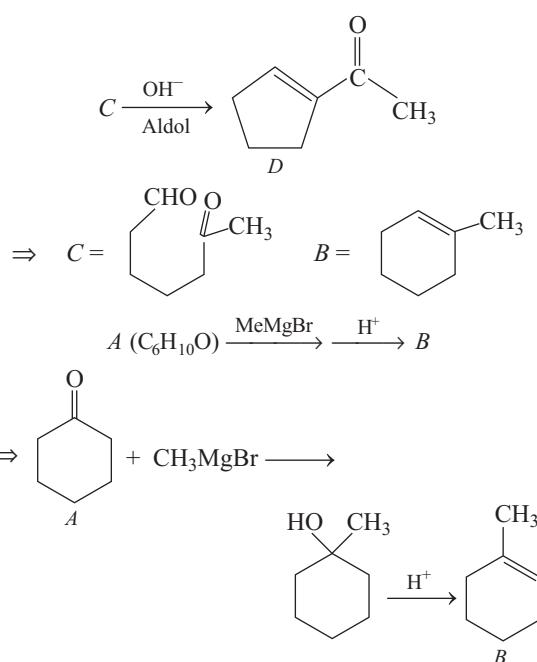


While in case of (4) and (5) they do not produce enantiomer due to the presence of stereogenic centre on ketone.

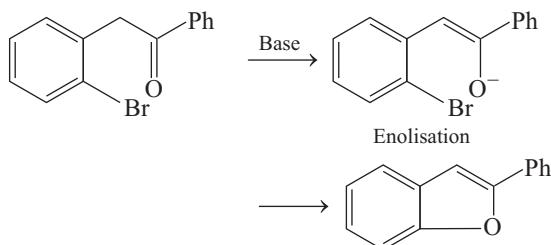


## 394 Aldehydes and Ketones

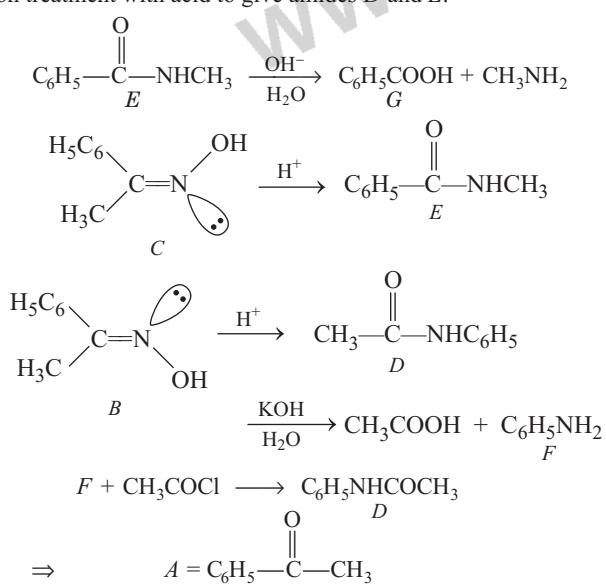
66.



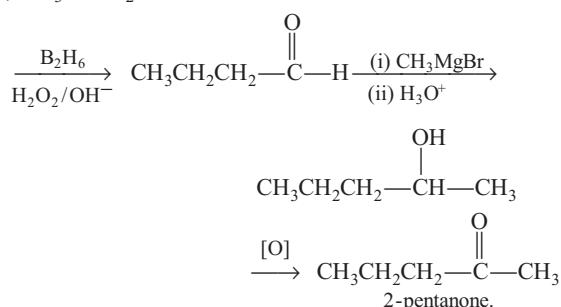
67.



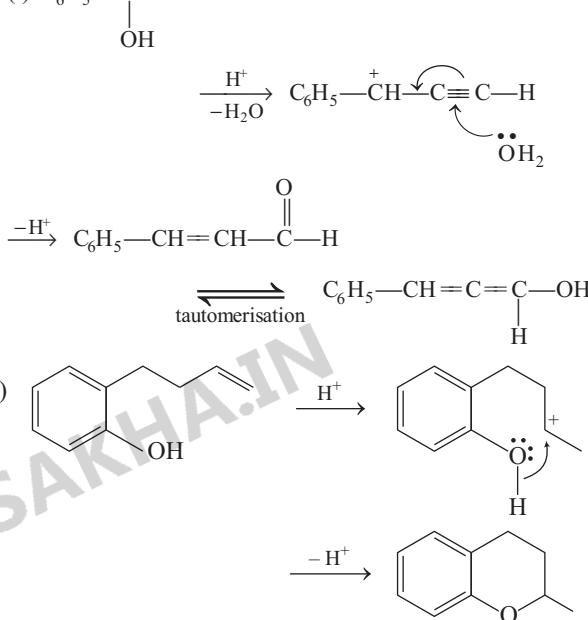
68. (a) *G* is benzoic acid  $\text{C}_6\text{H}_5\text{COOH}$ , *B* and *C* are two stereomeric oximes which undergo Beckmann's rearrangement on treatment with acid to give amides *D* and *E*.



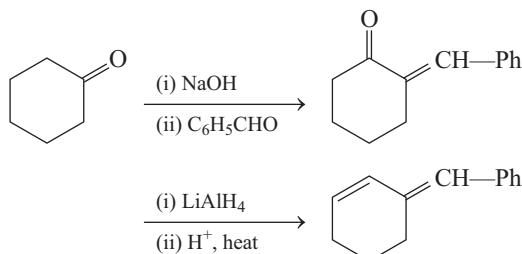
(b)  $\text{CH}_3\text{---CH}_2\text{---C}\equiv\text{CH}$



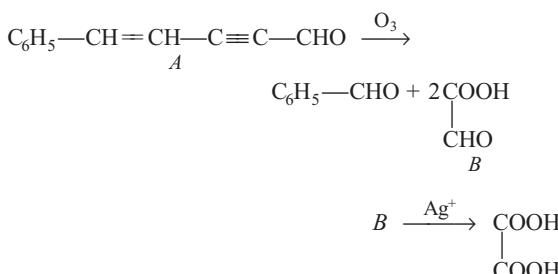
69. (i)

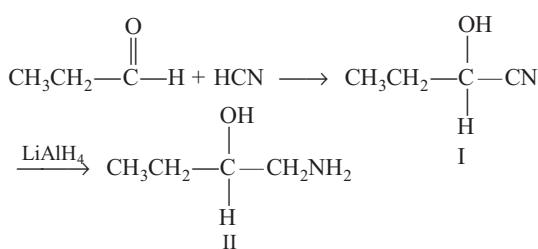
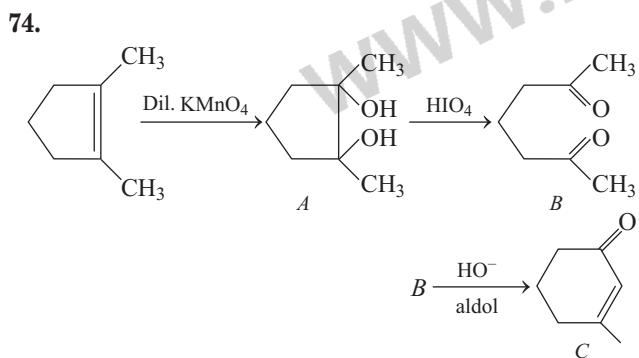
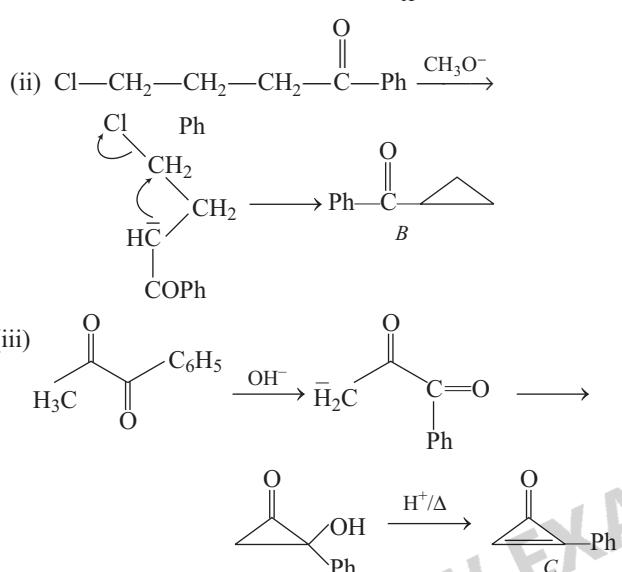
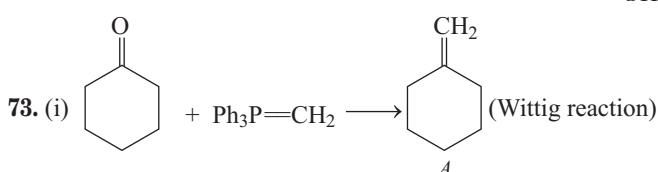
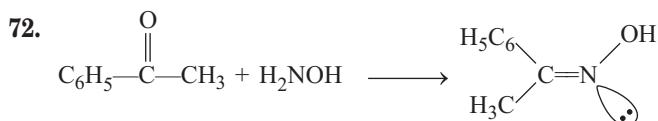


70.

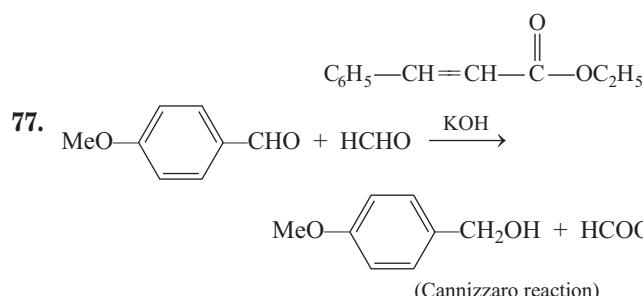
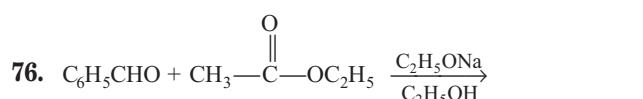


71. Aldehyde *A* does not have any  $\alpha$ -H but undergoes ozonolysis to give two moles of compound *B* and benzaldehyde. Compound *B* on oxidation gives oxalic acid, so *A* is

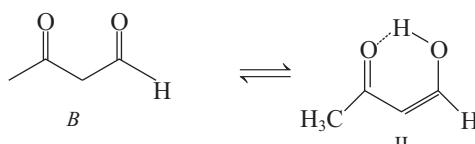




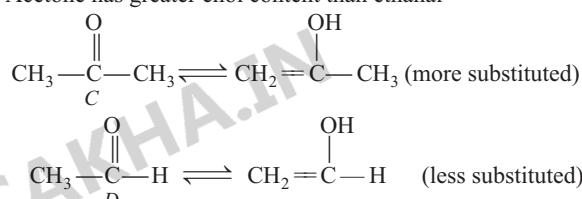
I is formed as racemic mixture.



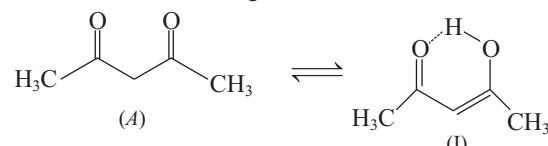
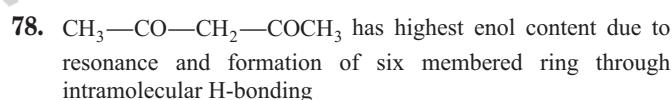
In cross-Cannizzaro reaction, methanol is always oxidised.



II is less stable than I because II is less substituted enol.  
Acetone has greater enol content than ethanal

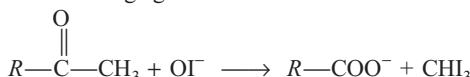
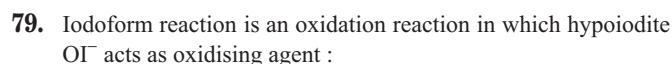


Therefore, overall enol-content order is  $D < C < B < A$

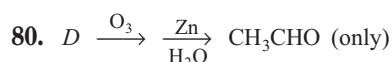


Also, enol content depends upon the number of substituents on double bond, greater the number of substituents, greater the stability, higher the enol content.

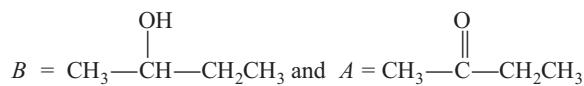
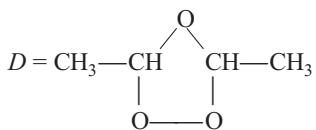
Therefore,  $\text{CH}_3\text{COCH}_2\text{CHO}$  forms next most stable enol



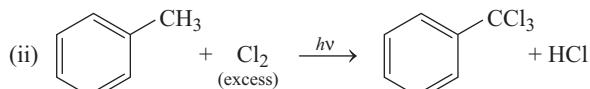
Iodide ( $\text{I}^-$ ) is a reducing agent, does not give iodoform reaction.

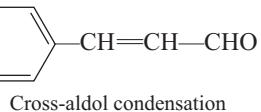


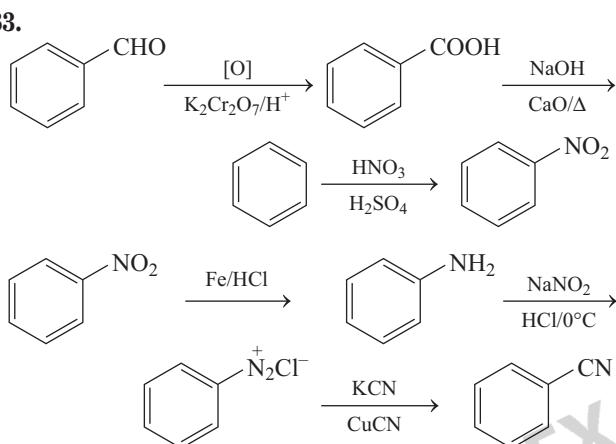
## 396 Aldehydes and Ketones



81. (i) Tollen's reagent gives grey precipitate of Ag, acetone does not.



82.  $\text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}}$    
Cross-alcohol condensation

83. 

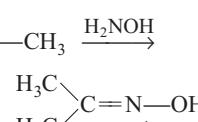
84.  $R-\overset{\text{O}}{\parallel}\text{C}-R + \text{PhNNNH}_2 \longrightarrow \begin{array}{c} R \\ | \\ R-\text{C}=\text{N}-\text{NHPh} \end{array}$   
Hydrazone

In acidic medium, hydrazine reacts to form salt and hydrazone is hydrolysed back to aldehyde/ketone.

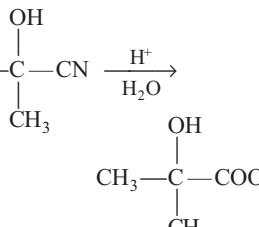
85.  $\text{CH}_3\text{CH}_2\text{CHO} \xrightarrow[\text{heat}]{\text{OH}^-} \text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\overset{\text{O}}{\parallel}\text{C}-\text{CHO}$   
Aldol followed by dehydration

86. Steric hindrance at carbonyl carbon determine the reactivity towards nucleophilic addition reaction. Greater the steric hindrance, smaller the reactivity.

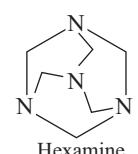


87.  $\text{CH}_3\text{CHO} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, \text{H}^+} \text{CH}_3\text{COOH} \xrightarrow{\text{Ca(OH)}_2} (\text{CH}_3\text{COO})_2\text{Ca}$   
 $(\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\text{heat}} \text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3 \xrightarrow{\text{H}_2\text{NOH}}$   


88.  $\text{Cl}_3\text{C}-\text{CHO} + \text{NaOH}(aq) \longrightarrow \text{Cl}_3\text{C}-\text{CH}_2\text{OH}$   
Cannizzaro reaction  
+  $\text{Cl}_3\text{C}-\text{COONa}$

89.  $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3 \xrightarrow{\text{HCN}} \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3-\text{C}-\text{CN} \end{array} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+}$   
  
 $\Rightarrow C = \text{CH}_3-\overset{\text{Br}}{\underset{\text{CH}_3}{\underset{|}{\text{C}}}}-\text{COOH}, B = \text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}-\text{COOH}$   
 $\Rightarrow A = \text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_3$

90.  $\text{H}-\overset{\text{O}}{\parallel}\text{C}-\text{H} + \text{CH}_3\text{MgBr} \xrightarrow{\text{Ether}}$   $\text{CH}_3\text{CH}_2\text{OMgBr}$   
 $\xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}$

91.  $6\text{CH}_2\text{O} + 4\text{NH}_3 \longrightarrow$    
“ $(\text{CH}_2)_6\text{N}_4$ ”  
Hexamine

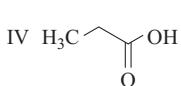
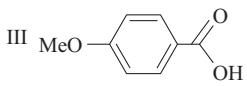
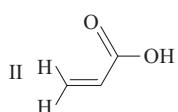
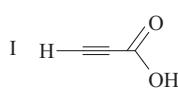
# 26

## Carboxylic Acids and Their Derivatives

### Topic 1 Carboxylic Acids

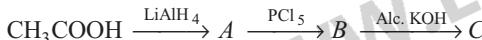
#### Objective Questions I (Only one correct option)

1. The correct order of acid strength of the following carboxylic acids is  
 (2019 Adv.)



- (a) III > II > I > IV  
 (b) I > II > III > IV  
 (c) II > I > IV > III  
 (d) I > III > II > IV

2. In the reaction,



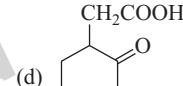
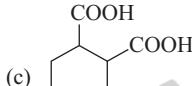
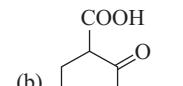
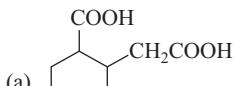
- The product C is  
 (2014 Main)  
 (a) acetaldehyde  
 (b) acetylene  
 (c) ethylene  
 (d) acetyl chloride

3. The compound that does not liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution, is  
 (2013 Adv.)
- (a) benzoic acid  
 (b) benzenesulphonic acid  
 (c) salicylic acid  
 (d) carboxylic acid (Phenol)

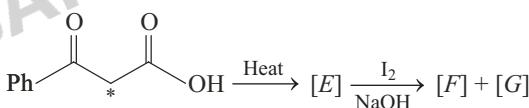
4. An organic compound A upon reacting with  $\text{NH}_3$  gives B. On heating, B gives C. C in the presence of KOH reacts with  $\text{Br}_2$  to give  $\text{CH}_3\text{CH}_2\text{NH}_2$ . A is  
 (2013 Main)

- (a)  $\text{CH}_3\text{COOH}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
 (c)  $\begin{matrix} \text{CH}_3 & \\ & \text{---} \text{CH} \text{---} \\ & | \\ & \text{CH}_3 \end{matrix}$   
 (d)  $\text{CH}_3\text{CH}_2\text{COOH}$

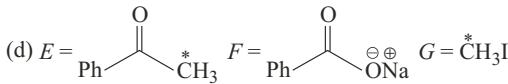
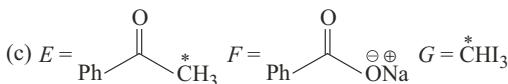
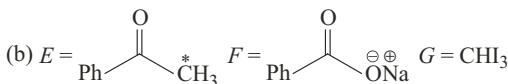
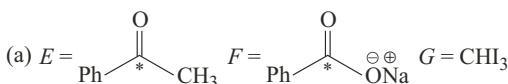
5. The compound that undergoes decarboxylation most readily under mild condition is  
 (2012)



6. In the following reaction sequence, the correct structures of E, F and G are



(\* implies  $^{13}\text{C}$  labelled carbon) (2008, 3M)



7. When benzene sulphonic acid and *p*-nitrophenol are treated with  $\text{NaHCO}_3$ , the gases released respectively, are

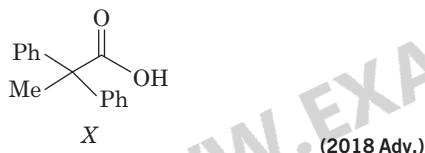
- (a)  $\text{SO}_2, \text{NO}_2$   
 (b)  $\text{SO}_2, \text{NO}$   
 (c)  $\text{SO}_2, \text{CO}_2$   
 (d)  $\text{CO}_2, \text{CO}_2$

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8. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be  
 (a) optically active mixture  
 (b) pure enantiomer  
 (c) *meso* compound  
 (d) racemic mixture  
 (2003, S, 1M)
9. Benzoyl chloride is prepared from benzoic acid by  
 (a)  $\text{Cl}_2, h\nu$   
 (b)  $\text{SO}_2\text{Cl}_2$   
 (c)  $\text{SOCl}_2$   
 (d)  $\text{Cl}_2, \text{H}_2\text{O}$   
 (2000, S, 1M)
10. When propionic acid is treated with aqueous sodium bicarbonate,  $\text{CO}_2$  is liberated. The C of  $\text{CO}_2$  comes from  
 (a) methyl group  
 (b) carboxylic acid group  
 (c) methylene group  
 (d) bicarbonate group  
 (1999, 2M)
11. Which of the following is basic ?  
 (a)  $\text{CH}_3\text{CH}_2\text{OH}$   
 (b)  $\text{H}_2\text{O}_2$   
 (c)  $\text{HOCH}_2\text{CH}_2\text{OH}$   
 (d)  $\text{CH}_3\text{COOH}$   
 (1980, 1M)

### Matching Type Questions

12. The desired product X can be prepared by reacting the major product of the reactions in List-I with one or more appropriate reagents in List-II.  
 (given, order of migratory aptitude : aryl > alkyl > hydrogen)

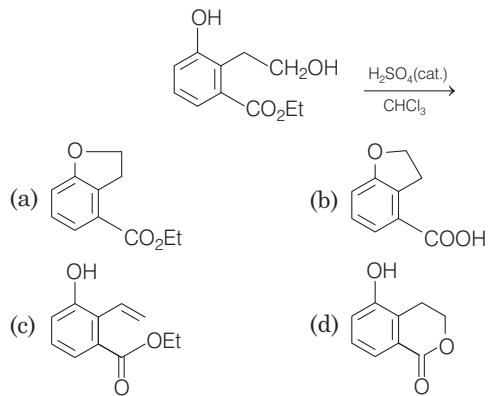


## Topic 2 Acid Derivatives

### Objective Questions I

(Only one correct option)

1. The major product of the following reaction is  
 (2019 Main, 9 April II)



| List-I | List-II                                  |
|--------|------------------------------------------|
| P.     | 1. $\text{I}_2, \text{NaOH}$             |
| Q.     | 2. $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ |
| R.     | 3. Fehling solution                      |
| S.     | 4. $\text{HCHO}, \text{NaOH}$            |
|        | 5. $\text{NaOBr}$                        |

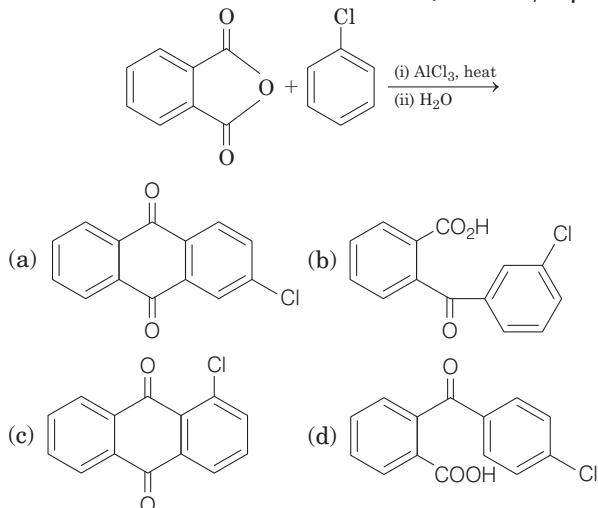
The correct option is

- (a) P  $\rightarrow$  1; Q  $\rightarrow$  2, 3; R  $\rightarrow$  1, 4; S  $\rightarrow$  2, 4  
 (b) P  $\rightarrow$  1, 5; Q  $\rightarrow$  3, 4; R  $\rightarrow$  4, 5; S  $\rightarrow$  3  
 (c) P  $\rightarrow$  1, 5; Q  $\rightarrow$  3, 4; R  $\rightarrow$  5; S  $\rightarrow$  2, 4  
 (d) P  $\rightarrow$  1, 5; Q  $\rightarrow$  2, 3; R  $\rightarrow$  1, 5; S  $\rightarrow$  2, 3

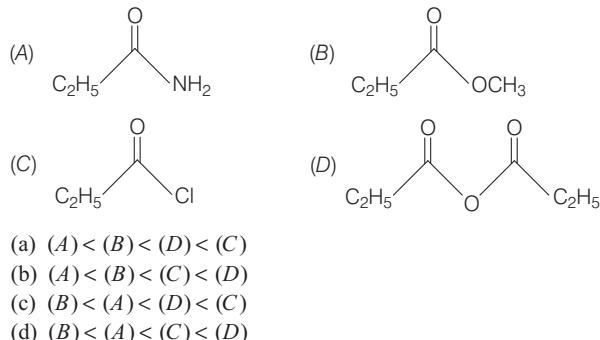
### Subjective Questions

13. How will you bring about the following conversion?  
 "Ethanal to 2-hydroxy-3-butenoic acid."  
 (1990, 2M)

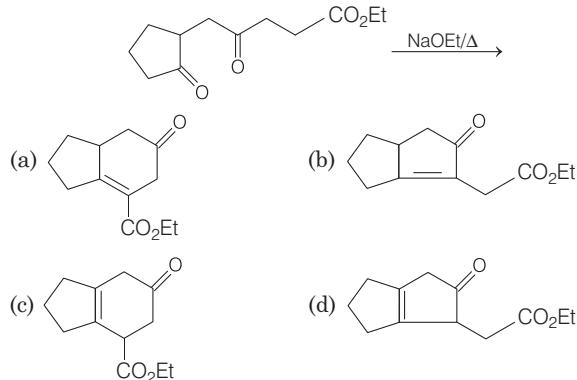
2. The major product of the following reaction is  
 (2019 Main, 8 April I)



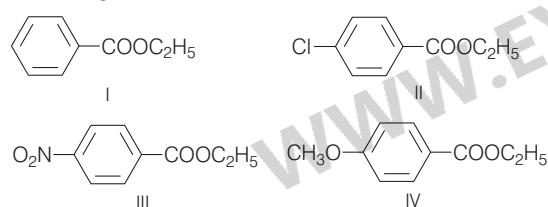
3. The increasing order of the reactivity of the following with  $\text{LiAlH}_4$  is  
 (2019 Main, 12 Jan II)



4. The major product obtained in the following reaction is  
 (2019 Main, 10 Jan II)

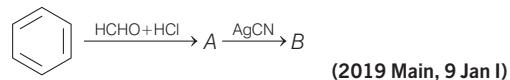


5. The decreasing order of ease of alkaline hydrolysis for the following esters is  
 (2019 Main, 10 Jan I)



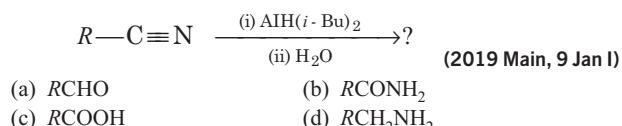
- (a) III > II > IV > I  
 (b) III > II > I > IV  
 (c) II > III > I > IV  
 (d) IV > II > III > I

6. The compounds *A* and *B* in the following reaction are, respectively

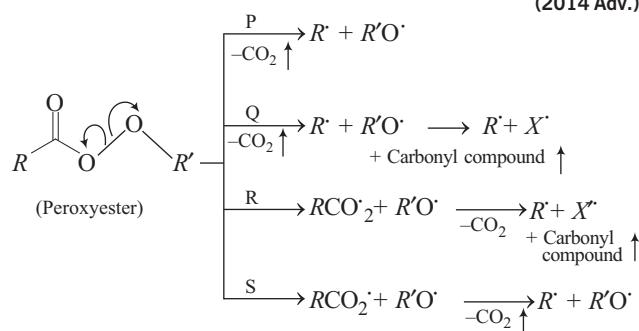


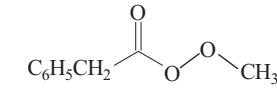
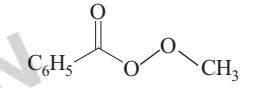
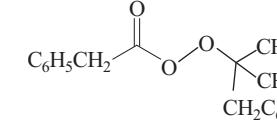
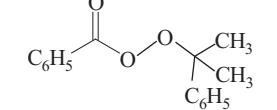
- (a) *A* = Benzyl alcohol, *B* = Benzyl isocyanide  
 (b) *A* = Benzyl alcohol, *B* = Benzyl cyanide  
 (c) *A* = Benzyl chloride, *B* = Benzyl isocyanide  
 (d) *A* = Benzyl chloride, *B* = Benzyl cyanide

7. The major product of following reaction is



8. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from Column I with an appropriate structure from Column II and select the correct answer using the code given below the lists.  
 (2014 Adv.)



|                     | Column I | Column II                                                                             |
|---------------------|----------|---------------------------------------------------------------------------------------|
| P. Pathway <i>P</i> | 1.       |    |
| Q. Pathway <i>Q</i> | 2.       |   |
| R. Pathway <i>R</i> | 3.       |  |
| S. Pathway <i>S</i> | 4.       |  |

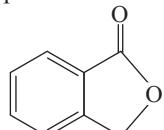
**Codes**

| P     | Q | R | S |
|-------|---|---|---|
| (a) 1 | 3 | 4 | 2 |
| (b) 2 | 4 | 3 | 1 |
| (c) 4 | 1 | 2 | 3 |
| (d) 3 | 2 | 1 | 4 |

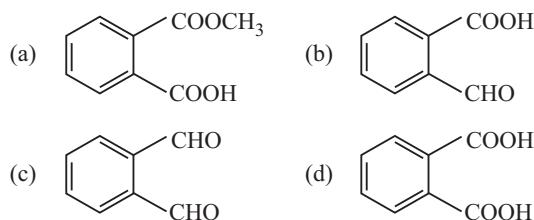
9. A compound with molecular mass 180 is acylated with  $\text{CH}_3\text{COCl}$  to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is  
 (2013 Main)

- (a) 2  
 (b) 5  
 (c) 4  
 (d) 6

10. Which of the following reactants on reaction with conc.  $\text{NaOH}$  followed by acidification gives the following lactone as the only product?  
 (2006, 5M)



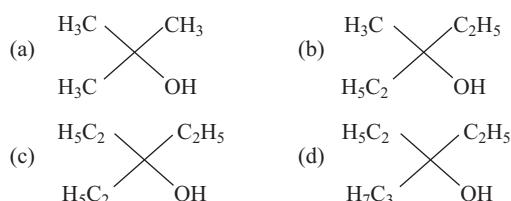
## 400 Carboxylic Acids and Their Derivatives



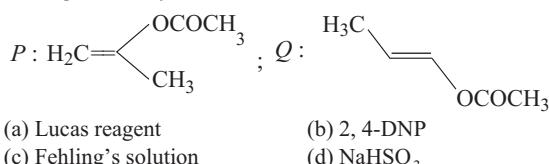
11. Benzamide on treatment with  $\text{POCl}_3$  gives (2004, S, 1M)

- (a) aniline (b) benzonitrile  
(c) chlorobenzene (d) benzyl amine

12. Ethyl ester  $\xrightarrow[\text{(excess)}]{\text{CH}_3\text{MgBr}}$   $P$ , the product ' $P$ ' will be (2003, S, 1M)



13. The product of acid hydrolysis of  $P$  and  $Q$  can be distinguished by (2003, S, 1M)



- (a) Lucas reagent (b) 2, 4-DNP  
(c) Fehling's solution (d)  $\text{NaHSO}_3$

14. Hydrogenation of benzoyl chloride in the presence of Pd on  $\text{BaSO}_4$  gives (1992, 1M)

- (a) benzyl alcohol (b) benzaldehyde  
(c) benzoic acid (d) phenol

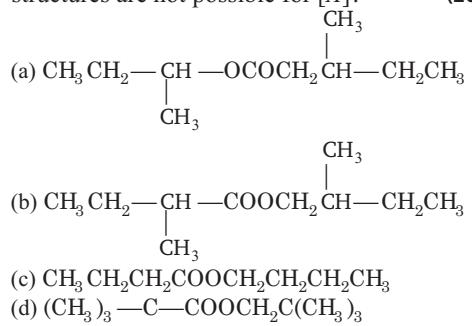
15. Acetamide is treated separately with the following reagents. Which one of these would give methyl amine? (1983, 1M)

- (a)  $\text{PCl}_5$  (b)  $\text{NaOH} + \text{Br}_2$   
(c) Soda lime (d) Hot conc.  $\text{H}_2\text{SO}_4$

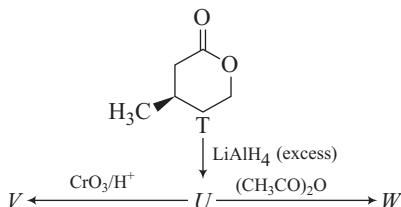
### Objective Questions I

(One or more than one correct options)

16. An organic compound [A], molecular formula  $\text{C}_{10}\text{H}_{20}\text{O}_2$  was hydrolysed with dilute sulphuric acid to give a carboxylic acid [B] and an alcohol [C]. Oxidation of [C] with  $\text{CrO}_3 - \text{H}_2\text{SO}_4$  produced [B]. Which of the following structures are not possible for [A]? (2020 Main, 3 Sep I)

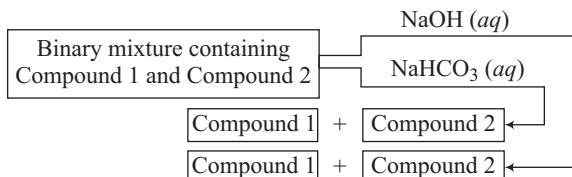


17. With reference to the scheme given, which of the given statement(s) about  $T$ ,  $U$ ,  $V$  and  $W$  is/are correct? (2012)



- (a)  $T$  is soluble in hot aqueous  $\text{NaOH}$   
(b)  $U$  is optically active  
(c) Molecular formula of  $W$  is  $\text{C}_{10}\text{H}_{18}\text{O}_4$   
(d)  $V$  gives effervescence on treatment with aqueous  $\text{NaHCO}_3$

18. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. (2012)



- (a)  $\text{C}_6\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{COOH}$   
(b)  $\text{C}_6\text{H}_5\text{COOH}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$   
(c)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{OH}$   
(d)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

19. Reaction of  $R\text{CONH}_2$  with a mixture of  $\text{Br}_2$  and  $\text{KOH}$  gives  $R-\text{NH}_2$  as the main product. The intermediates involved in this reaction are (1992, 1M)

- (a)  $\text{RCONHBr}$  (b)  $\text{RNHBr}$   
(c)  $\text{R}-\text{N}=\text{C}=\text{O}$  (d)  $\text{RCONBr}_2$

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is a correct explanation of Statement I.  
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.  
(c) Statement I is true; Statement II is false.  
(d) Statement I is false; Statement II is true.

20. **Statement I**  $p$ -hydroxybenzoic acid has a lower boiling point than  $o$ -hydroxybenzoic acid.

**Statement II**  $o$ -hydroxybenzoic acid has intramolecular hydrogen bonding. (2007, 3M)

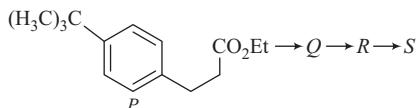
21. **Statement I** Acetic acid does not undergo haloform reaction.  
**Statement II** Acetic acid has no alpha hydrogen. (1998, 2M)

### Passage Based Questions

#### Passage 1

The reaction of compound  $P$  with  $\text{CH}_3\text{MgBr}$  (excess) in  $(\text{C}_2\text{H}_5)_2\text{O}$  followed by addition of  $\text{H}_2\text{O}$  gives  $Q$ . The compound  $Q$  on treatment with  $\text{H}_2\text{SO}_4$  at  $0^\circ\text{C}$  gives  $R$ . The reaction of  $R$  with  $\text{CH}_3\text{COCl}$  in the

presence of anhydrous  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  followed by treatment with  $\text{H}_2\text{O}$  produces compound  $S$ . [Et in compound  $P$  is ethyl group]



**22.** The product  $S$  is

- (a) (b) (2017 Adv.)  
 (c)   
 (d)

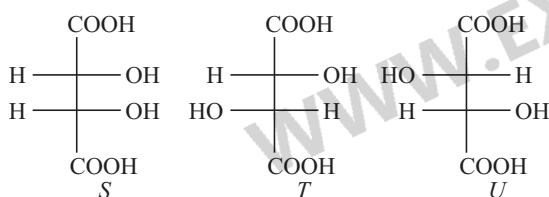
**23.** The reactions,  $Q$  to  $R$  and  $R$  to  $S$ , are

- (a) Aromatic sulfonation and Friedel-Crafts acylation  
 (b) Friedel-Crafts alkylation and Friedel-Crafts acylation  
 (c) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation  
 (d) Dehydration and Friedel-Crafts acylation

### Passage 2

$P$  and  $Q$  are isomers of dicarboxylic acid  $\text{C}_4\text{H}_4\text{O}_4$ . Both decolorize  $\text{Br}_2/\text{H}_2\text{O}$ . On heating,  $P$  forms the cyclic anhydride.

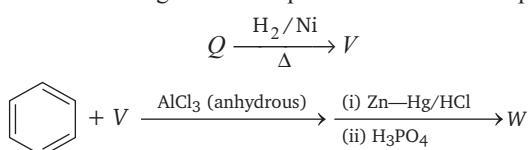
Upon treatment with dilute alkaline  $\text{KMnO}_4$ ,  $P$  as well as  $Q$  could produce one or more than one form  $S$ ,  $T$  and  $U$ . (2013 Adv.)



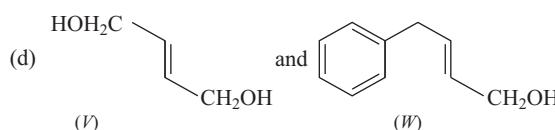
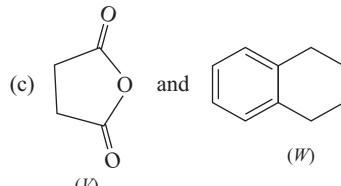
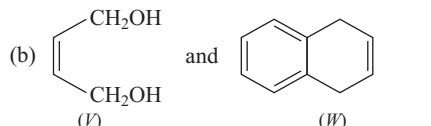
**24.** Compounds formed from  $P$  and  $Q$  are, respectively

- (a) Optically active  $S$  and optically active pair ( $T, U$ )  
 (b) Optically inactive  $S$  and optically inactive pair ( $T, U$ )  
 (c) Optically active pair ( $T, U$ ) and optically active  $S$   
 (d) Optically inactive pair ( $T, U$ ) and optically inactive  $S$

**25.** In the following reaction sequences  $V$  and  $W$  are respectively

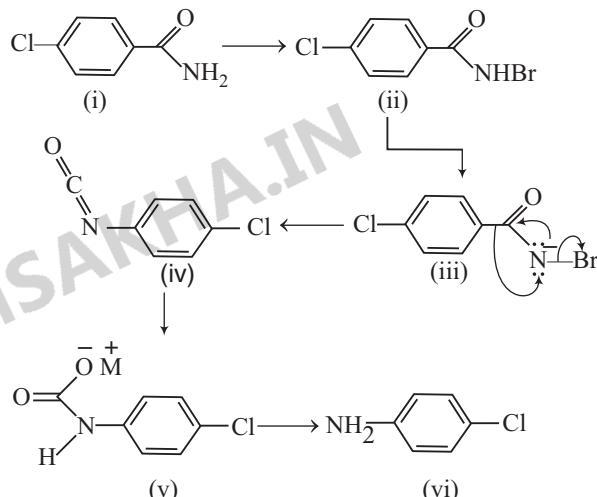


- (a) and



### Passage 3

$\text{RCONH}_2$  is converted into  $\text{RNH}_2$  by means of Hofmann's bromamide degradation.



In this reaction,  $\text{RCONHBr}$  is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann's degradation reaction is an intramolecular reaction. (2006, 3 × 4M = 12M)

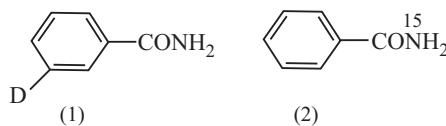
**26.** How can the conversion of (i) to (ii) be brought about?

- (a)  $\text{KBr}$  (b)  $\text{KBr} + \text{CH}_3\text{ONa}$   
 (c)  $\text{KBr} + \text{KOH}$  (d)  $\text{Br}_2 + \text{KOH}$

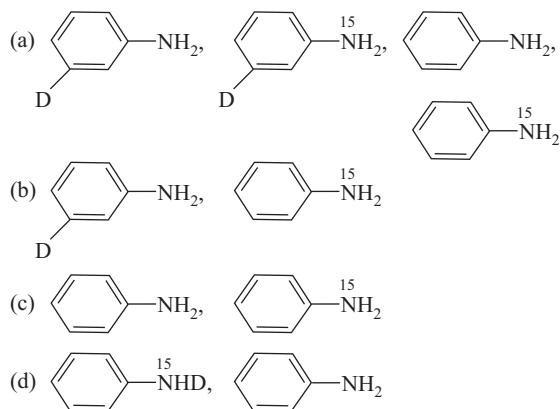
**27.** Which is the rate determining step in Hofmann's bromamide degradation?

- (a) Formation of (i) (b) Formation of (ii)  
 (c) Formation of (iii) (d) Formation of (iv)

**28.** What are the constituent amines formed when the mixture of (1) and (2) undergoes Hofmann's bromamide degradation?



## 402 Carboxylic Acids and Their Derivatives



### Fill in the Blank

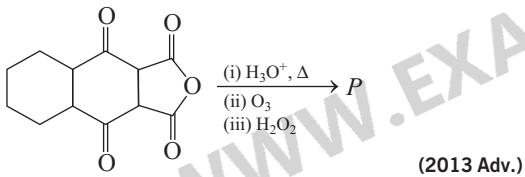
29. Formic acid when heated with conc. H<sub>2</sub>SO<sub>4</sub> produces ..... (1983, 1M)

### True/False

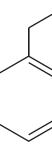
30. The boiling point of propanoic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. (1991, 1M)
31. Hydrolysis of an ester in the presence of a dilute acid is known as saponification. (1983, 1M)

### Integer Answer Type Question

32. The total number of carboxylic acid groups in the product *P* is



### Subjective Questions

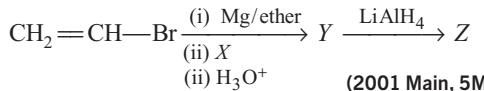
33. 
- $\xrightarrow[\text{DMF}]{\text{KCN}} (A) \xrightarrow[\text{C}_6\text{H}_5\text{CHO}]{\text{C}_2\text{H}_5\text{ONa/EtOH}} (B) \xrightarrow[\text{Heat}]{\text{H}_3\text{O}^+/\Delta} (C)$
- $\xrightarrow[\text{CH}_3\text{NH}_2]{\text{SOCl}_2} (D)$
- Identify *A* to *D*. (2004, M)

34. Compound *A* of molecular formula C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>Cl exists in keto form and predominantly in enolic form *B*. On oxidation with KMnO<sub>4</sub>, *A* gives *m*-chlorobenzoic acid. Identify *A* and *B*. (2003 Main, 2M)

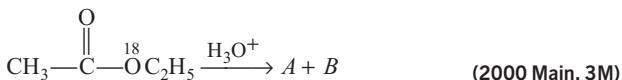
35. ( $\pm$ ) 2-phenylpropanoic acid on treatment with (+) 2-butanol gives (*A*) and (*B*). Deduce their structures and also establish stereochemical relation between them. (2003)

36. Identify *X* and *Y* in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H<sub>2</sub><sup>\*</sup>CO) as one of the products when

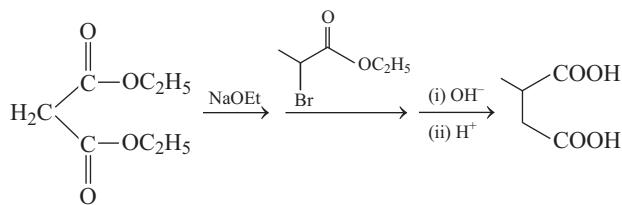
compound (*Z*) is treated with HBr and subsequently ozonolysed. Mark the C\* carbon in the entire scheme.



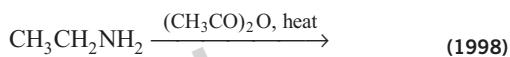
37. Write the structures of the products *A* and *B*.



38. Explain briefly the formation of the products giving the structures of the intermediates

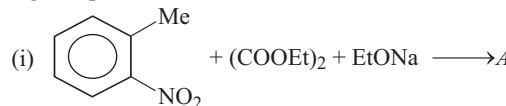


39. Write the structures of the products :



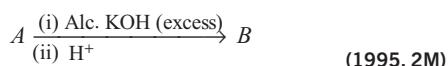
40. An ester *A* (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of *A* and *B*. Show the reactions involved. (1998)

41. Complete the following, giving the structures of the principal organic products



42. A hydrocarbon *A* of the formula C<sub>8</sub>H<sub>10</sub>, on ozonolysis gives compound *B* (C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>) only. The compound *B* can also be obtained from the alkyl bromide *C* (C<sub>3</sub>H<sub>5</sub>Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify *A*, *B* and *C* and also give equations for the reactions. (1996, 3M)

43. Complete the following sequence of reactions with appropriate structures



44. Which of the following carboxylic acids undergoes decarboxylation easily ? Explain briefly. (1995, 2M)

- (i) C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>COOH      (ii) C<sub>6</sub>H<sub>5</sub>COCOOH  
 (iii) C<sub>6</sub>H<sub>5</sub>CH(OH)COOH      (iv) C<sub>6</sub>H<sub>5</sub>CH(NH<sub>2</sub>)COOH

- 45.** Predict the major product in the following reaction :

$$\text{C}_6\text{H}_5-\text{CH}_2\text{COCH}_3 \xrightarrow[\text{(ii) H}^+]{\text{(i) CH}_3\text{MgBr (excess)}} \quad \text{(1994, 1M)}$$

**46.** In the following reactions, identify the compounds *A*, *B*, *C* and *D*.

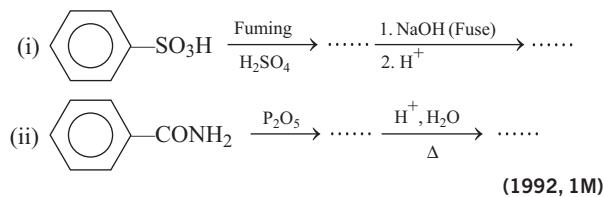
  - (i)  $\text{PCl}_5 + \text{SO}_2 \longrightarrow A + B$
  - (ii)  $A + \text{CH}_3\text{COOH} \longrightarrow C + \text{SO}_2 + \text{HCl}$
  - (iii)  $2C + (\text{CH}_3)_2\text{Cd} \longrightarrow 2D + \text{CdCl}_2 \quad \text{(1994, 1M} \times 4 = 4\text{M})$

**47.** Complete the following sequence of the reactions with appropriate structures

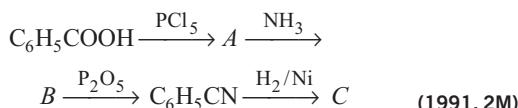
  - (i)   $\xrightarrow[\text{H}_2\text{SO}_4]{\text{Fuming}} \dots \xrightarrow{\text{1. NaOH (Fuse)}} \dots \xrightarrow{\text{2. H}^+} \dots$
  - (ii)   $\xrightarrow{\text{P}_2\text{O}_5} \dots \xrightarrow[\Delta]{\text{H}^+, \text{H}_2\text{O}} \dots$

**(1992, 1M)**

**48.** In the following identify the compounds/reaction conditions represented by the alphabets *A*, *B*, and *C* :



- 48.** In the following identify the compounds/reaction conditions represented by the alphabets A, B, and C:





- 53.** A liquid  $X$ , having a molecular formula  $C_6H_{12}O_2$  is hydrolysed with water in the presence of an acid to give a carboxylic acid  $Y$  and an alcohol  $Z$ . Oxidation of  $Z$  with chromic acid gives  $Y$ . What are the structures of  $X$ ,  $Y$  and  $Z$ ? (1986, 3M)

**54.** An ester  $A$  ( $C_4H_8O_2$ ) on treatment with excess of methyl magnesium chloride followed by acidification, gives an alcohol  $B$  as the sole organic product. Alcohol  $B$ , on oxidation with  $NaOCl$  followed by acidification, gives acetic acid. Deduce structures of  $A$  and  $B$ . Show the reactions involved. (1998)

**55.** Complete the following with appropriate structures :  

$$(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$$
 (1986, 1M)

**56.** Arrange the following in order of their increasing ease of hydrolysis : (1986, 1M)  
 $CH_3COOC_2H_5, CH_3COCl, (CH_3CO)_2O, CH_3CONH_2$

**57.** Give reasons in one or two sentences for the following :  
“Formic acid is a stronger acid than acetic acid.” (1985, 1M)

**58.** Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis.  
“Propionic anhydride from propionaldehyde”  
 $[AgNO_3, NH_4OH, P_2O_5]$  (1984, 2M)

**59.** Give reasons for the following in one or two sentences.  
“Acetic acid can be halogenated in the presence of  $P$  and  $Cl_2$ , but formic acid cannot be halogenated in the same way.”  
Why? (1983, 1M)

**60.** State with balanced equation, what happens when, “Acetic anhydride reacts with phenol in presence of a base.” (1982, 1M)

**61.** Write the structural formula of main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. (1981, 1/2 M)

**62.** Write the chemical equation to show what happens when, “Ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified”. (1981, 2 M)

## Answers

## Topic 1

- |        |         |         |         |
|--------|---------|---------|---------|
| 1. (b) | 2. (c)  | 3. (d)  | 4. (d)  |
| 5. (b) | 6. (c)  | 7. (d)  | 8. (d)  |
| 9. (c) | 10. (d) | 11. (a) | 12. (d) |

Topic 2

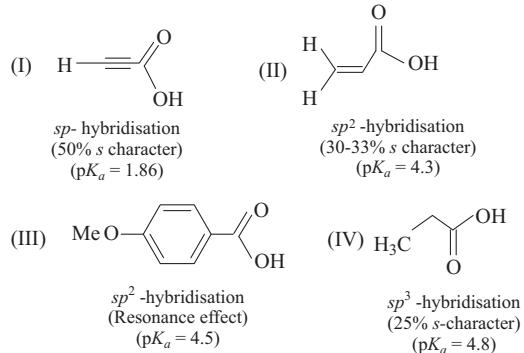
1. (d)      2. (d)      3. (a)      4. (b)  
5. (b)      6. (c)      7. (a)      8. (a)

- |                          |           |             |             |
|--------------------------|-----------|-------------|-------------|
| 9. (b)                   | 10. (c)   | 11. (b)     | 12. (a)     |
| 13. (c)                  | 14. (b)   | 15. (b)     | 16. (a,c)   |
| 17. (a,c,d)              | 18. (b,d) | 19. (a,c)   | 20. (d)     |
| 21. (c)                  | 22. (a)   | 23. (c)     | 24. (b)     |
| 25. (a)                  | 26. (d)   | 27. (d)     | 28. (b)     |
| 29. ( $H_2O$ and CO gas) |           | 30. (False) | 31. (False) |
| 32. (2)                  |           |             |             |

# Hints & Solutions

# Topic 1 Carboxylic Acids

1. Acidic nature depends upon nature of electron withdrawing group and electronegativity. Electronegativity further depends on % *s* character. Higher the *s*-character, greater will be the electronegativity and hence tendency to loose H increases thus acidic character also increases.



Hence, acidic order I > II > III > IV.

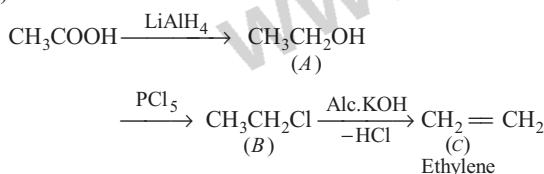
II is more acidic than III since electron donating group ( $-\text{OCH}_3$ ) is attached to benzene ring in III which decreases the acidic character.

On the other hand,  $pK_a$  value also determined acidic nature, lower  $pK_a$  value gives maximum acidic character.

Hence, option (b) is correct.

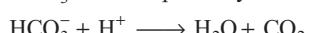
- 2.** This problem is based on successive reduction, chlorination and elimination reaction. To solve such problem, use the function of the given reagents.

- (i) LiAlH<sub>4</sub> causes reduction
  - (ii) PCl<sub>5</sub> causes chlorination
  - (iii) Alc. KOH causes elimination reaction



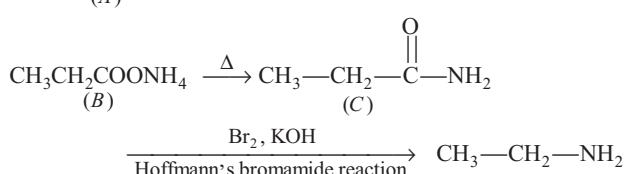
- 3. PLAN**  $\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^-$

$\text{HCO}_3^-$  is decomposed by acid releasing  $\text{CO}_2$ ,

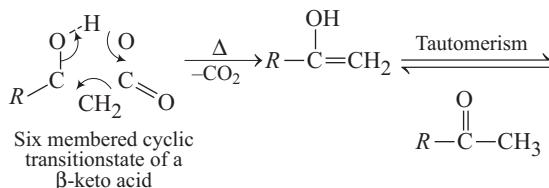


If acid is stronger than  $\text{HCO}_3^-$  then  $\text{CO}_2$  is released. Phenol is less acidic and thus does not liberate  $\text{CO}_2$  with  $\text{NaHCO}_3$ .

4.  $\text{CH}_3\text{CH}_2-\overset{\text{(1)}}{\underset{\text{(2)}}{\text{C}}}(\text{O})-\text{OH} \xrightarrow{\text{NH}_3}$

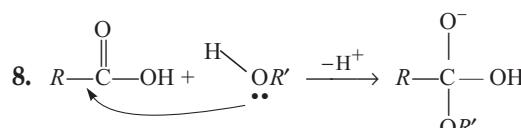
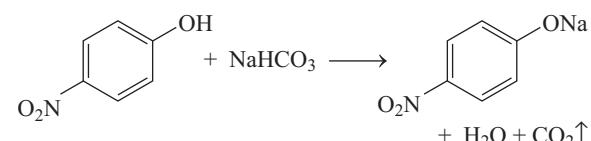
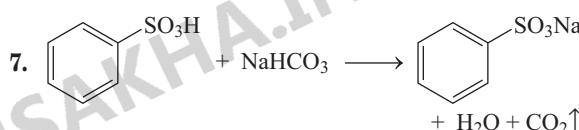
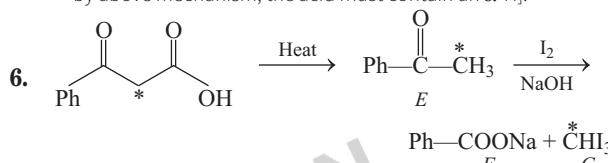


5. It is a  $\beta$ -keto acid which undergo decarboxylation in very mild condition, i.e. on simple heating. This occur through a six member cyclic transition state as

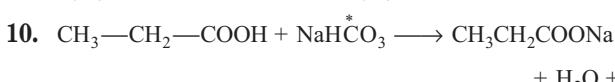


## NOTE

- Ordinary carboxylic acid require soda-lime catalyst for decarboxylation.
  - Final step of decarboxylation in the above shown mechanism involve tautomerism, therefore, for decarboxylation of  $\beta$ -keto acid by above mechanism, the acid must contain an  $\alpha$ -H].



Reaction occur at planar  $sp^2$  carbon giving racemic mixture of product.

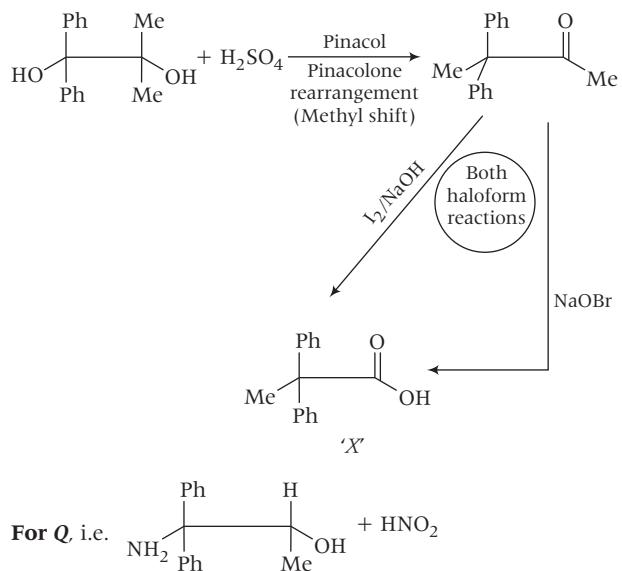


11. Ethanol is the weakest acid among these, hence it is most basic.

- 12. (d)**  
**For P, i.e.**  + H<sub>2</sub>SO<sub>4</sub>

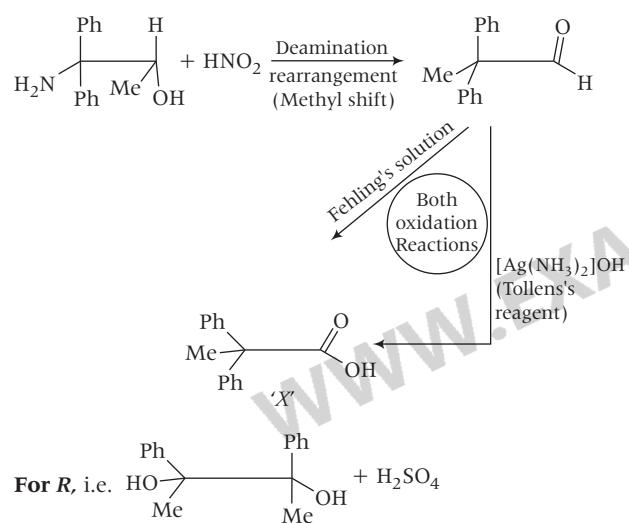
The correct match is 1 i.e.,  $\text{I}_2$ ,  $\text{NaOH}$  and 5 i.e.,  $\text{NaOBr}$ .

The reactions proceed as



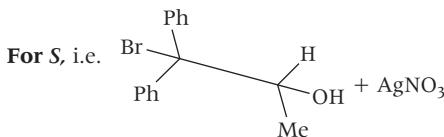
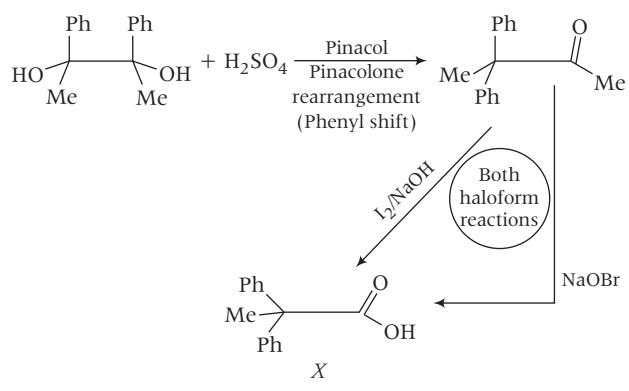
The correct match is 2 i.e.  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$  and 3 i.e., Fehling's solution.

The reactions proceed as



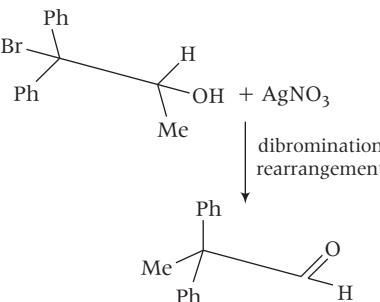
The correct match is 1, 5 again.

The reaction proceed as

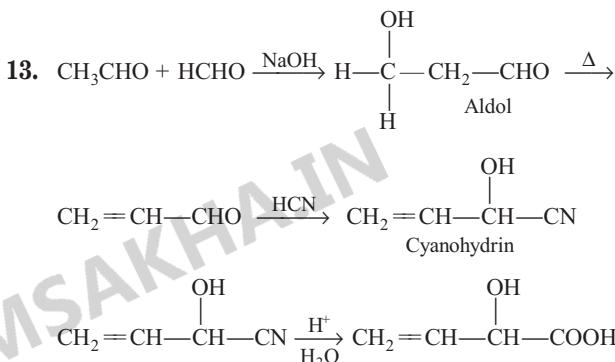


The correct match is 2, 3.

The reaction proceed as

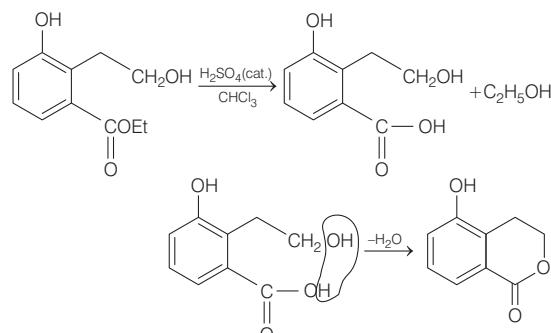


Rest procedure is same as seen for Q above i.e., via oxidation.



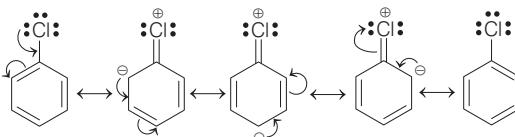
## Topic 2 Acid Derivatives

- Given reaction involves acidic hydrolysis of esters followed by the intramolecular cyclisation. The chemical equation is as follows:



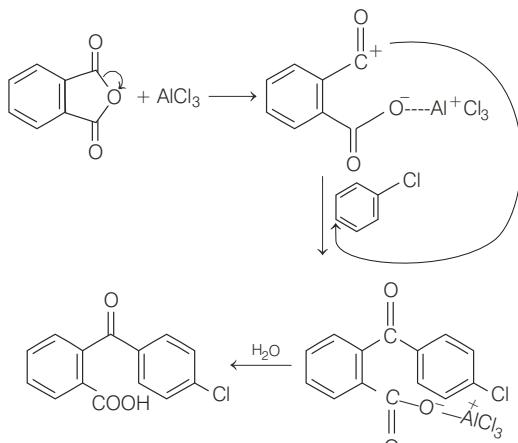
- The major product of the given reaction is (d).

This reaction proceed via Friedel-Crafts acylation. Here, —Cl group present on chlorobenzene is *ortho*- and *para*-directing. It can be easily understood by resonating structures of chlorobenzene.



## 406 Carboxylic Acids and Their Derivatives

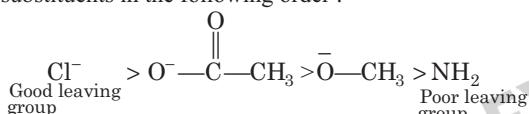
The given reaction proceed as follows :



3. All the given compounds are acid derivatives, thus contain carbonyl group in them. LiAlH<sub>4</sub> reduces these compounds through nucleophilic substitution *via* addition elimination ( $S_N E$ ) reaction. The rate of reaction depends upon the following factors :

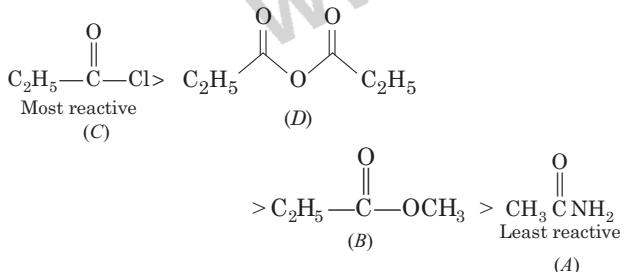
- (i) Size of alkyl group.
- (ii) Steric hinderance around the  $>\text{C}=\text{O}$  group.
- (iii) (+)ve charge on the C-atom of  $>\text{C}=\text{O}$  group.

The alkyl groups are more or less same in the given compounds. Thus, the reactivity order of given compounds depends upon 2nd and 3rd factor written above. The cumulative effect of these two factors results to leaving group ability (LGA) of the substituents in the following order :

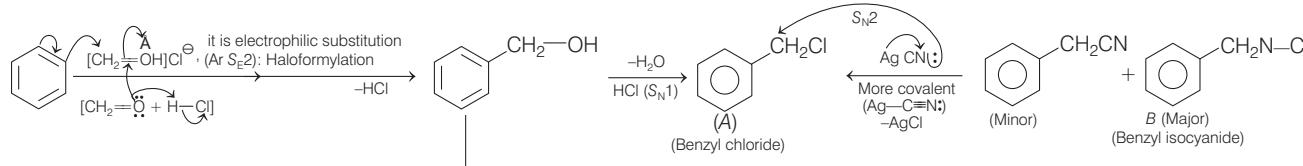


This leaving group ability (weak conjugate base) corresponds directly to the reactivity order.

Hence, the correct reactivity order is:

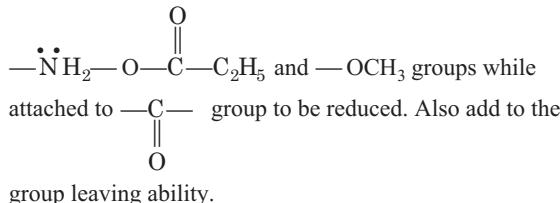


6. The mechanism of the given reaction is as follows:

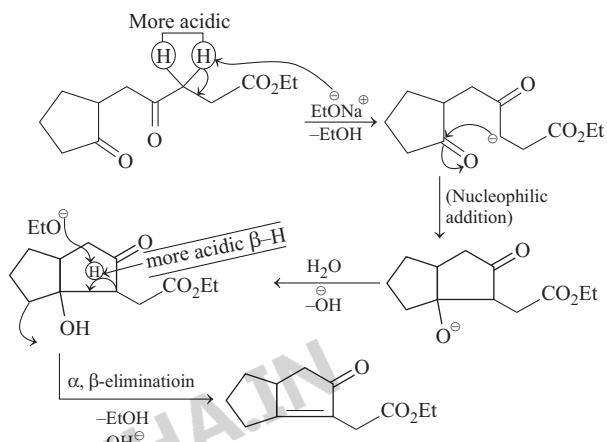


Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

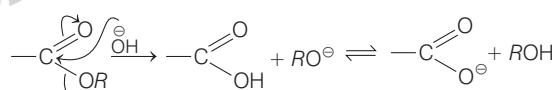
Note The  $-I$  effect of  $-\text{Cl}$  and  $+m$  effects of



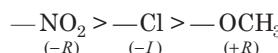
4. In presence of strong base, acidic H can easily be removed that result in formation of anion. The resulting anion undergoes intramolecular nucleophilic addition which on hydrolysis followed by heating gives the required product.



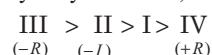
5. Alkaline hydrolysis of an ester (carboxylic acid derivative) follows acyl S<sub>N</sub>2 mechanism.



Rate of S<sub>N</sub>2 mechanism depends on the polarity of  $>\text{C}=\text{O}$  group of  $-\text{COOR}$  group. Electron withdrawing group ( $-R > -I$ ) increases the rate of S<sub>N</sub>2 reaction whereas electron donating group ( $+R > +I$ ) decreases the rate of S<sub>N</sub>2 reaction. Here, the nature of functional groups attached *para* to the benzene ring are:

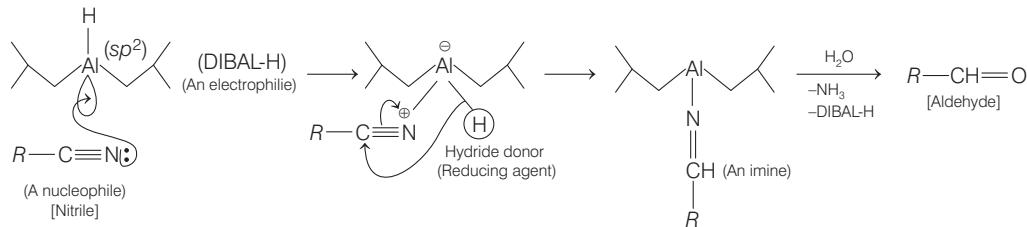


So, the order of hydrolysis will be,



7. **Key Idea** DIBAL-H is diisobutyl aluminium hydride,  $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH}$ . It is a selective reducing agent. It reduces carboxylic acids, carboxylic acid derivatives and nitriles into aldehydes. It is an electrophilic reducing agent.

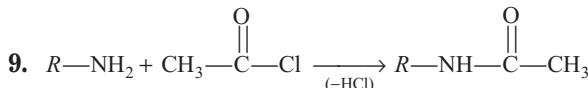
The mechanism of the reaction is as follows:



So,  $\text{R}-\overset{\parallel}{\underset{\text{O}}{\text{C}}}\text{H}$  is the correct answer.

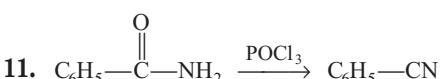
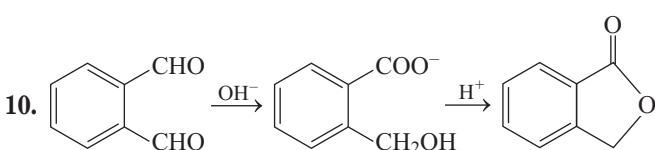
8. **PLAN** This problem can be solved by using the stability of radical obtained after fragmentation of peroxyester.  
Allylic radical are more stable than alkyl radical, so when there is a possibility of formation of allyl radical, it will undergo fragmentation through formation of allyl radical. i.e. fragmentation produces stable radical.  
On the basis of stability of radical, fragmentation can be done as

| Column I | Column II                                                                                                              | Explanation                                                                                                                                                                                                                      |
|----------|------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| P.       | $\text{C}_6\text{H}_5\text{H}_2\text{C}(\text{O})\text{OOCCH}_3$                                                       | 1. $\text{C}_6\text{H}_5-\dot{\text{C}}\text{H}_2 + \text{CO}_2 + \text{CH}_3\text{O}^\bullet$                                                                                                                                   |
| Q.       | $\text{C}_6\text{H}_5\text{H}_2\text{C}(\text{O})\text{OOCCH}_2\text{C}(\text{CH}_3)(\text{CH}_2\text{C}_6\text{H}_5)$ | 3. $\text{C}_6\text{H}_5-\dot{\text{C}}\text{H}_2 + \text{CO}_2 + \text{Ph}-\text{CH}_2-\overset{\bullet}{\text{C}}(\text{CH}_3)-\text{CH}_3 \rightarrow \text{Ph}-\dot{\text{C}}\text{H}_2 + \text{CH}_3-\text{CO}-\text{CH}_3$ |
| R.       | $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OOCCH}_2\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)$                      | 4. $\text{C}_6\text{H}_5-\dot{\text{C}}\text{O}_2 + \text{CH}_3-\overset{\bullet}{\text{C}}(\text{CH}_3)-\text{CH}_3 \xrightarrow{-\text{CO}_2} \text{Ph} + \text{CH}_3-\text{CO}-\text{Ph} + \text{CH}_3^\bullet + \text{CO}_2$ |
| S.       | $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OOCCH}_3$                                                                 | 2. $\text{C}_6\text{H}_5-\dot{\text{C}}\text{O}_2 + \text{CH}_3\text{O}^\bullet \rightarrow \text{C}_6\text{H}_5^\bullet + \text{CO}_2$                                                                                          |

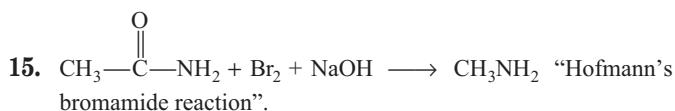
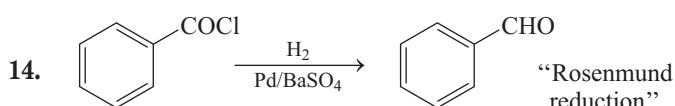
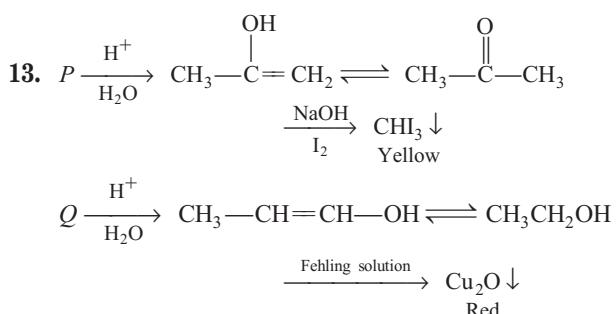
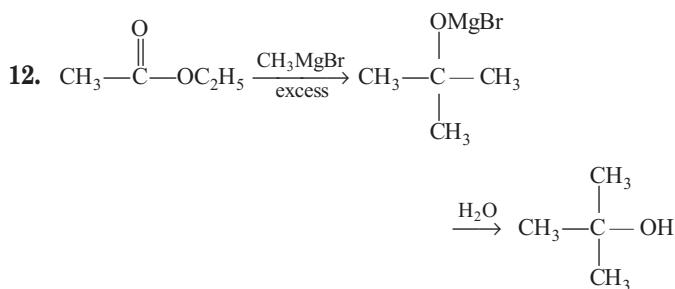


Since, each  $-\text{COCH}_3$  group displace one H atom in the reaction of one mole of  $\text{CH}_3-\overset{\text{O}}{\text{C}}-\text{Cl}$  with one  $-\text{NH}_2$  group, the molecular mass increases with 42 unit.

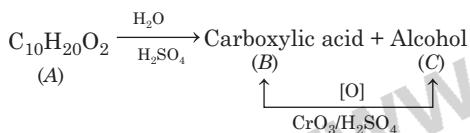
Since the mass increases by  $(390 - 180) = 210$ , hence the number of  $-\text{NH}_2$  group is  $\frac{210}{42} = 5$ .



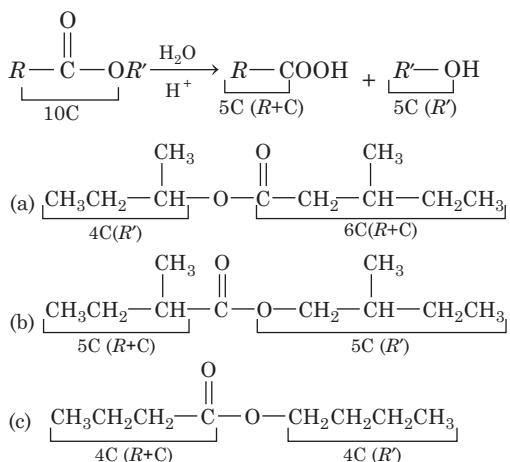
## 408 Carboxylic Acids and Their Derivatives



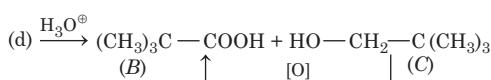
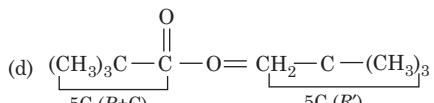
16. A can be written as :  $(\text{CH}_3)_3\text{C}-\text{COOCH}_2\text{C}(\text{CH}_3)_3$  ]



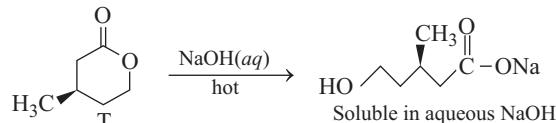
From the informations given, it is clear that A is an ester which contain 10 carbon atoms. Again, C on oxidation gives B. It indicates B and C contains equal number of carbon atom, i.e. each of B and C contains 5 carbon atom.



Note It is not having the molecular formula of A ( $\text{C}_{10}\text{H}_{20}\text{O}_2$ ). Its molecular formula ( $\text{C}_8\text{H}_{16}\text{O}_2$ ).



17. (a) T undergoes an ester hydrolysis in hot aqueous alkali as

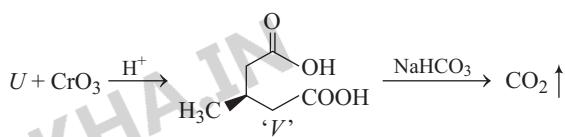


(b)  $\text{LiAlH}_4$  reduces ester to alcohol as

“U” No chiral carbon optically inactive.

(c) U on treatment with excess of acetic anhydride forms a diester as

(d) U on treatment with  $\text{CrO}_3|\text{H}^+$  undergo oxidation to diacid which gives effervescence with  $\text{NaHCO}_3$ .



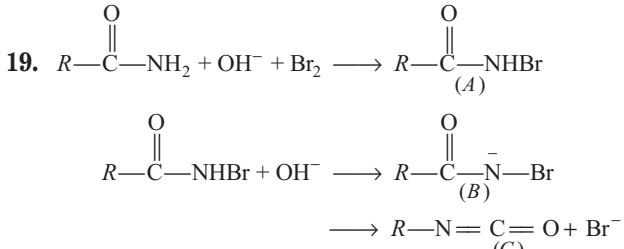
18. For separation by differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.

(a) Both phenol and benzoic acid forms salt with  $\text{NaOH}$ , hence this mixture can't be separated.

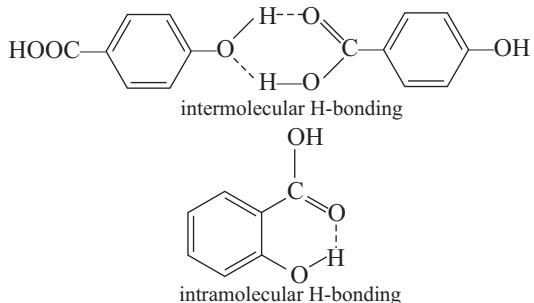
(b) Benzoic acid forms salt with  $\text{NaOH}$  while benzyl alcohol does not, hence the mixture can be separated using  $\text{NaOH}$ . Also benzoic acid forms salt with  $\text{NaHCO}_3$  but benzyl alcohol does not, hence  $\text{NaHCO}_3$  can be used for separation.

(c) Neither benzyl alcohol nor phenol forms salt with  $\text{NaHCO}_3$ , mixture cannot be separated using  $\text{NaHCO}_3$ .

(d)  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$  forms salt with  $\text{NaOH}$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  does not, hence mixture can be separated using  $\text{NaOH}$ .  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$  forms salt with  $\text{NaHCO}_3$ .  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  does not, hence mixture can be separated using  $\text{NaHCO}_3$ .

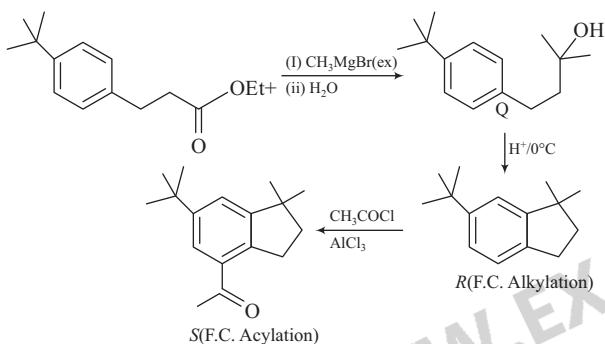


20. *p*-hydroxy benzoic acid has higher boiling point than *o*-hydroxy benzoic acid because former prefers intermolecular H-bonding while the latter prefer intramolecular H-bonding.



21. Compounds with  $\text{CH}_3-\overset{\text{O}}{\text{C}}-$  or  $\text{CH}_3-\text{CH}(\text{OH})-$  group gives haloform reaction but this reaction is given only by aldehydes, ketones and alcohols, so acetic acid does not give haloform reaction. However acetic acid has three  $\alpha$ -H, therefore, statement I is true but statement II is false.

#### Passage-1



22. (a)      23. (c)

24. **PLAN** Alkenes decolourise  $\text{Br}_2$  water

*cis*-isomer  $\xrightarrow{\text{dil-KMnO}_4}$  Meso isomers by *syn* addition  
*trans*-isomer  $\xrightarrow{\text{dil-KMnO}_4}$  *d*(+) and *l*(-) isomers by *syn* addition thus, racemic mixture.  
 Formation of anhydride from dicarboxylic acid indicates *cis*-isomer.

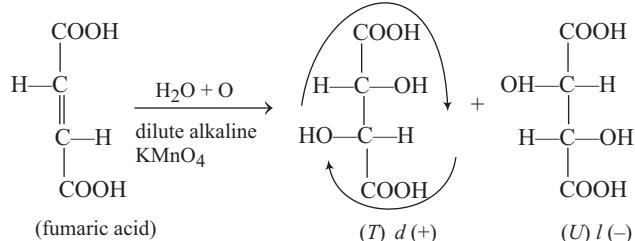
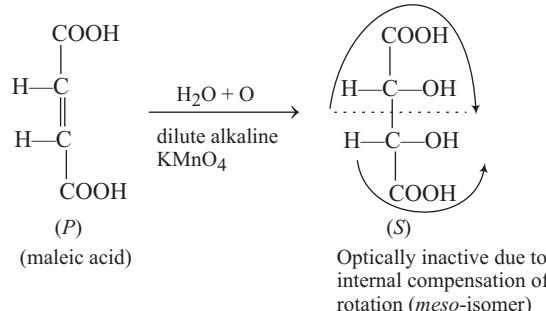
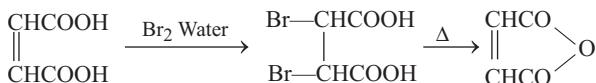
*P* and *Q* are isomers of dicarboxylic acids.

*P, Q*  $\xrightarrow{\text{Br}_2 \text{ water}}$  decolourised

*P* and *Q* have ( $\text{C}=\text{C}$ ) bond

*P*  $\xrightarrow{\Delta}$  anhydride

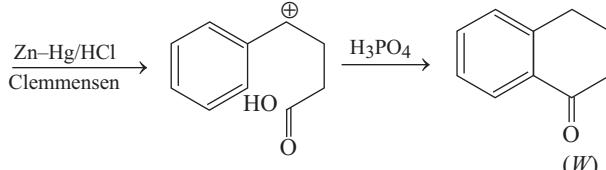
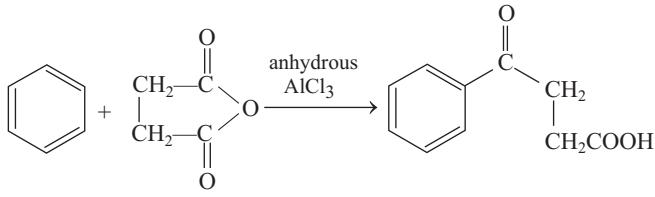
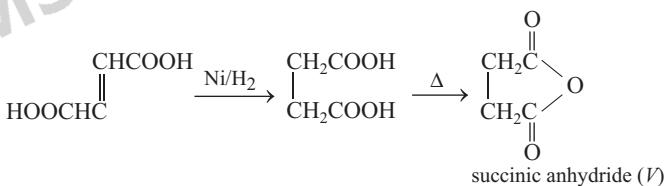
Thus, *P* is *cis*-isomer.



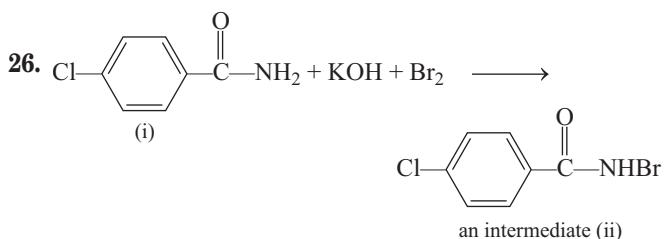
*T* and *U* (in 1 : 1 molar ratio) form optically inactive (racemic mixture) due to external compensation.

25. **PLAN**  $\text{Ni}/\text{H}_2$  reduces ( $\text{C}=\text{C}$ ) bond.

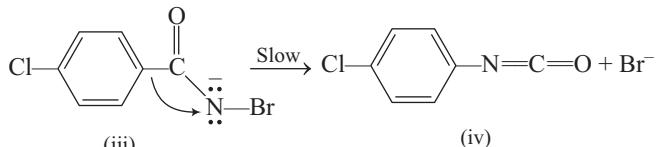
Benzene undergoes Friedel-Crafts reaction  $\text{Zn-Hg/HCl}$  reduces carbonyl group (Clemmensen reduction)



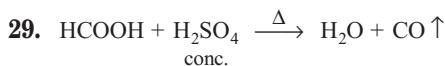
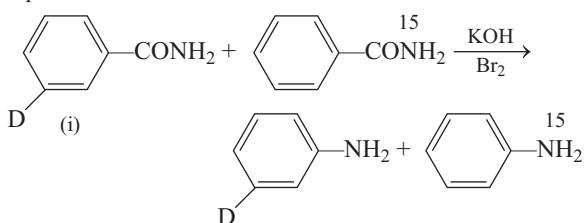
## 410 Carboxylic Acids and Their Derivatives



27. Rearrangement of (iii) to (iv) is the rate determining step :



28. The rate determining step of Hofmann's bromamide reaction is unimolecular rearrangement of bromamide anion (iii) and no cross-products are formed when mixture of amides are taken.

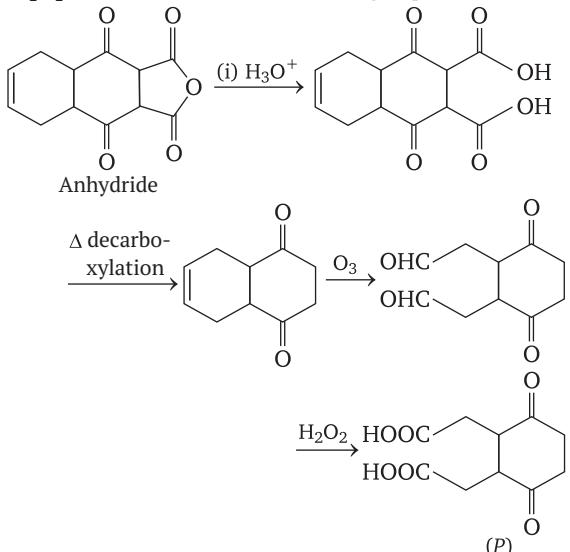


30. Propanoic acid has higher boiling point than *n*-butanol because of more exhaustive H-bonding in former case.

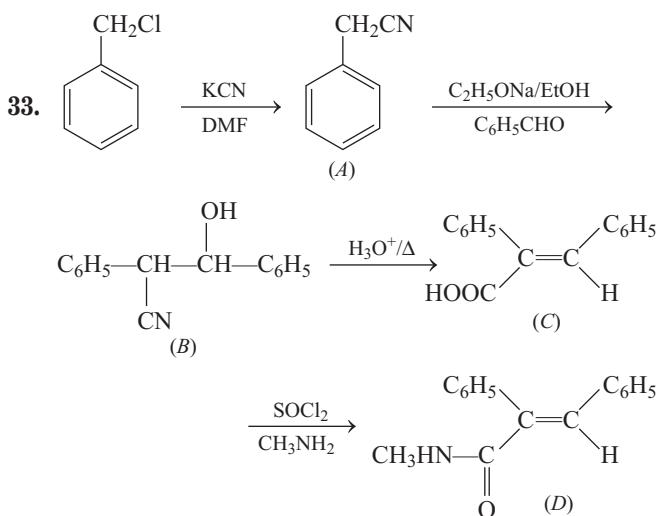
31. Saponification is hydrolysis of ester in presence of dilute base rather in presence of dilute acid.

32. **PLAN** Reactant is cyclic anhydride and changes to dicarboxylic acid on hydrolysis.

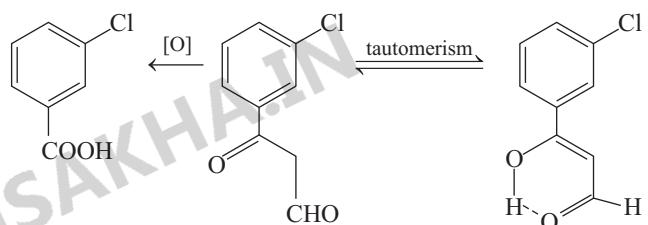
Also there is decarboxylation on heating if there is keto group w.r.t  $-\text{COOH}$  group. Ozonolysis cleaves  $(\text{C}=\text{C})$  bond and  $\text{H}_2\text{O}_2$  oxidises  $-\text{CHO}$  to  $-\text{COOH}$  group.



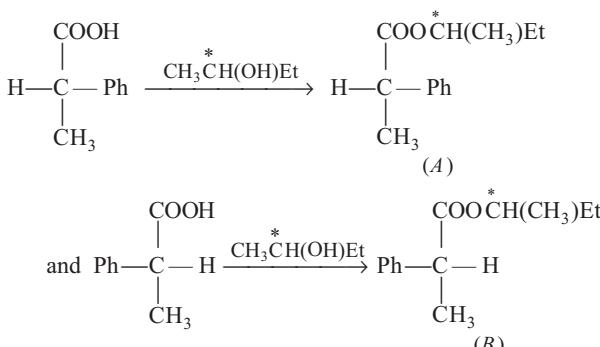
Thus, number of  $-\text{COOH}$  groups in P = 2.



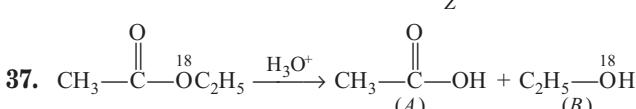
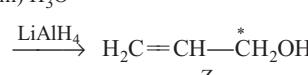
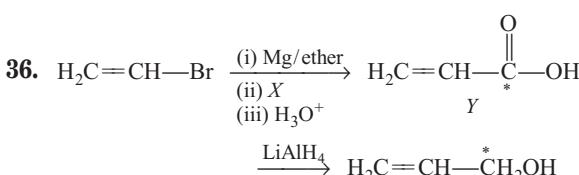
34. Compound A of molecular formula  $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$  exist in keto and predominantly in enolic form B. Hence, A must be a carbonyl compound which contain  $\alpha$ -H. Enolic forms of B predominates because of presence of intramolecular H-bonding.

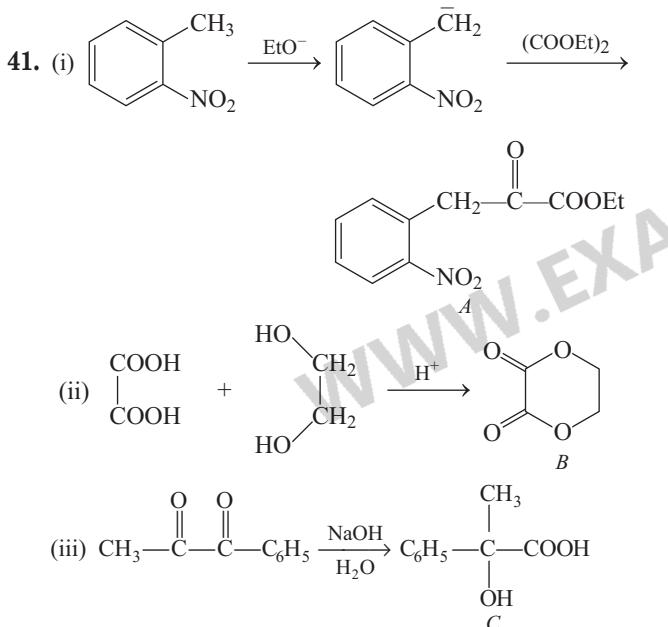
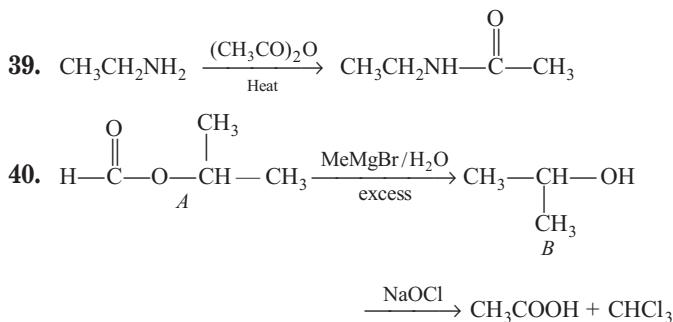
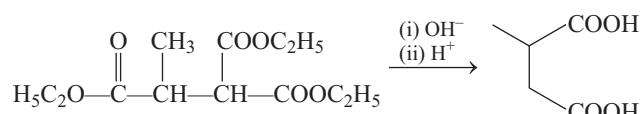
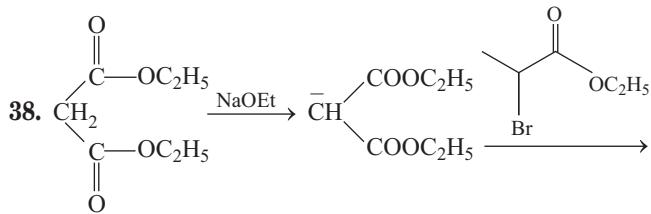


35. The two stereoisomers of 2-phenyl propanoic acid in the racemic mixture are :

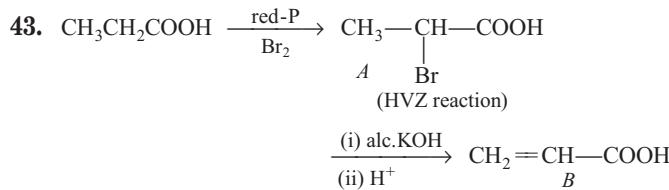
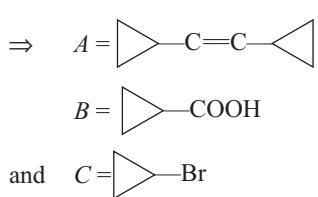


Here A and B are diastereomers.

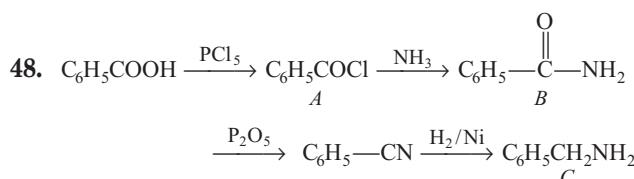
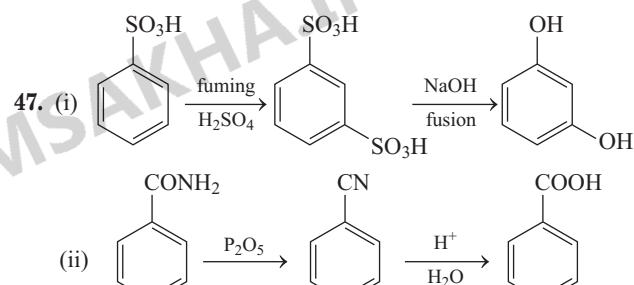
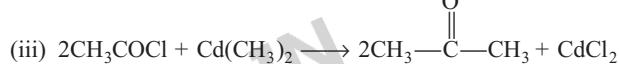
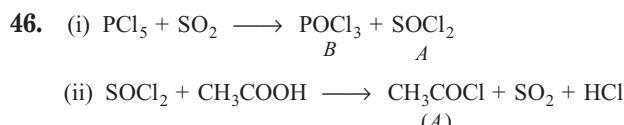
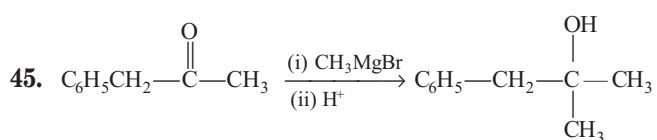
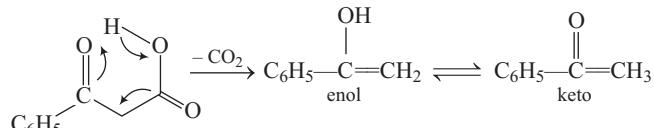




42. B is  $\text{C}_3\text{H}_5\text{COOH}$  and A is  $\text{C}_3\text{H}_5-\text{C}\equiv\text{C}-\text{C}_3\text{H}_5$   
Also A on ozonolysis gives B indicates that there is no olefinic bond in  $\text{C}_3\text{H}_5$ -unit of A and it is cyclopropyl group.

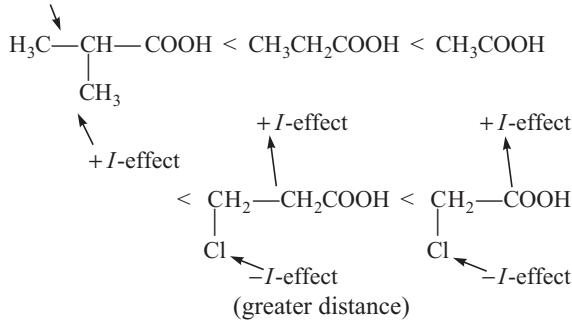


44. A  $\beta$ -keto acid undergo very fast decarboxylation

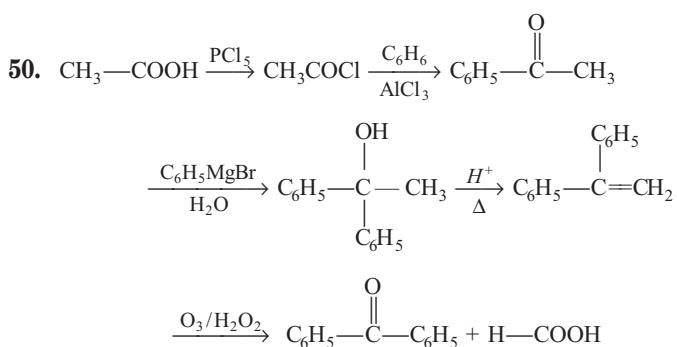


49. Electron withdrawing inductive effect increases acid strength while electron donating inductive effect decreases acid strength.

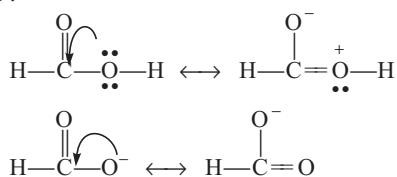
+ I-effect



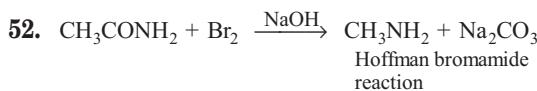
## 412 Carboxylic Acids and Their Derivatives



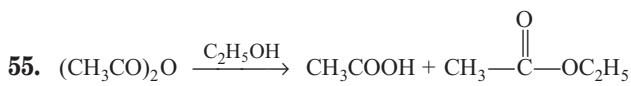
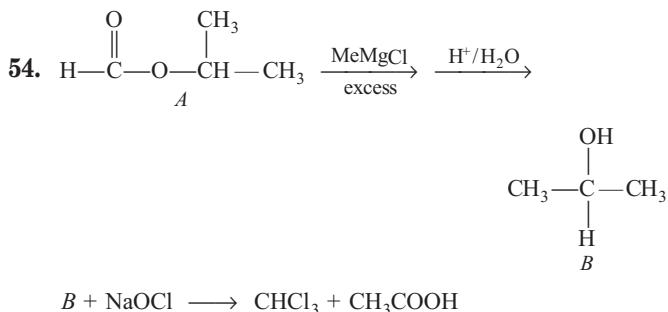
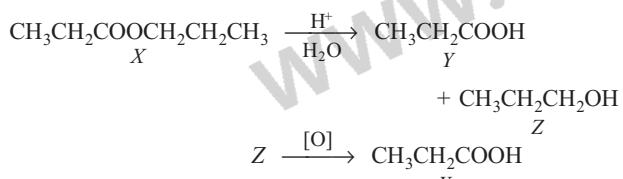
51. Both formic acid and sodium formate exhibit the phenomenon of resonance as :



In formic acid, the extent of delocalisation is less compared to sodium formate because of charge separation in the former case. Due to this reason, the bond length between carbon and  $sp^3$  oxygen in formic acid is slightly greater than the same between carbon and  $sp^2$  oxygen. In formate ion, there is no separation of charge and both the resonance structures are equivalent giving equal bond length of both carbon oxygen bonds.



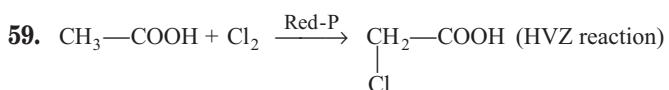
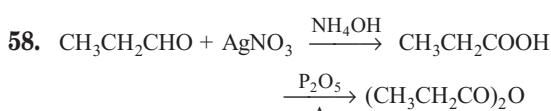
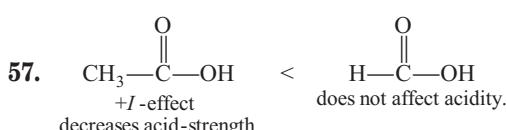
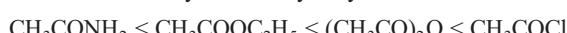
53. X is an ester and both its acid and alcohol fragments have same number of carbons. Hence, X is :



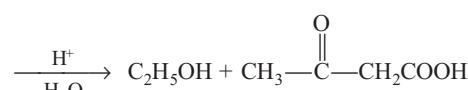
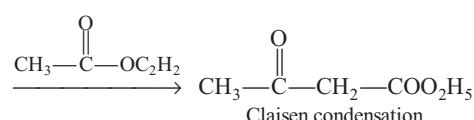
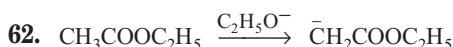
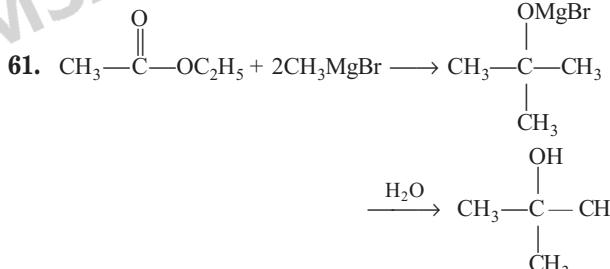
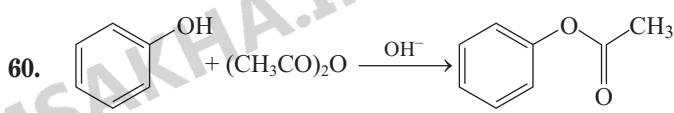
56. Among acid derivatives, the reactivity towards nucleophilic acyl substitution is in the order of :



Hydrolysis is an example of nucleophilic acyl substitution, hence the reactivity towards hydrolysis is :



For this reaction to occur, presence of a  $\alpha$ -H is essential requirement. Formic acid does not have any  $\alpha$ -H, fails in HVZ reaction.

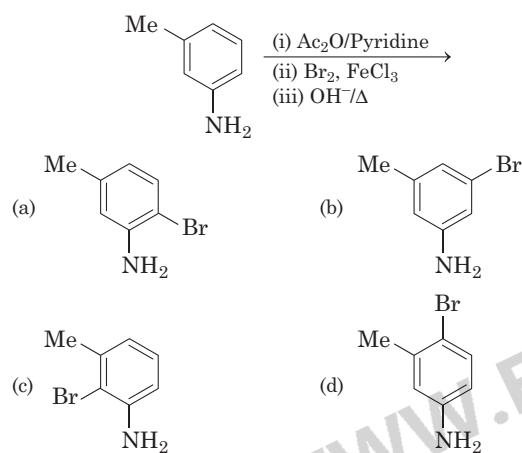


27

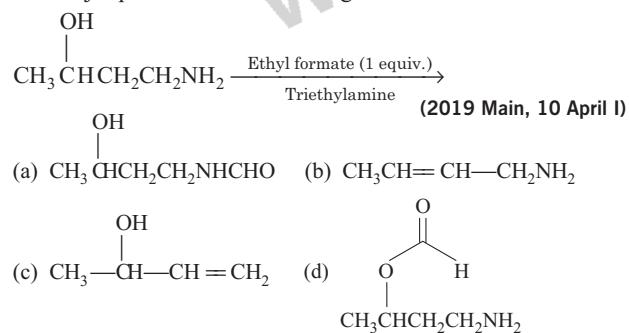
# **Aliphatic Compounds Containing Nitrogen**

## **Objective Questions I (Only one correct option)**

- 1.** The final major product of the following reaction is  
**(2020 Main, 5 Sep II)**



- 2.** The major product of the following reaction is

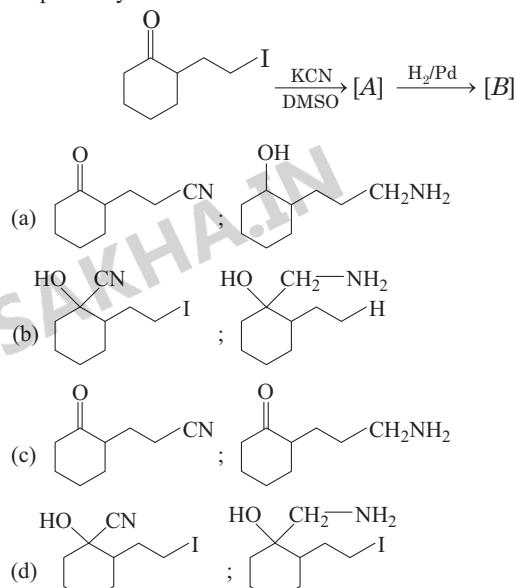


3. Ethylamine ( $C_2H_5NH_2$ ) can be obtained from






5. The major products *A* and *B* for the following reactions are, respectively (2019 Main, 9 April II)



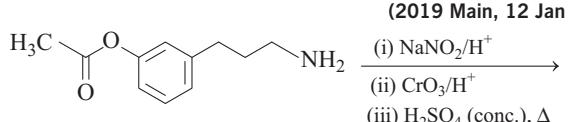
6. Which of the following amines can be prepared by Gabriel phthalimide reaction? (2019 Main, 8 April)



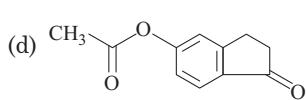
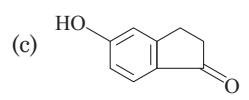
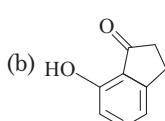
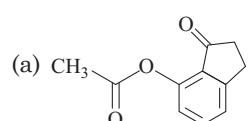
7. In the following compounds, the decreasing order of basic strength will be **(2019 Main, 8 April I)**

- (a)  $\text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > (\text{C}_2\text{H}_5)_2\text{NH}$   
 (b)  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{NH}_3 > \text{C}_2\text{H}_5\text{NH}_2$   
 (c)  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$   
 (d)  $\text{NH}_2 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH}$

- 8.** The major product of the following reaction is



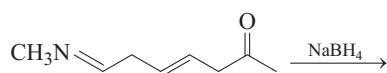
## 414 Aliphatic Compounds Containing Nitrogen



9. A compound 'X' on treatment with  $\text{Br}_2 / \text{NaOH}$ , provided  $\text{C}_3\text{H}_9\text{N}$ , which gives positive carbylamine test. Compound 'X' is  
 (2019 Main, 11 Jan II)

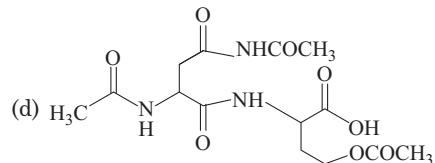
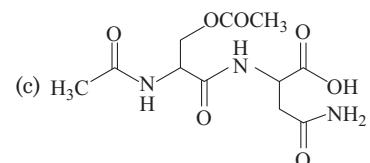
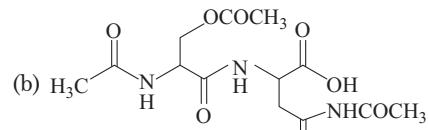
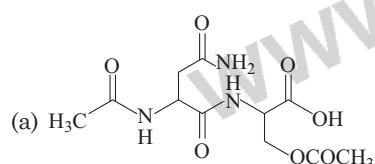
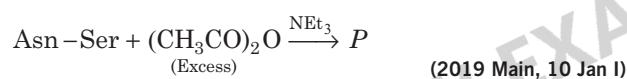
- (a)  $\text{CH}_3\text{COCH}_2\text{NHCH}_3$       (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$   
 (c)  $\text{CH}_3\text{CON}(\text{CH}_3)_2$       (d)  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{NH}_2$

10. The major product of the following reaction is  
 (2019 Main, 10 Jan II)

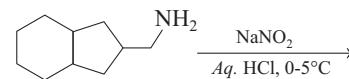


- (a)
- (b)
- (c)
- (d)

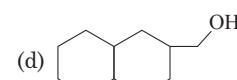
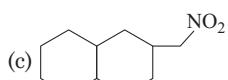
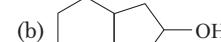
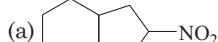
11. The correct structure of product 'P' in the following reaction is



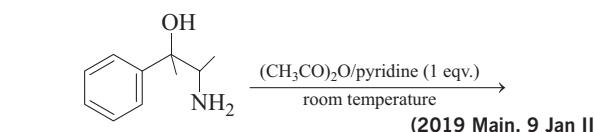
12. The major product formed in the reaction given below will be



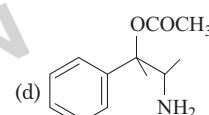
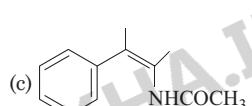
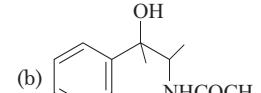
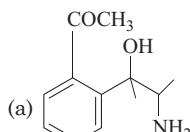
(2019 Main, 10 Jan I)



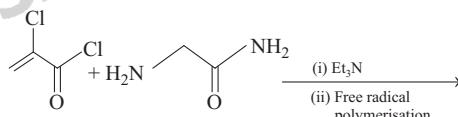
13. The major product obtained in the following reaction is



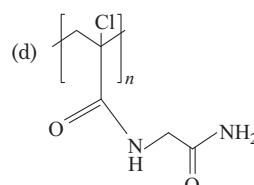
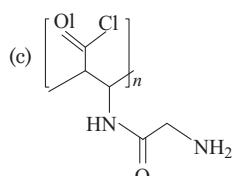
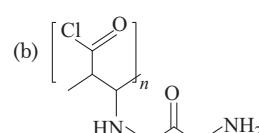
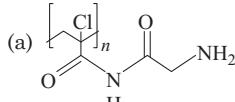
(2019 Main, 9 Jan II)



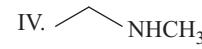
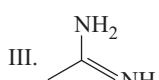
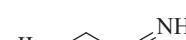
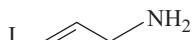
14. Major product of the following reaction is



(2019 Main, 9 Jan I)



15. The increasing order of basicity of the following compounds is



(2018 Main)

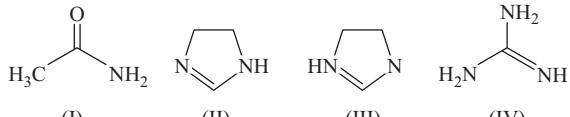
- (a) (I) < (II) < (III) < (IV)

- (c) (II) < (I) < (IV) < (III)

- (b) (II) < (I) < (III) < (IV)

- (d) (IV) < (II) < (I) < (III)

- 16.** The order of basicity among the following compounds is  
**(2017 Adv.)**



- (a) II > I > IV > III  
 (b) I > IV > III > I  
 (c) IV > I > II > I  
 (d) IV > I > II > III

- 17.** In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br<sub>2</sub> used per mole of amine produced are  
**(2016 Main)**

- (a) four moles of NaOH and two moles of Br<sub>2</sub>  
 (b) two moles of NaOH and two moles of Br<sub>2</sub>  
 (c) four moles of NaOH and one mole of Br<sub>2</sub>  
 (d) one mole of NaOH and one mole of Br<sub>2</sub>

- 18.** Considering the basic strength of amines in aqueous solution, which one has the smallest pK<sub>b</sub> value?  
**(2014 Main)**

- (a) (CH<sub>3</sub>)<sub>2</sub>NH (b) CH<sub>3</sub>NH<sub>2</sub> (c) (CH<sub>3</sub>)<sub>3</sub>N (d) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>

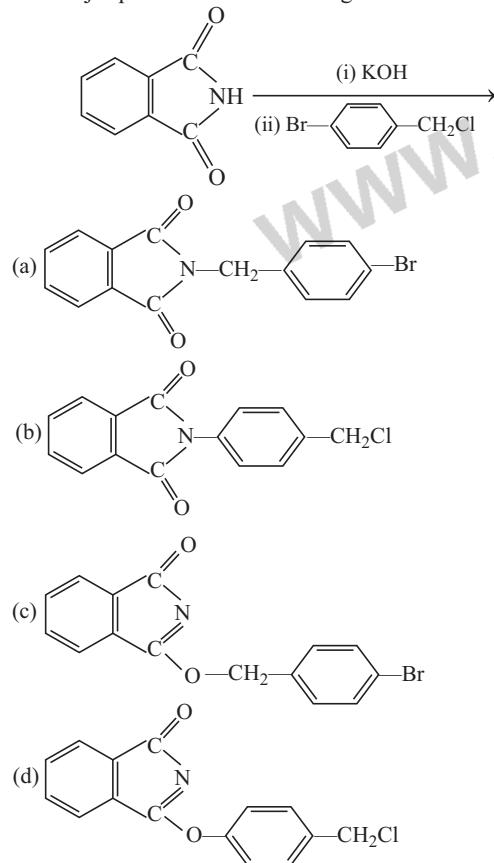
- 19.** On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is  
**(2014 Main)**

- (a) an alkanol (b) an alkanediol  
 (c) an alkyl cyanide (d) an alkyl isocyanide

- 20.** The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was  
**(2013 Main)**

- (a) methyl isocyanate (b) methylamine  
 (c) ammonia (d) phosgene

- 21.** The major product of the following reaction is  
**(2011)**



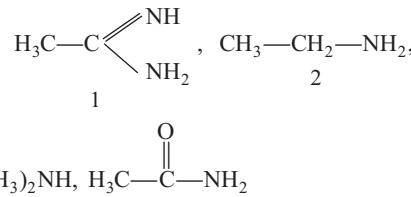
- 22.** CH<sub>3</sub>NH<sub>2</sub> + CHCl<sub>3</sub> + KOH → Nitrogen containing compound + KCl + H<sub>2</sub>O. Nitrogen containing compound is  
**(2006)**

- (a) CH<sub>3</sub>CN (b) CH<sub>3</sub>NHCH<sub>3</sub>  
 (c) CH<sub>3</sub>— $\bar{N} \equiv \dot{C}$  (d) CH<sub>3</sub>— $\dot{N} \equiv \bar{C}$

- 23.** Benzamide on treatment with POCl<sub>3</sub> gives  
**(2004)**

- (a) aniline (b) benzonitrile  
 (c) chlorobenzene (d) benzyl amine

- 24.** The correct order of basicities of the following compounds is



- (a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4  
 (c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

- 25.** A positive carbylamine test is given by  
**(1999, 2M)**

- (a) N, N-dimethylaniline (b) 2, 4-dimethylaniline  
 (c) N-methyl-o-methylaniline (d) *p*-methylbenzylamine

- 26.** *p*-chloroaniline and anilinium hydrochloride can be distinguished by  
**(1998, 2M)**

- (a) Sandmeyer reaction (b) NaHCO<sub>3</sub>  
 (c) AgNO<sub>3</sub> (d) Carbylamine test

- 27.** Carbylamine test is performed in alc. KOH by heating a mixture of  
**(1984, 1M)**

- (a) chloroform and silver powder  
 (b) trihalogenated methane and a primary amine  
 (c) an alkyl halide and a primary amine  
 (d) an alkyl cyanide and a primary amine

- 28.** Acetamide is treated separately with the following reagents. Which of these would give methylamine?  
**(1983, 1M)**

- (a) PCl<sub>5</sub> (b) Soda lime  
 (c) NaOH + Br<sub>2</sub> (d) Hot, conc. H<sub>2</sub>SO<sub>4</sub>

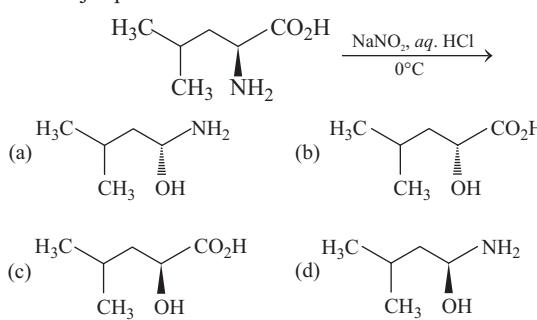
- 29.** The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine, is  
**(1981, 1M)**

- (a) methylamine (b) ethylamine  
 (c) diethylamine (d) triethylamine

### Objective Question II

(Only one more than one correct option)

- 30.** The major product of the reaction is



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31. A positive carbylamine test is given by (1999, 2M)  
 (a) N, N-dimethyl aniline      (b) 2, 4-dimethyl aniline  
 (c) N-methyl-*o*-methyl aniline      (d) *p*-methyl benzyl amine

### Fill in the Blank

32.  $(\text{CH}_3\text{OH}_2^+)$  is ..... acidic than  $(\text{CH}_3\text{NH}_3^+)$ . (1997 C, 1M)

### Match the Column

33. Match each of the compounds in Column I with its characteristic reaction(s) in Column II. (2016, Adv.)

| Column I                                                      | Column II                                                                     |
|---------------------------------------------------------------|-------------------------------------------------------------------------------|
| (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$              | (p) Reduction with Pd - C/H <sub>2</sub>                                      |
| (B) $\text{CH}_3\text{CH}_2\text{OOCCH}_3$                    | (q) Reduction with $\text{SnCl}_2/\text{HCl}$                                 |
| (C) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$             | (r) Development of foul smell on treatment with chloroform and alcoholic KOH. |
| (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ | (s) Reduction with diisobutylaluminium hydride (DIBAL-H)                      |
|                                                               | (t) Alkaline hydrolysis                                                       |

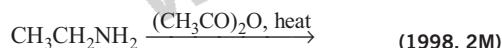
### Subjective Questions

34.  $\text{C}_5\text{H}_{13}\text{N} \xrightarrow[\substack{-\text{N}_2 \\ X}]{\text{NaNO}_2, \text{HCl}} Y$  (tertiary alcohol + other products)  
 optically active

Find *X* and *Y*. Is *Y* optically active? Write the intermediate steps (2005, 4M)

35. Give reasons for the following in one or two sentences.  
 Dimethylamine is a stronger base than trimethylamine. (1998, 2M)

36. Following reaction gives two products. Write the structures of the products.



37. Give the structure of *A*. ‘*A* ( $\text{C}_3\text{H}_9\text{N}$ ) reacts with benzenesulphonyl chloride to give a solid, insoluble in alkali’. (1993, 1M)

38. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic KOH. A 0.295 g sample of the substance dissolved in *aq.* HCl and treated with  $\text{NaNO}_2$  solution at 0°C, liberated a colourless, odourless gas whose volume corresponds to 112 mL at STP.

After evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance assuming that it contains one N-atom per molecule. (1993, 4M)

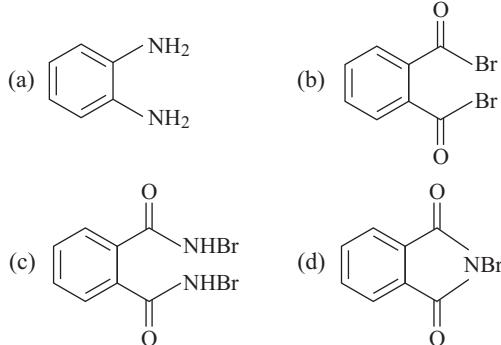
39. Arrange the following in increasing order of basic strength: methylamine, dimethylamine, aniline, N-methylaniline. (1988, 1M)
40. Give a chemical test and the reagent used to distinguish between the following : “Ethylamine and diethylamine”. (1988, 1M)
41. For nitromethane molecule, write structures  
 (i) showing significant resonance stabilisation  
 (ii) indicating tautomerism (1986, 1M + 1M = 2M)
42. State the equation for the preparation of following compounds : *n*-propyl amine from ethyl chloride. (1982, 2 × 1M = 2M)

### Passage Based Questions

Treatment of compound *O* with  $\text{KMnO}_4/\text{H}^+$  gave *P*, which on heating with ammonia gave *Q*. The compound *Q* on treatment with  $\text{Br}_2/\text{NaOH}$  produced *R*. On strong heating, *Q* gave *S*, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound *T*. (2016 Adv.)



43. The compound *R* is

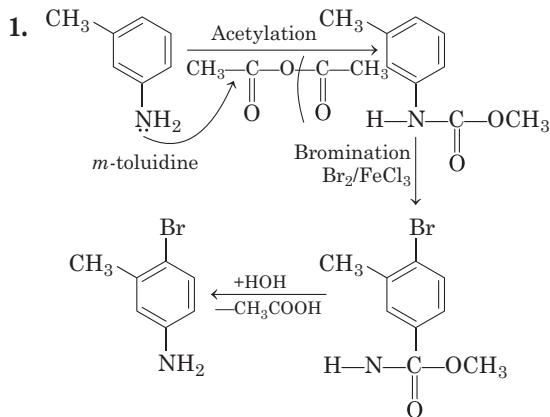


44. The compound *T* is  
 (a) glycine      (b) alanine      (c) valine      (d) serine

### Answers

- |                                               |         |         |            |
|-----------------------------------------------|---------|---------|------------|
| 1. (d)                                        | 2. (a)  | 3. (b)  | 4. (c)     |
| 9. (b)                                        | 10. (c) | 11. (a) | 12. (*)    |
| 17. (c)                                       | 18. (a) | 19. (d) | 20. (a)    |
| 25. (d)                                       | 26. (c) | 27. (b) | 28. (c)    |
| 33. A → p, q, s, t; B → p, s, t; C → p; D → r | 43. (a) | 44. (b) |            |
|                                               |         |         | 5. (c)     |
|                                               |         |         | 6. (a)     |
|                                               |         |         | 7. (c)     |
|                                               |         |         | 8. (c)     |
|                                               |         |         | 13. (b)    |
|                                               |         |         | 14. (d)    |
|                                               |         |         | 15. (c)    |
|                                               |         |         | 16. (d)    |
|                                               |         |         | 21. (a)    |
|                                               |         |         | 22. (d)    |
|                                               |         |         | 23. (b)    |
|                                               |         |         | 24. (b)    |
|                                               |         |         | 29. (c)    |
|                                               |         |         | 30. (c)    |
|                                               |         |         | 31. (b,d)  |
|                                               |         |         | 32. (more) |

# Hints & Solutions



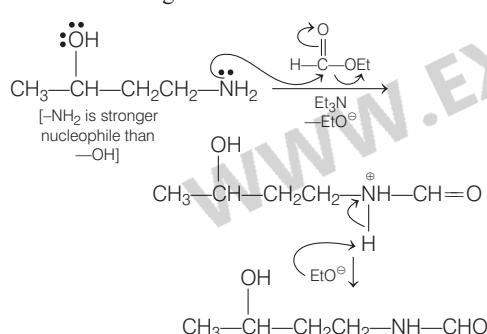
The basic nature of *m*-toluidine is not greatly affected by the —CH<sub>3</sub> group.

—NH—C(=O)—OCH<sub>3</sub> is moderately activating group, its activating nature overcome weak activating —CH<sub>3</sub> group.

Due to bulky nature of —NHC(=O)CH<sub>3</sub> attack happen *para* to —NHCO—CH<sub>3</sub>.

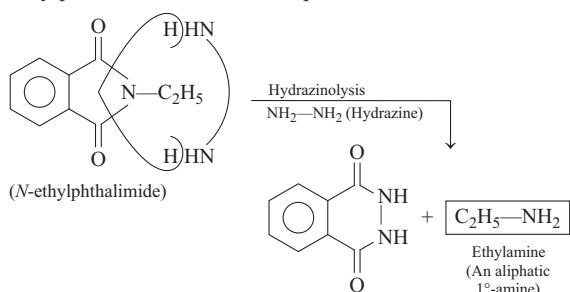
Here, NH<sub>2</sub> group has been protected by forming its acetyl derivative and as such it does not interfere in the bromination.

2. The mechanism of the given reaction is as follows:



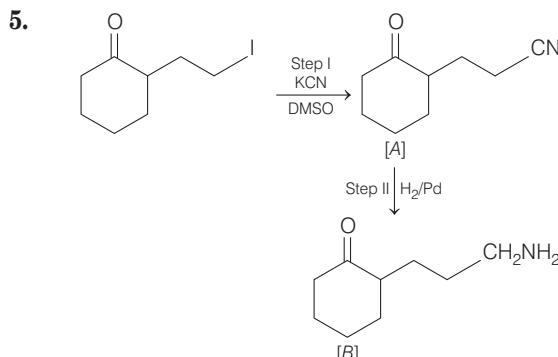
The basic mechanism of the reaction is acyl S<sub>N</sub>2 because the nucleophile, CH<sub>3</sub>(OH)CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> attacks the sp<sup>2</sup> carbon of the ester (H—CO<sub>2</sub>Et) and gets substituted.

3. The reaction for the production of ethylamine from *N*-ethylphthalimide can be takes place as follows:



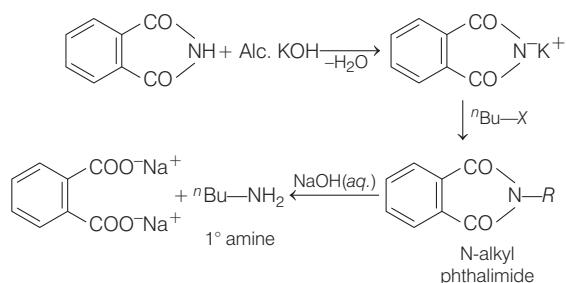
This reaction is the second step of Gabriel phthalimide synthesis for the preparation of aliphatic 1°-amines and amino acid. In this step concentrated alkali can also be used in place of hydrazine.

4. Hinsberg's reagent is C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl (benzene sulphonyl chloride). This reagent is used to distinguish between primary, secondary and tertiary amines.



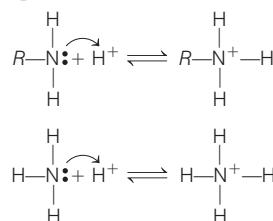
**Step I** involves the nucleophilic substitution reaction in which I (Iodine) is substituted by —CN group. In **Step II**, H<sub>2</sub>/Pd reagent is used for reduction process. Here, —CN group reduces itself to —CH<sub>2</sub>NH<sub>2</sub>.

6. *n*-butylamine (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) can be prepared by Gabriel phthalimide reaction. This method produces only primary amines without the traces of secondary or tertiary amines. In this method, phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.



Triethylamine, *t*-butylamine and *neo*-pentylamine cannot be prepared by Gabriel phthalimide reaction.

7. Basic strength can be compared by the reaction of an alkanamine and ammonia with proton.



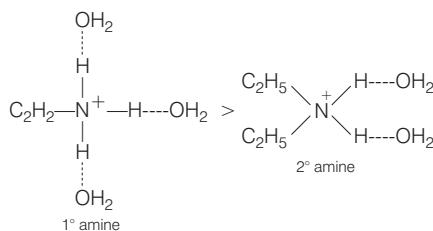
Basicity of an amine in aqueous solution depends upon the solubility of ammonium cation formed by accepting proton from

## 418 Aliphatic Compounds Containing Nitrogen

water. The stability of ammonium cation depends upon the following factors.

- (a) + I effect
- (b) Steric effect
- (c) Solvation effect

In first case, on increasing the size of alkyl group + I effect increases and the positive charge of ammonium cation gets dispersed more easily. Therefore, order of basicity is 2° amine > 1° amine > ammonia. In second case, substituted ammonium cation is also stabilised by solvation with water molecules. Greater the size of ion, lesser will be the solvation and less stabilised is the ion.



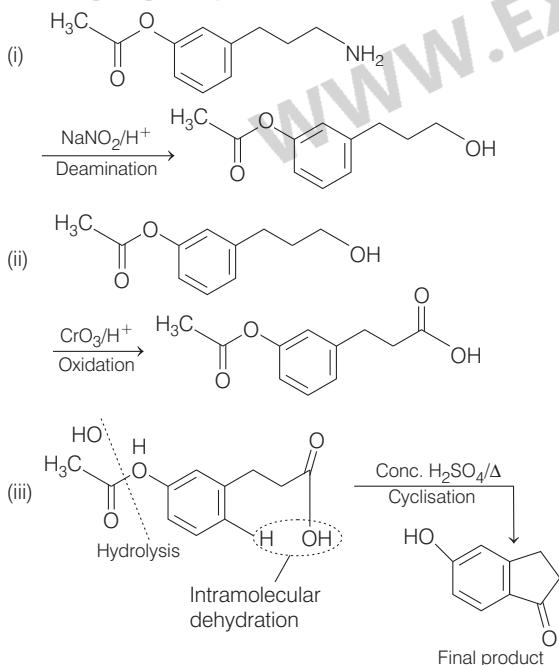
Considering both steric and solvation effect, it can be concluded that greater the number of H-atoms on the N-atom, greater will be the H-bonding and hence more stable is the ammonium cation. But in case of  $\text{---C}_2\text{H}_5$  group, + I effect predominates over H-bonding. Therefore, order is 2° amine > 1° amine > ammonia i.e.  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$ .

### 8. Key Idea

The reaction involves:

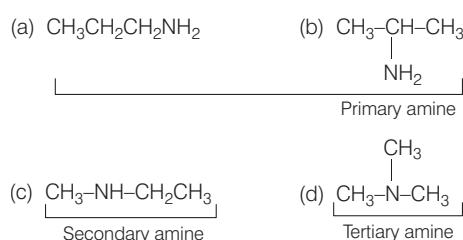
- A. Deamination in step (i)
- B. Oxidation in step (ii)
- C. Hydrolysis in step (iii)

The complete pathway of reactions is as follows:

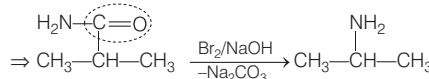
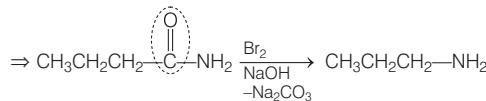


Thus, option (c) is the correct answer.

9. The molecular formula,  $\text{C}_3\text{H}_9\text{N}$  refers to four structural isomers of amines

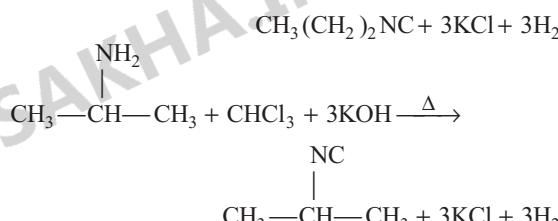
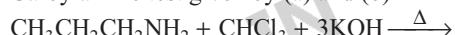


Here, only (a) and (b) (primary amines) can be prepared from their respective amides by Hoffmann bromamide ( $\text{Br}_2/\text{NaOH}$ ) method and can give positive carbonylamine test.



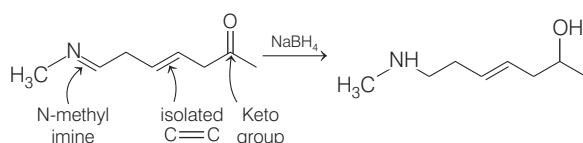
So, 'X' can be  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CONH}_2$  (a) or  $\text{CH}_3\text{CH}(\text{CONH}_2)\text{CH}_3$  (b).

Carbonylamine test given by (a) and (b)



As (b) is not among the given options So, it is ruled out and compound (X) is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$ .

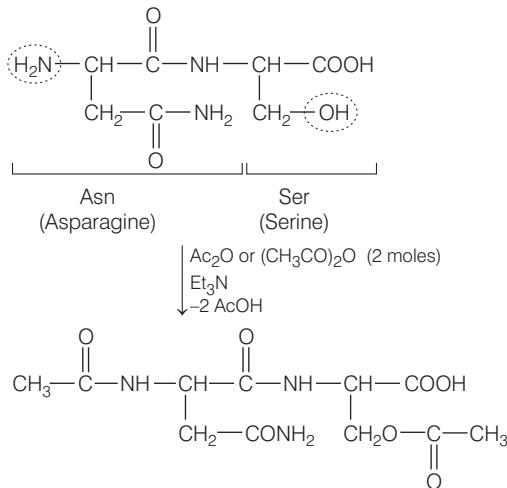
10.  $\text{NaBH}_4$  is a selective reducing agent. It can reduce  $\text{C=O}$  group into alcohol, N-methyl imine group,  $\text{Me}-\text{N}=\text{CH}-$  into 2°-amine but cannot reduce an isolated  $\text{C=C}$ .



11. Acetylation by  $\text{Ac}_2\text{O}/\text{Et}_3\text{N}$  is possible with  $-\text{NH}_2$  (1°-amine) and  $-\text{OH}$  (alcohol) groups only, but not with ' $-\text{NH}_2$ ' part of

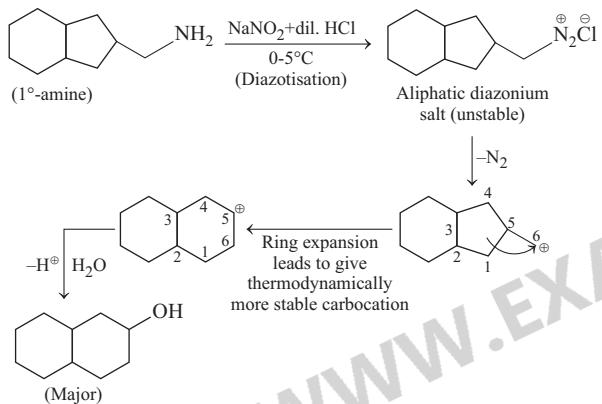
$\text{---C}(=\text{O})-\text{NH}_2$  (amide) groups, because the lp of nitrogen in amide group is involved in resonance with  $\text{C=O}$  part.





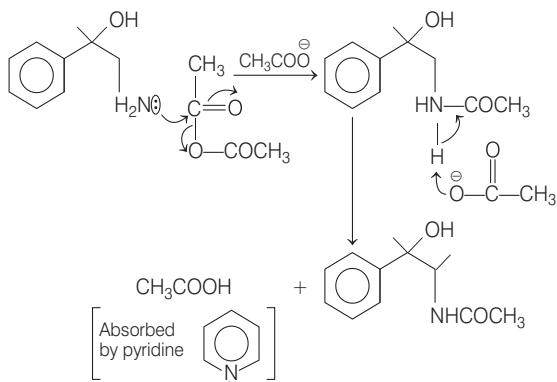
12. No option is the correct answer.

Amines in presence of  $\text{NaNO}_2 + \text{dil. HCl}$  undergoes diazotisation. The diazotised product readily loses nitrogen gas with the formation of carbocation. The resulting carbocation rearranges itself to give the expanded ring.

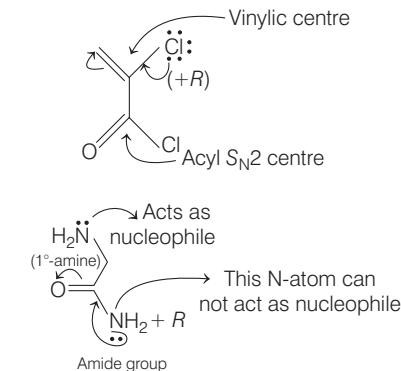


13. Rate of acetylation :  $-\text{NH}_2 > -\text{OH}$  because N-bases are stronger than O-bases. Size of N-atom is larger than O-atom and at the same time, N atom is less electronegative than O-atom. So,

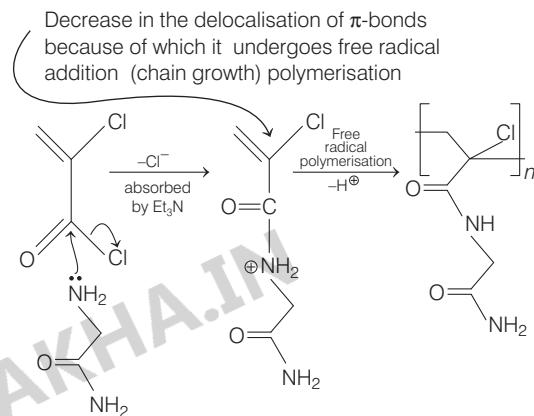
N-atom of the  $-\text{NH}_2$  group can donate its lone pair of electrons (Lewis basicity) more easily than that of O atom of the  $-\ddot{\text{O}}\text{H}$  group.



14. The analysis of both the substrates :



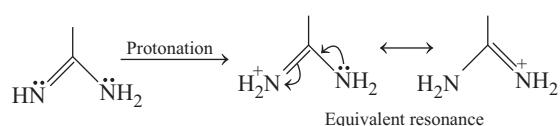
So, the reaction can take place as follows:



15. **Key Idea** Among the given compounds the basic nature depends upon their tendency to donate electron pair.

Among the given compounds in  $\text{CH}_2=\text{NH}_2$ , Nitrogen is  $sp^2$ -hybridised. This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen. Thus making compound least basic.

Among the rest  $\text{CH}_2=\text{NH}_2$  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with  $\pi$  bond i.e. As a result of this conjugation the cation formed after protonation becomes resonance stabilised



This equivalent resonance in cation makes  $\text{CH}_2=\text{NH}_2$  most basic among all.

$\text{CH}_2=\text{NH}_2$  Categorisation is very simple between rest two as

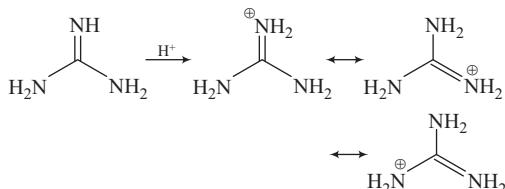
$\text{CH}_3\text{N}-\text{CH}_3$  (primary amine) is less basic than (secondary amine)

Hence, the correct order is

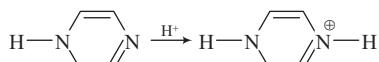
(II)  $<$  (I)  $<$  (IV)  $<$  (III) i.e. option (c) is correct.

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16. IV is most basic as conjugate acid is stabilised by resonance of two  $\text{—NH}_2$ .

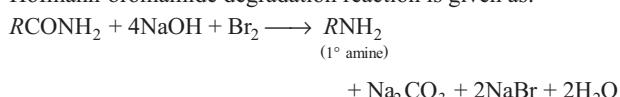


III is least basic as



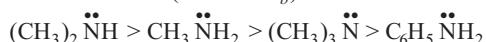
Destabilised by  $-I$ -effect of  $sp^2$ -carbons.

17. Hofmann-bromamide degradation reaction is given as:



Hence, four moles of NaOH and one mole of  $\text{Br}_2$  are used.

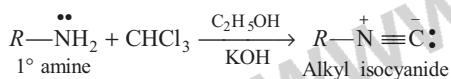
18. This problem can be solved by using the concept of effect of steric hindrance, hydration and H-bonding in basic strength of amines. Order of basic strength of aliphatic amine in aqueous solution is as follows (order of  $K_b$ )



As we know,  $pK_b = -\log K_b$

So,  $(\text{CH}_3)_2\ddot{\text{N}}$  will have smallest  $pK_b$  value. In case of phenyl amine, N is attached to  $sp^2$ -hybridised carbon, hence it has highest  $pK_b$  and least basic strength.

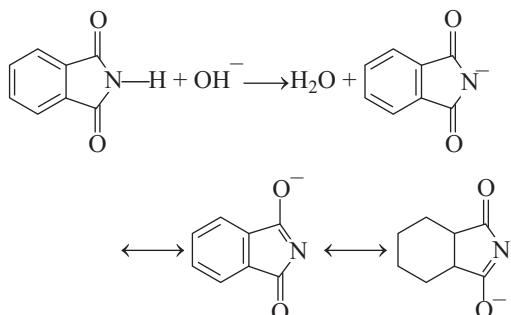
19. This reaction is an example of carbylamine test which includes conversion of amine to isocyanide.



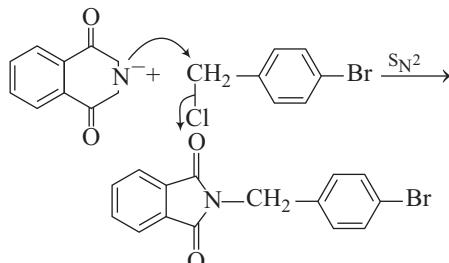
**NOTE** The mechanism of this reaction included rearrangement of nitrene in which migration of alkyl group from carbon to nitrogen takes place.

20. Methyl isocyanate  $\text{CH}_3\text{—N}=\text{C}=\text{O}$  (MIC) gas was leaked from the storage tank of the union carbide plant in Bhopal gas tragedy.

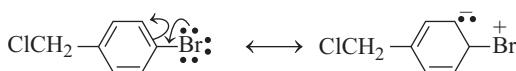
21. It is the first step of Gabriel's phthalimide synthesis. The hydrogen bonded to nitrogen is sufficiently acidic due to two  $\alpha$ -carbonyls.



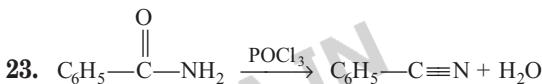
The conjugate base formed above act as nucleophile in the subsequent step of reaction. As shown above, the nucleophile exist in three resonating form, one may think of oxygen being the donor atom in the nucleophilic attack. However, nitrogen act as donor as it is better donor than oxygen.



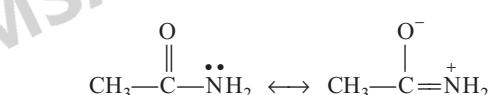
Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C—Br bond, hence difficult to break.



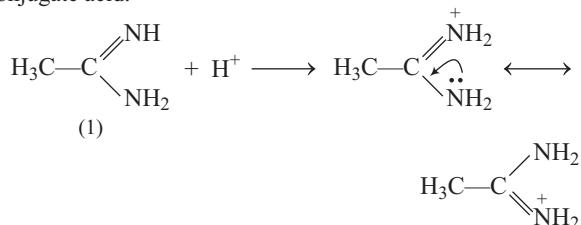
22.  $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \longrightarrow \text{CH}_3\text{—N}^+ \equiv \bar{\text{C}} : + \text{KCl} + \text{H}_2\text{O}$  isocyanide



24. 4, (acetamide) is least basic because lone pair of nitrogen is involved in delocalisation.



'1' is most basic due to formation of resonance stabilised conjugate acid.



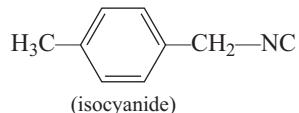
3 (secondary amine) is stronger base than 2 (primary amine).

Hence, overall order of basic strength is :

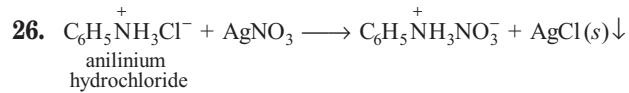
$$1 > 3 > 2 > 4$$

25.  $\text{H}_3\text{C—C}_6\text{H}_4\text{—CH}_2\text{NH}_2 + \text{CHCl}_3 \xrightarrow{\text{KOH}}$

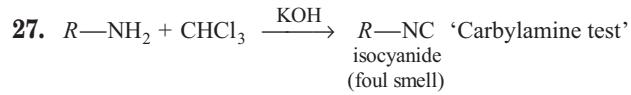
*p*-methyl benzylamine  
(a primary amine)



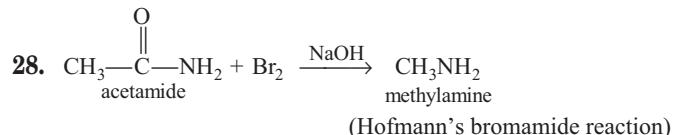
Carbylamine test is not given by secondary or tertiary amine.



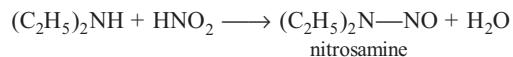
No such precipitate of  $\text{AgCl}(s)$  would be formed with *p*-chloroaniline.



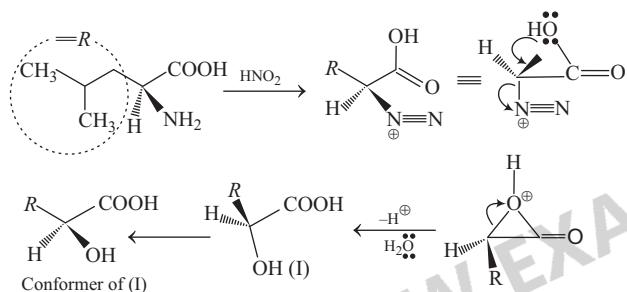
The above test is characteristic of primary amine and used to distinguish primary amine from other amines.



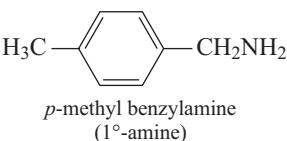
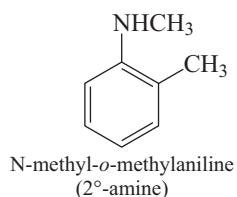
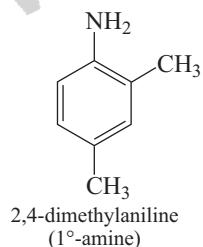
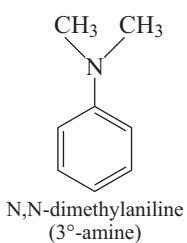
29. A secondary amine, on treatment with aqueous nitrous acid at low temperature produces oily nitrosamine.



30. Reaction proceeds *via* diazonium salt with neighbouring group participation.

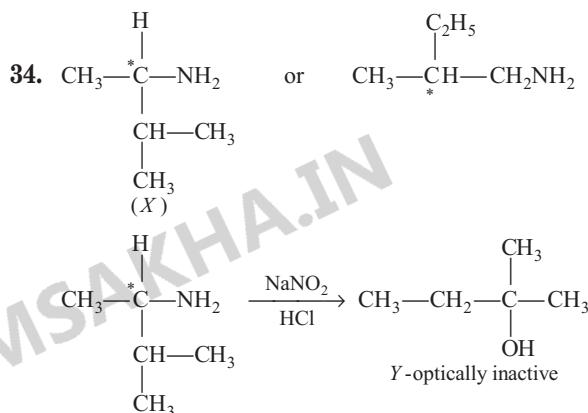


31. Carbylamine test is given by primary amines only.



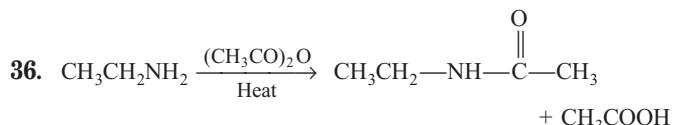
32. More :  $\text{CH}_3\text{NH}_2$  is stronger base than  $\text{CH}_3\text{OH}$ .

|     | Column I                                                  | Column II                                                                                                                                                                             |
|-----|-----------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (A) | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ :            | Gives amine with Pd-C/H <sub>2</sub><br>Gives aldehyde with SnCl <sub>2</sub> /HCl<br>Gives amide with diisobutyl-aluminium hydride.<br>Gives carboxylic acid on alkaline hydrolysis. |
| (B) | $\text{CH}_3\text{CH}_2\text{OCOCH}_3$ : ester            | Reduced to alcohol with Pd - C/H <sub>2</sub> Reduced with diisobutylaluminium hydride into aldehyde. Undergo alkaline hydrolysis.                                                    |
| (C) | $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$             | Reduced to butanol when treated with Pd-C/H <sub>2</sub> .                                                                                                                            |
| (D) | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ | A primary amine, gives carbylamine test.                                                                                                                                              |

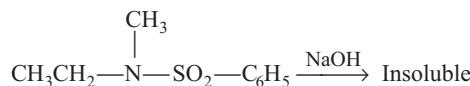


Above reaction proceeds *via* carbocation intermediate, hence rearrangement takes place.

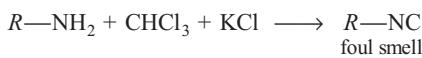
35. Conjugate acid of dimethylamine is more stable than conjugate base of triethyl amine due to exhaustive H-bonding with water.



37. A must be a secondary amine :



38. Starting compound is a primary amine.



## 422 Aliphatic Compounds Containing Nitrogen

$$\text{Moles of } \text{N}_2 = \frac{112}{22500} = 5 \times 10^{-3}$$

$\therefore$  One mole of  $\text{N}_2$  is obtained from 1.0 mole of  $R-\text{NH}_2$ , mole of  $R-\text{NH}_2 = 5 \times 10^{-3}$

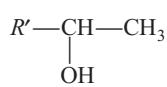
$\Rightarrow 5 \times 10^{-3} \text{ mol } R-\text{NH}_2 \text{ weigh} = 0.295 \text{ g}$

$$1 \text{ mole of } R-\text{NH}_2 \text{ will weigh} = \frac{0.295}{5 \times 10^{-3}} = 59 \text{ g}$$

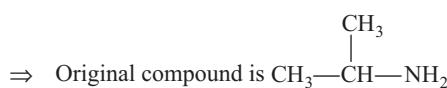
In  $R-\text{NH}_2$ ,  $-\text{NH}_2$  has molar mass = 16

$\Rightarrow R-$  has molar mass = 43

Also, the alcohol  $R-\text{OH}$  gives iodoform test; it must have the following skeleton :

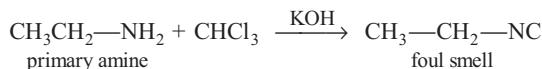


$\Rightarrow R'$  — has molar mass = 15 ( $\text{CH}_3$ )

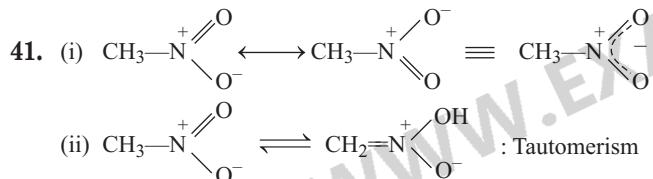
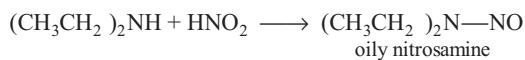


39. Aniline > N-methylaniline < methylamine < dimethylamine.

40. Carbylamine test given only by primary amine.

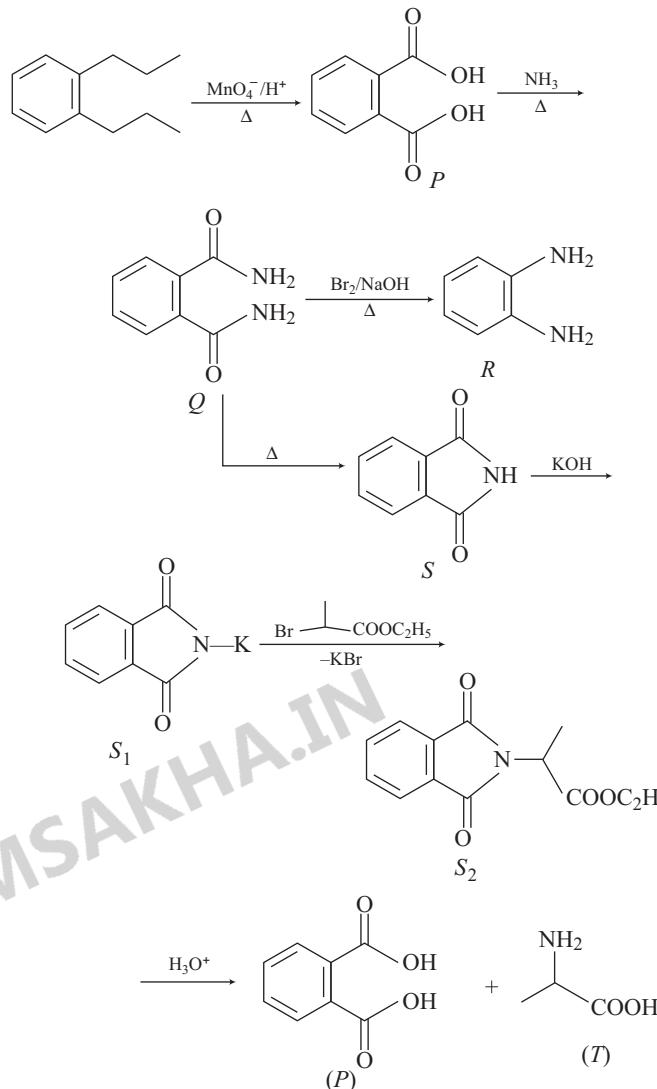


Nitrosamine test is given only by secondary amine.



43. (a)

### 44. Explanation



# 28

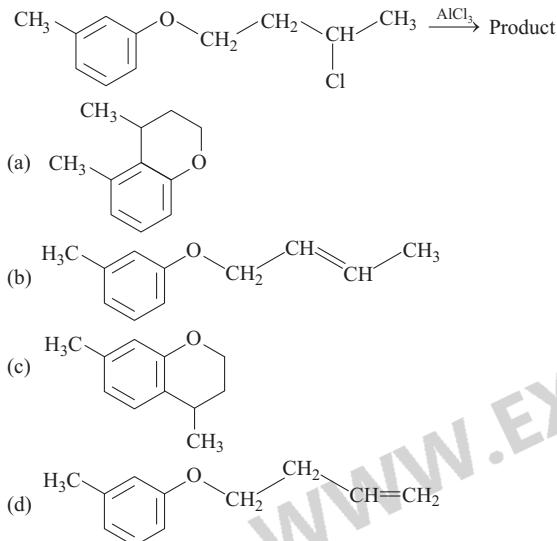
## Benzene and Alkyl Benzene

### Objective Questions I (Only one correct option)

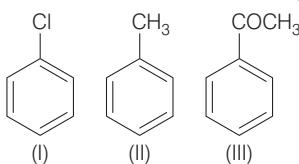
1. The number of  $sp^2$ -hybrid orbitals in a molecule of benzene is  
 (2020 Main, 9 Jan II)

(a) 24      (b) 12      (c) 18      (d) 6

2. The major product obtained in the given reaction is  
 (2019 Main, 10 April II)

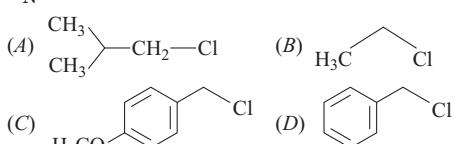


3. The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is  
 (2019 Main, 10 April I)



(a) III < I < II      (b) II < I < III  
 (c) III < II < I      (d) I < III < II

4. Increasing order of reactivity of the following compounds for  $S_N1$  substitution is  
 (2019 Main, 9 April II)

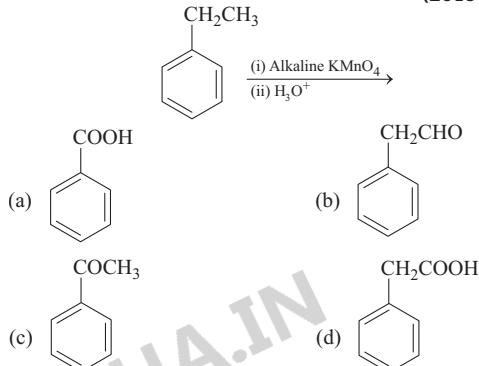


(a) (A) < (B) < (D) < (C)      (b) (B) < (C) < (D) < (A)  
 (c) (B) < (A) < (D) < (C)      (d) (B) < (C) < (A) < (D)

5.

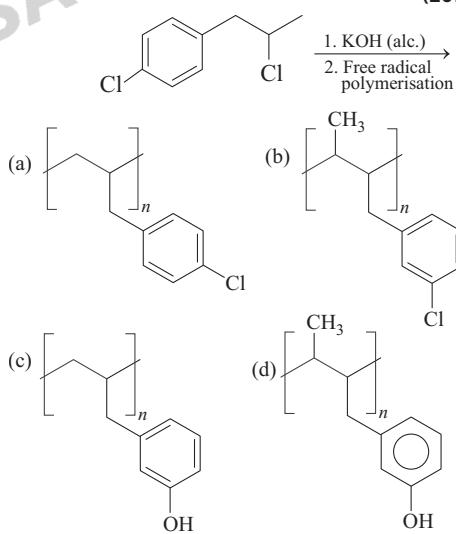
The major product of the following reaction is

(2019 Main, 9 April I)

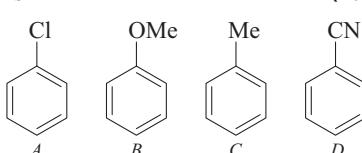


6. The major product of the following reaction is

(2019 Main, 9 April I)



7. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is  
 (2019 Main, 9 April I)



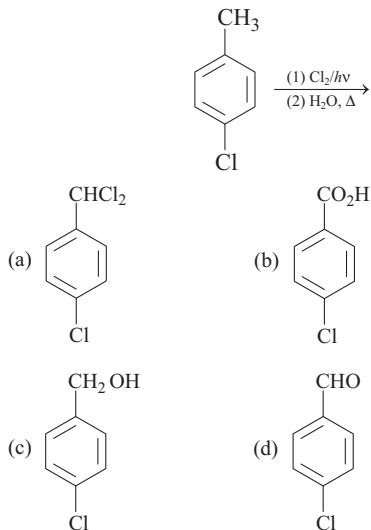
(a) A < B < C < D      (b) B < C < A < D  
 (c) D < A < C < B      (d) D < B < A < C

## 424 Benzene and Alkyl Benzene

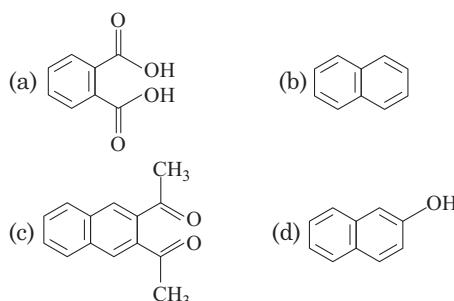
8. Polysubstitution is a major drawback in (2019 Main, 8 April II)

- (a) Friedel-Craft's alkylation
- (b) Reimer-Tiemann reaction
- (c) Friedel-Craft's acylation
- (d) Acetylation of aniline

9. The major product of the following reaction is (2019 Main, 8 April II)



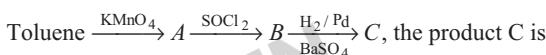
10. Among the following four aromatic compounds, which one will have the lowest melting point? (2019 Main, 12 Jan I)



11. Which of the following compounds is not aromatic? (2019 Main, 9 Jan II)



12. In the following sequence of reactions (2015 Main)



- (a)  $\text{C}_6\text{H}_5\text{COOH}$
- (b)  $\text{C}_6\text{H}_5\text{CH}_3$
- (c)  $\text{C}_6\text{H}_5\text{CH}_3\text{OH}$
- (d)  $\text{C}_6\text{H}_5\text{CHO}$

13. Match the four starting materials given in Column I with the corresponding reaction schemes provided in Column II and select the correct answer using the code given below the lists.

| Column I |                            | Column II |                                                                                                                                                                                                                                                             |
|----------|----------------------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A.       | $\text{H} \equiv \text{H}$ | p.        | <b>Scheme I</b><br>(i) $\text{KMnO}_4$ , $\text{HO}^-$ , heat (ii) $\text{H}^+$ , $\text{H}_2\text{O}$<br>? $\xrightarrow{\text{iii) SOCl}_2 \text{ iv) NH}_3} \text{C}_7\text{H}_6\text{N}_2\text{O}_3$                                                    |
| B.       |                            | q.        | <b>Scheme II</b><br>(i) $\text{Sn}/\text{HCl}$ (ii) $\text{CH}_3\text{COCl}$ (iii) Conc. $\text{H}_2\text{SO}_4$<br>? $\xrightarrow{\text{iv) HNO}_3 \text{ v) Dil. H}_2\text{SO}_4, \text{ heat vi) HO}^-} \text{C}_6\text{H}_6\text{N}_2\text{O}_2$       |
| C.       |                            | r.        | <b>Scheme III</b><br>(i) Red hot iron, 873 K (ii) fuming $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ , heat<br>? $\xrightarrow{\text{iii) H}_2\text{S.NH}_3 \text{ iv) NaNO}_2, \text{ H}_2\text{SO}_4 \text{ v) hydrolysis}} \text{C}_6\text{H}_5\text{NO}_3$ |
| D.       |                            | s.        | <b>Scheme IV</b><br>(i) Conc. $\text{H}_2\text{SO}_4, 60^\circ\text{C}$<br>? $\xrightarrow{\text{ii) Conc. HNO}_3, \text{ conc. H}_2\text{SO}_4 \text{ iii) Dil. H}_2\text{SO}_4, \text{ heat}} \text{C}_6\text{H}_5\text{NO}_4$                            |

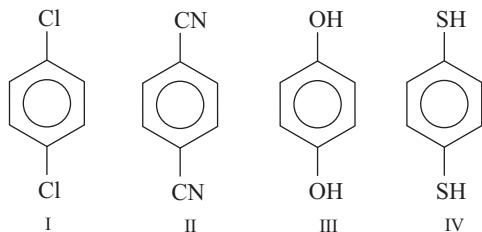
### Codes

- |       |   |   |   |
|-------|---|---|---|
| A     | B | C | D |
| (a) p | s | q | r |
| (c) r | s | q | p |

- |       |   |   |   |
|-------|---|---|---|
| A     | B | C | D |
| (b) r | p | s | q |
| (d) s | p | r | q |

(2014 Adv.)

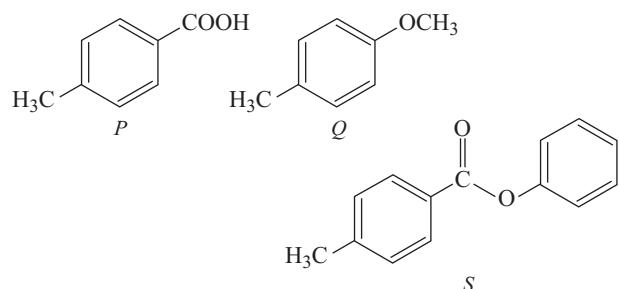
14. For which of the following molecule significant  $\mu \neq 0$ ?



- (a) Only I      (b) I and II  
 (c) Only III      (d) III and IV

(2014 Main)

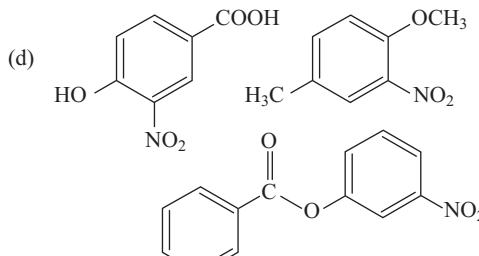
15. The compounds P, Q and S



were separately subjected to nitration using  $HNO_3 / H_2SO_4$  mixture. The major product formed in each case respectively, is

(2010)

- (a)   
 (b)   
 (c)

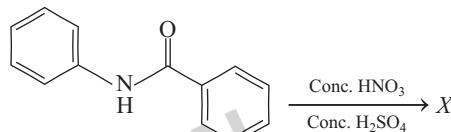


16. In the reaction, the products are,

(2010)

- (a) and  $H_2$       (b) and  $CH_3Br$   
 (c) and  $CH_3OH$       (d) and  $CH_3Br$

17. In the following reaction,



The product X is

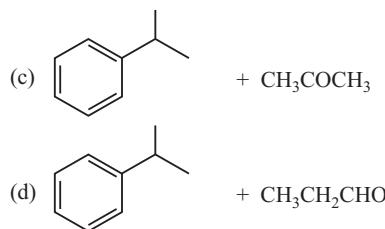
- (a)   
 (b)   
 (c)   
 (d)

18.  $P \xrightarrow{(i) O_2/\Delta, (ii) H_3O^+} Q + \text{Phenol}$

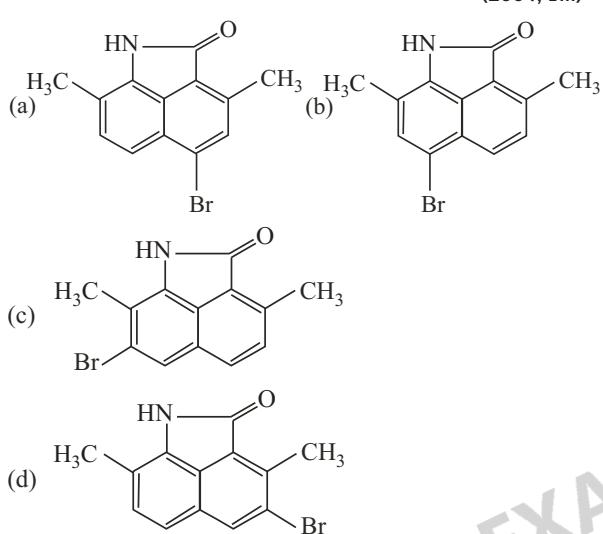
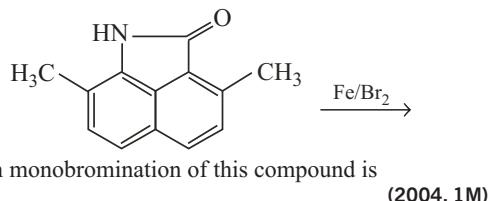
P and Q are respectively

- (a) +  $CH_3CH_2CHO$   
 (b) +  $CH_3COCH_3$

## 426 Benzene and Alkyl Benzene



19.



20. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds

Benzene (1), Toluene (2), Chlorobenzene (3) and Nitrobenzene (4) (2002)

- (a) 1 > 2 > 3 > 4      (b) 4 > 3 > 2 > 1  
 (c) 2 > 1 > 3 > 4      (d) 2 > 3 > 1 > 4

21. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of SbCl<sub>5</sub>, due to the formation of (1999, 2M)

- (a) carbanion      (b) carbene  
 (c) free-radical      (d) carbocation

22. Benzyl chloride (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl) can be prepared from toluene by chlorination with (1998, 2M)

- (a) SO<sub>2</sub>Cl<sub>2</sub>      (b) SOCl<sub>2</sub>      (c) Cl<sub>2</sub>      (d) NaOCl

23. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives (1990, 1M)

- (a) o-cresol      (b) p-cresol  
 (c) 2, 4-dihydroxy toluene      (d) benzoic acid

24. The reaction of toluene with chlorine in the presence of ferric chloride (FeCl<sub>3</sub>) gives predominantly (1986, 1M)

- (a) benzoyl chloride      (b) m-chlorotoluene  
 (c) benzyl chloride      (d) o- and p-chlorotoluene

25. The compound that is most reactive towards electrophilic substitution is (1985, 1M)

- (a) toluene      (b) benzene  
 (c) benzoic acid      (d) nitrobenzene

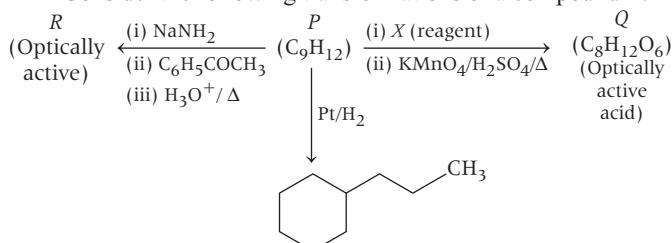
26. Among the following, the compound that can be most readily sulphonated is (1982)

- (a) benzene      (b) nitrobenzene  
 (c) toluene      (d) chlorobenzene

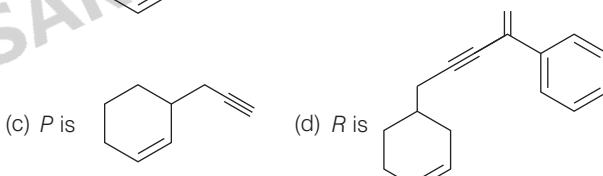
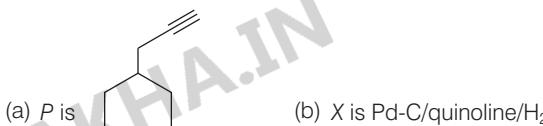
### Objective Questions II

(One or more than one correct option)

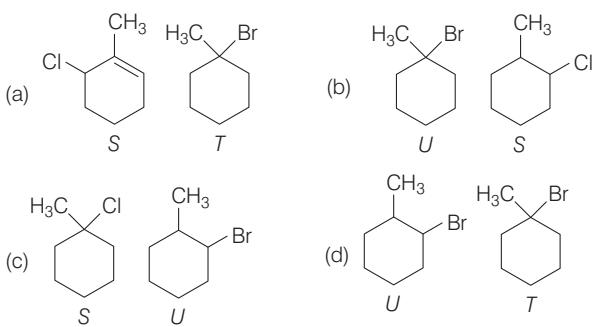
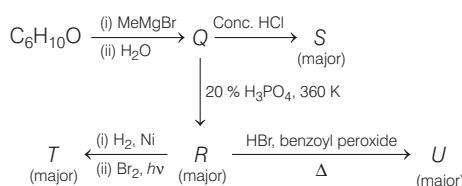
27. Consider the following transformations of a compound P.



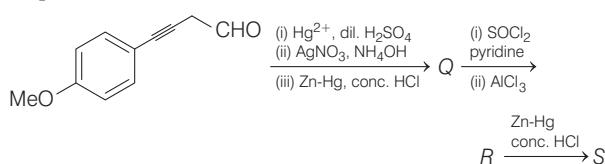
Choose the correct option(s).



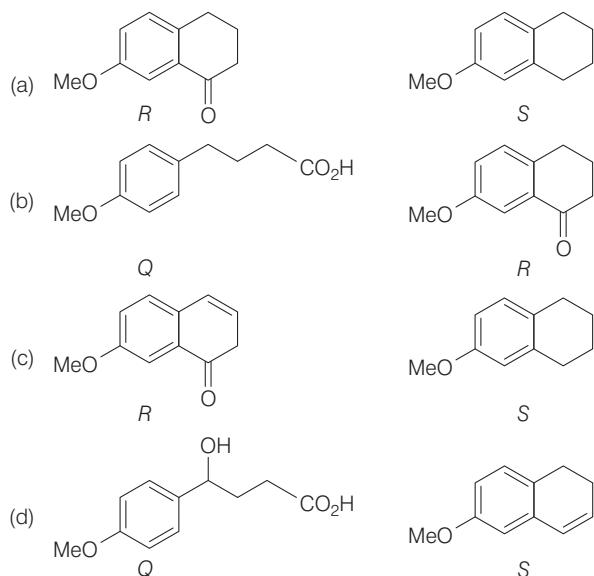
28. Choose the correct option(s) for the following set of reactions. (2019 Adv.)



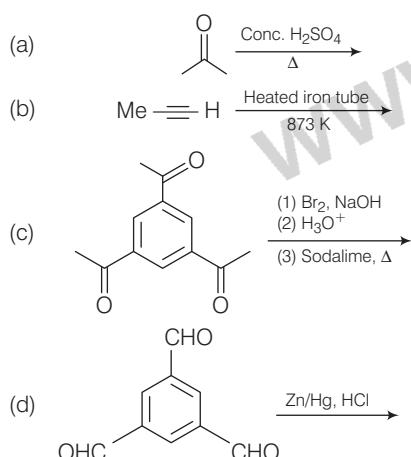
29. Choose the correct option(s) for the following reaction sequence  
(2019 Adv.)



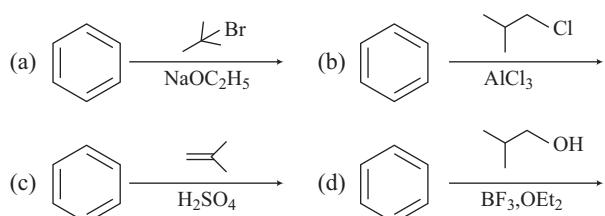
Consider Q, R and S as major products.



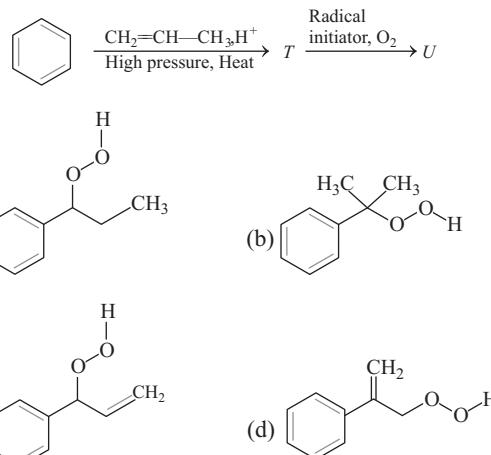
30. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)  
(2018 Adv.)



31. Among the following reaction(s), which gives(give) *tert*-butyl benzene as the major product?  
(2016 Adv.)



32. The major product U in the following reaction is (2015 Adv.)



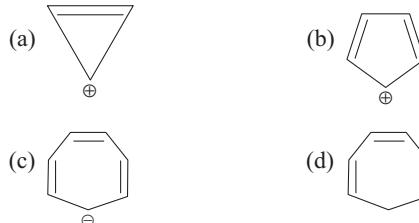
33. Which of the following molecules, in pure form, is/are unstable at room temperature?  
(2012)



34. An aromatic molecule will  
(1999, 3M)

- (a) have  $4n\pi$ -electrons
- (b) have  $(4n + 2)\pi$ -electrons
- (c) be planar
- (d) be cyclic

35. Which compound(s) out of the following is/are not aromatic?  
(2019 Main, 11 Jan I)



36. Toluene, when treated with  $\text{Br}_2/\text{Fe}$ , gives *p*-bromotoluene as the major product because the  $\text{CH}_3$  group  
(1999, 3M)

- (a) is *para*-directing
- (b) is *meta*-directing
- (c) activates the ring by hyperconjugation
- (d) deactivates the ring

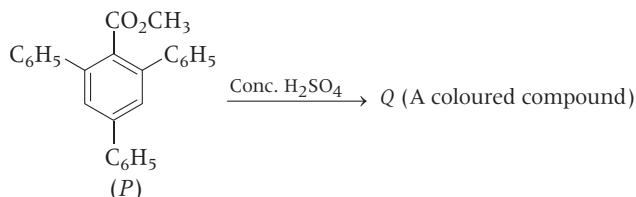
37. A new carbon–carbon bond formation is possible in  
(1998)

- (a) Cannizzaro's reaction
- (b) Friedel-Craft's alkylation
- (c) Clemmensen reduction
- (d) Reimer-Tiemann reaction

## 428 Benzene and Alkyl Benzene

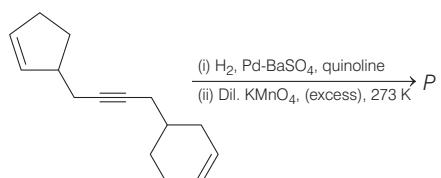
### Numerical Answer Type Questions

38. In the following reaction, compound *Q* is obtained from compound *P* via an ionic intermediate.



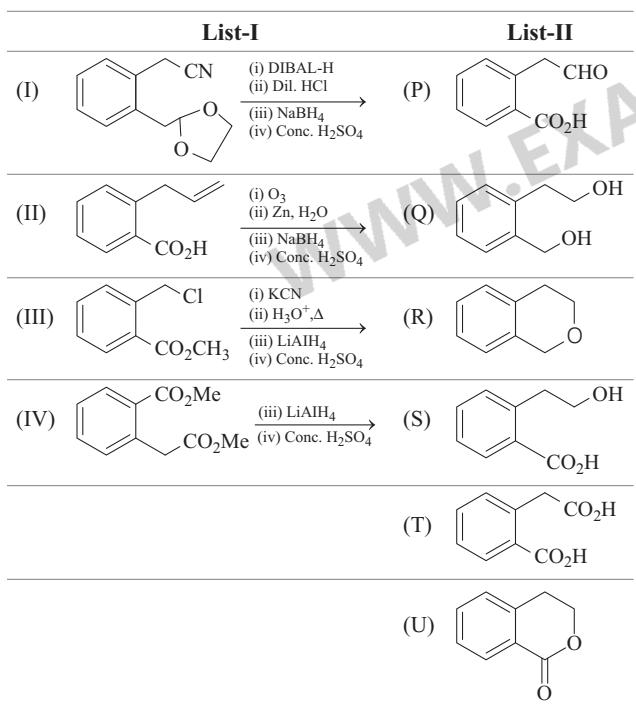
What is the degree of unsaturation of *Q*? (2020 Adv.)

39. Total number of hydroxyl groups present in a molecule of the major product *P* is ..... (2019 Adv.)



### Match the Columns

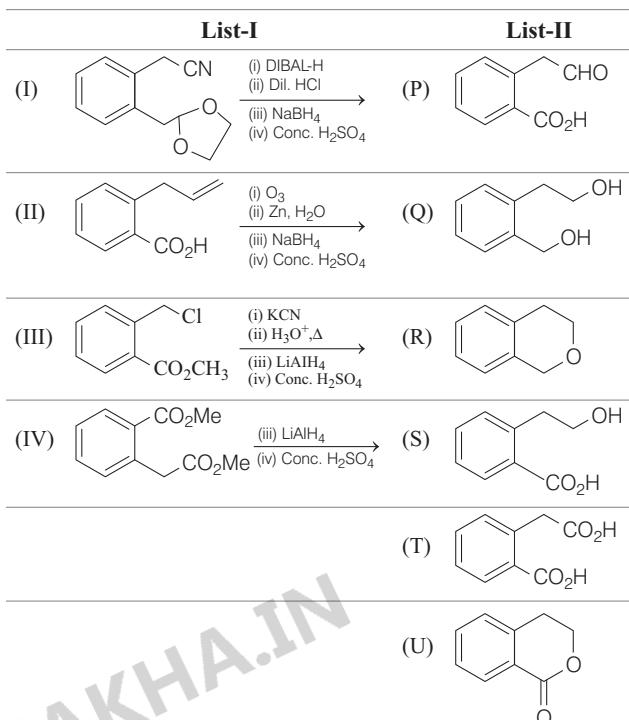
40. List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.



Which of the following options has correct combination considering List-I and List-II? (2019 Adv.)

- (a) (III), (S), (R)      (b) (IV), (Q), (R)  
 (c) (III), (T), (U)      (d) (IV), (Q), (U)

41. List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.



Which of the following options has correct combination considering List-I and List-II? (2019 Adv.)

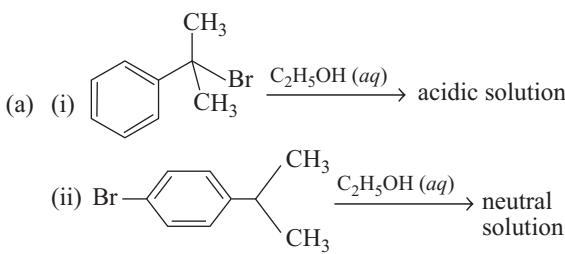
- (a) (II), (P), (S), (U)  
 (b) (I), (Q), (T), (U)  
 (c) (II), (P), (S), (T)  
 (d) (I), (S), (Q), (R)

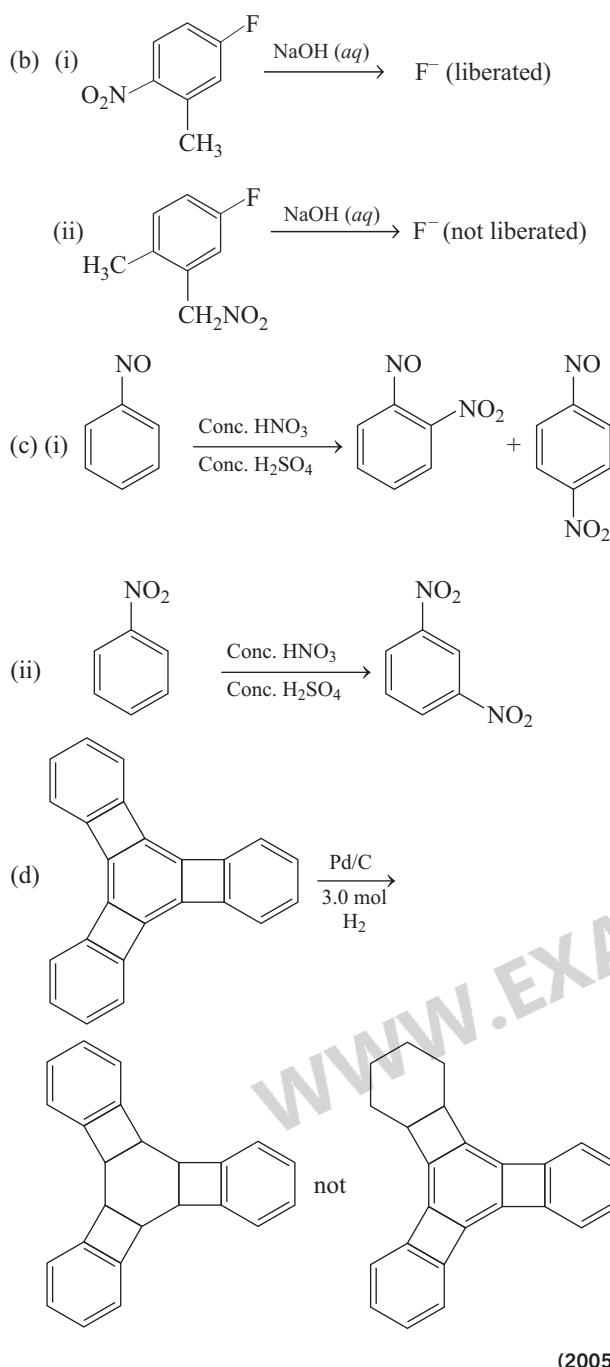
### True or False

42. An electron donating substituent in benzene orients the incoming electrophilic group to the *meta*-position. (1987, 1M)
43. In benzene, carbon uses all the three *p*-orbitals for hybridisation. (1987, 1M)

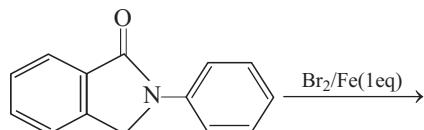
### Subjective Questions

44. Explain the followings :





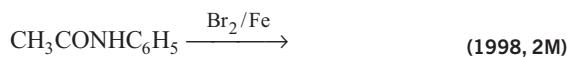
45. 7-bromo-1, 3, 5-cycloheptatriene exists as ionic species in aqueous solution while 5-bromo-1,3-cyclopentadiene doesn't ionise even in presence of  $\text{Ag}^+(aq)$ . Explain. (2004)
46. What would be the major product in the following reaction? (2000, Main, 1M)



47. Give reasons for the following :  
 (i) *tert*-butylbenzene does not give benzoic acid on treatment with acidic  $\text{KMnO}_4$ .  
 (ii) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bond. (2000)

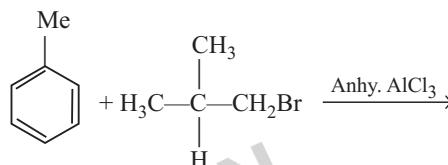
48. Show the steps to carry out the following transformations.  
 (i) Ethylbenzene  $\rightarrow$  benzene  
 (ii) Ethylbenzene  $\rightarrow$  2-phenylpropionic acid

49. Write the structures of the products.



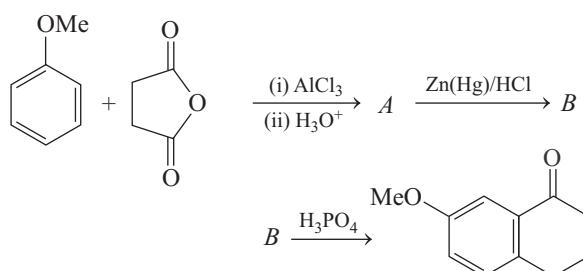
50. Give reasons for the following in one or two sentences  
 "Nitrobenzene does not undergo Friedel-Craft's alkylation." (1998, 2M)

51. Complete the following, giving the structures of the principal organic products. (1997)

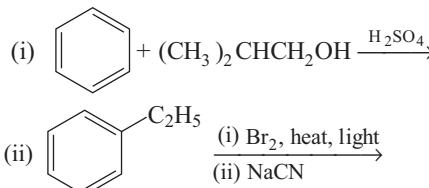


52. Toluene reacts with bromine in the presence of the light to give benzyl bromide, while in presence of  $\text{FeBr}_3$  it gives *p*-bromotoluene. Give explanation for the above observation. (1996)

53. Predict the structures of the intermediates/products in the following reaction sequences (1996)

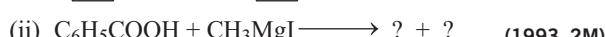
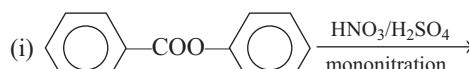


54. Predict the major product in the following reactions (1994)



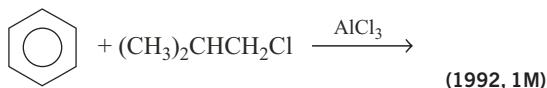
55. Give reason for the following 'In acylium ion the structure  $R-\text{C}\equiv\text{O}^+$  is more stable than  $R-\text{C}^+=\text{O}$ ' (1994, 1M)

56. Identify the major product in the following reactions :



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57. Write the structure of the major organic product expected from the following reaction

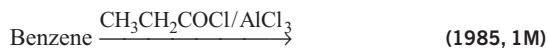


58. Give reasons in two or three sentences only for the following: Phenyl group is known to exert negative inductive effect, but each phenyl ring in biphenyl ( $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$ ) is more reactive than benzene towards electrophilic substitution.
- (1992, 1M)

59. Arrange the following in increasing order of reactivity towards sulphonation with fuming sulphuric acid.  
Benzene, toluene, methoxy benzene, chlorobenzene.
- (1988, 1M)

60. Answer the following with suitable equation wherever necessary  
(i) How can you prepare benzene from lime ?  
(ii) How will you convert toluene to *m*-nitrobenzoic acid ?
- (1987, 2M)

61. Write down the main product of the following reaction



62. How many sigma and pi-bonds are present in a benzene molecule ?
- (1985, 1M)

63. Write down the reaction involved in the preparation of following using the reagents indicated against in parenthesis. "Ethyl benzene from benzene."

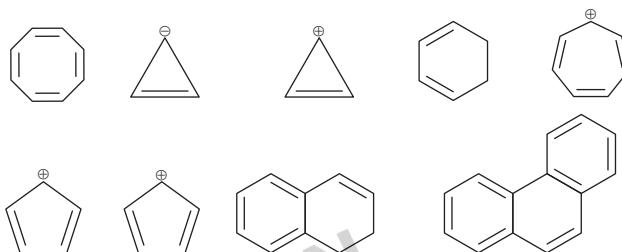
$[\text{C}_2\text{H}_5\text{OH}, \text{PCl}_5, \text{anhyd. AlCl}_3]$  (1984, 2M)

64. Show with balanced equation what happens when the *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH.
- (1984, 1M)

65. Give reasons for the following in one or two sentences : 'Although benzene is highly unsaturated, normally it does not undergo addition reaction.'
- (1983, 1M)

### Integer Type Question

66. Among the following, the number of aromatic compound(s) is



### Answers

- |         |         |         |         |           |             |             |               |
|---------|---------|---------|---------|-----------|-------------|-------------|---------------|
| 1. (c)  | 2. (c)  | 3. (a)  | 4. (c)  | 25. (a)   | 26. (c)     | 27. (b,c)   | 28. (c,d)     |
| 5. (a)  | 6. (a)  | 7. (c)  | 8. (a)  | 29. (a,b) | 30. (a,b,d) | 31. (b,c,d) | 32. (b)       |
| 9. (d)  | 10. (b) | 11. (b) | 12. (d) | 33. (b,c) | 34. (b,c,d) | 35. (b,c,d) | 36. (a,c)     |
| 13. (c) | 14. (d) | 15. (c) | 16. (d) | 37. (b,d) | 38. (18)    | 39. (6)     | 40. (b)       |
| 17. (b) | 18. (c) | 19. (b) | 20. (c) | 41. (a)   | 42. False   | 43. False   | 62. (12σ, 3π) |
| 21. (d) | 22. (a) | 23. (d) | 24. (d) | 66. (5)   |             |             |               |

## Hints & Solutions

1. In benzene, every carbon atom is  $sp^2$ -hybridised.

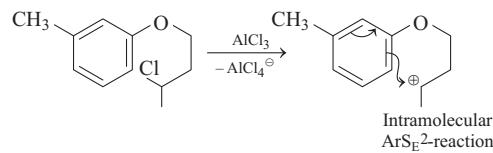


Each  $sp^2$ -hybridised atom has three  $sp^2$  hybrid orbitals.

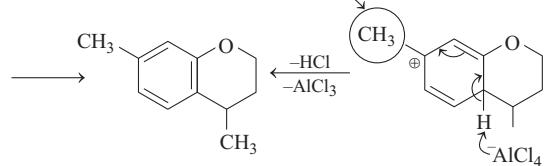
∴ Total number of  $sp^2$  hybrid orbitals in a molecule of benzene is

$$= 6 \times 3 = 18$$

2. The given reaction takes place as follows :

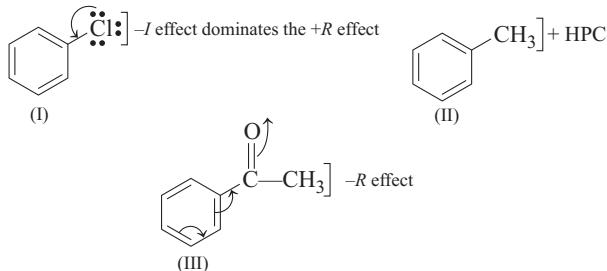


It will stabilise the carbocation by (+ve) hyperconjugation

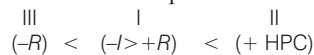


- 3. Key Idea** In electrophilic aromatic substitution ( $\text{ArS}_{\text{E}}2$ ) reaction, the aromatic (benzene nucleus here) compound (substrate) acts as a nucleophile which gets attacked by an electrophile in the rate determining step (rds).

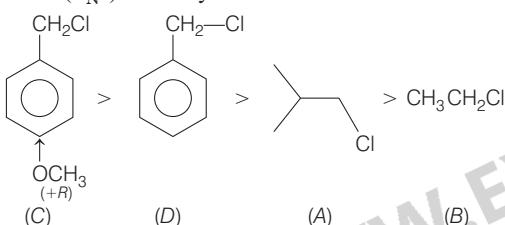
Higher electron density on the nucleophile, i.e. benzene nucleus will fasten the rate of the reaction. Electron-donating groups (EDG) will increase electron density in benzene nucleus by any or both of their  $+R/M$  and hyperconjugative (HPC) effects. Now, let us consider the given substrate.



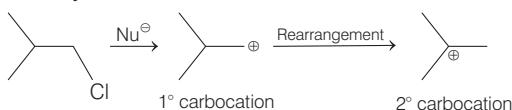
As  $-R$  effect is more powerful than  $-I$  effect, the order of their reactivity, towards an electrophile will be



- 4.** Reactivity of substitution nucleophilic unimolecular ( $\text{S}_{\text{N}}1$ ) reaction depends on the formation of carbocation. Greater the stability of carbocation, greater will be its ease of formation of alkyl halide and faster will be the rate of reaction. So, the correct order of ( $\text{S}_{\text{N}}1$ ) reactivity is

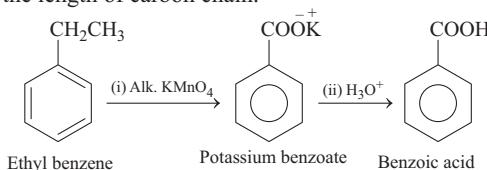


In compound *C*, the carbocation formed is stabilised by activating group ( $-\text{OCH}_3$ ). Compound *D* forms benzyl carbocation ( $\text{C}_6\text{H}_5-\text{CH}_2^+$ ) that is stabilised by resonance. Compound *A* produces a primary carbocation that further rearranges itself to secondary carbocation.

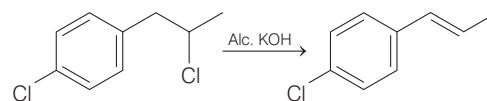


Compound *B* produces primary carbocation which is least stable among all the given options.

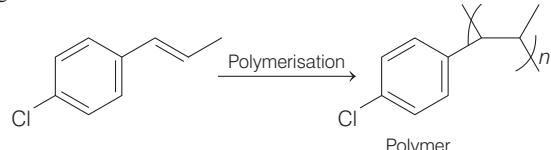
- 5.** The major product of the given reaction is benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ). On vigorous oxidation of alkyl benzene with acidic or alkaline  $\text{KMnO}_4$ , aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to  $-\text{COOH}$  group irrespective of the length of carbon chain.



- 6.** In presence of alc. KOH, the given halide undergoes elimination reaction



The alkene produced undergoes polymerisation *via* free radical mechanism. This process involve three steps, i.e. initiation, propagation and termination.

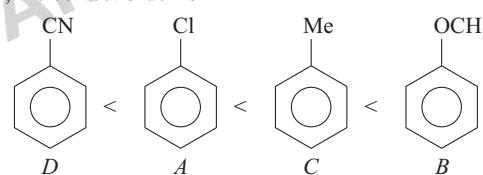


- 7.** Aromatic electrophilic substitution reactions are fast in those compounds in which the attacking site possess high electron density. Electron withdrawing groups (EWGs) reduces the electron density in the benzene ring due to its strong  $-I$  effect and makes further substitution difficult. Hence, called as deactivating groups. While electron releasing groups (ERGs) increases the electron density in the benzene due to resonance. Therefore, activates the benzene ring for the attack by an electrophile. Hence, called as activating groups.

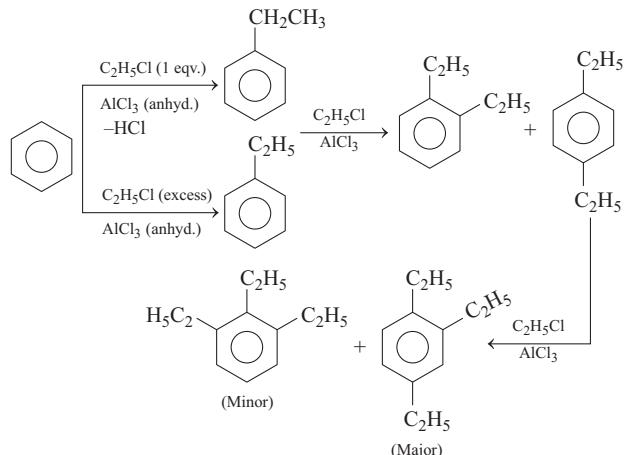
In given options, Activating groups are  $-\text{CH}_3 < -\ddot{\text{O}}\text{CH}_3$   
( $+I, +R$ ) Strong  $+R$  effect

Deactivating groups are  $-\text{CN} > -\text{Cl}$   
 $-\text{CN}$  Strong  $-I$  effect  $-\text{Cl}$   $-I > -R$

So, the correct order is

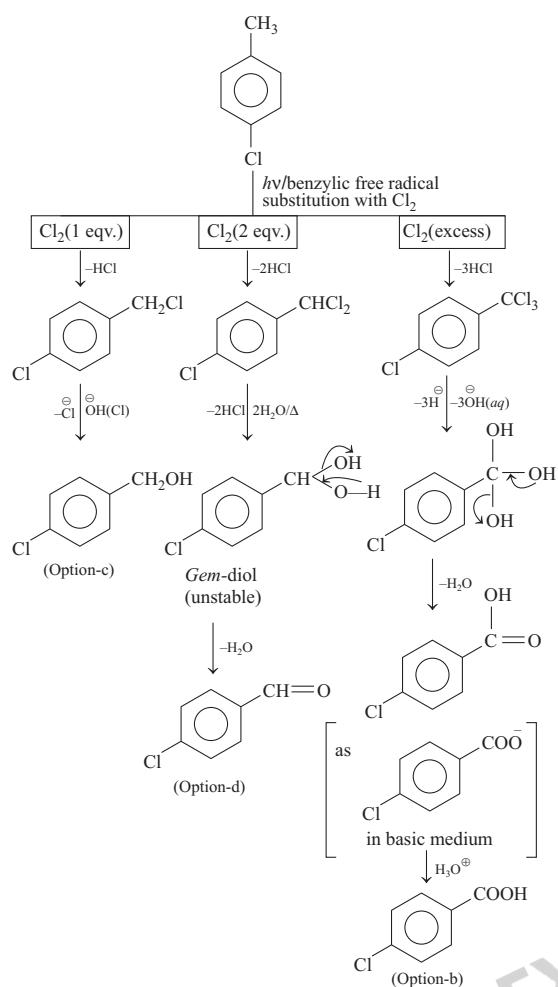


- 8.** Through aromatic electrophilic substitution mechanism ( $\text{ArS}_{\text{E}}2$ ) when mono-alkylation (Friedel-Craft's reaction) is performed, we get mono-alkylated benzene. As, the alkyl group is ring activating (towards  $\text{ArS}_{\text{E}}2$ ) in nature, again *o*- and *p*-substituted alkyl benzene will be obtained and so on. e.g.



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9.



So, considering the second reaction condition, Cl<sup>-</sup>, H<sub>2</sub>O, Δ in the statement of the question, the correct answer is option (d).

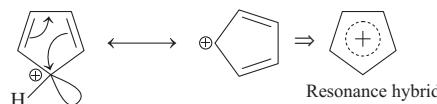
10. Melting point of a compound depends on size and force of attraction between the molecules. Compound (c) has largest size and also possess weak intermolecular association due to dipole - dipole interactions.

Compound (a) is a dicarboxylic acid and possess high melting point due to intermolecular hydrogen bonding.

As a result, it exist as associated molecule. Compound (d) is an alcohol and possess intermolecular H-bonding. No interactions are present in hydrocarbon (naphthalene) compound (b).

Hence, melting point is lowest for naphthalene ( $\approx 80^{\circ}\text{C}$ ), i.e. compound (b).

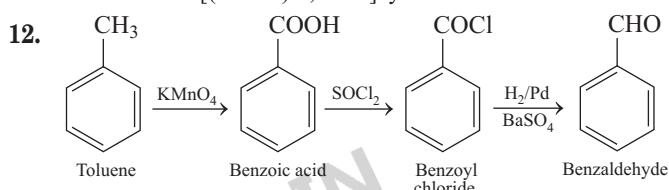
11. Aromaticity of a compound can be decided by Huckel's rule. In cyclopentadienyl cation (b), resonance takes place as follows:



Hence,

 is anti-aromatic does not follow

Huckel's rule as it has conjugated  $4\pi$ -electron ( $4n\pi, n=1$ ) system. Rest of the species are aromatic as each of them belongs to  $6\pi$ -electron [ $(4n+2)\pi, n=1$ ] system.



13. **PLAN** This problem can be solved by using the various concepts synthesis of benzene, electrophilic substitution reaction and directive influence of various substituents, including oxidation and reduction.

$\Rightarrow$  —OH and —NH<sub>2</sub> are *o/p*-directing groups.

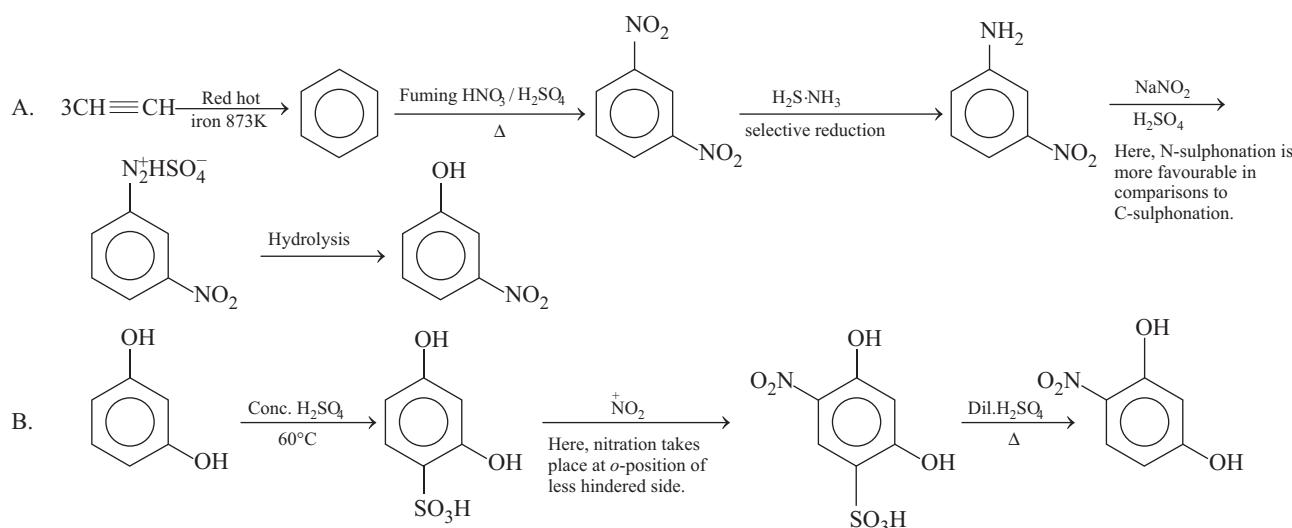
$\Rightarrow$  N-acetylation is more favourable than C-acylation.

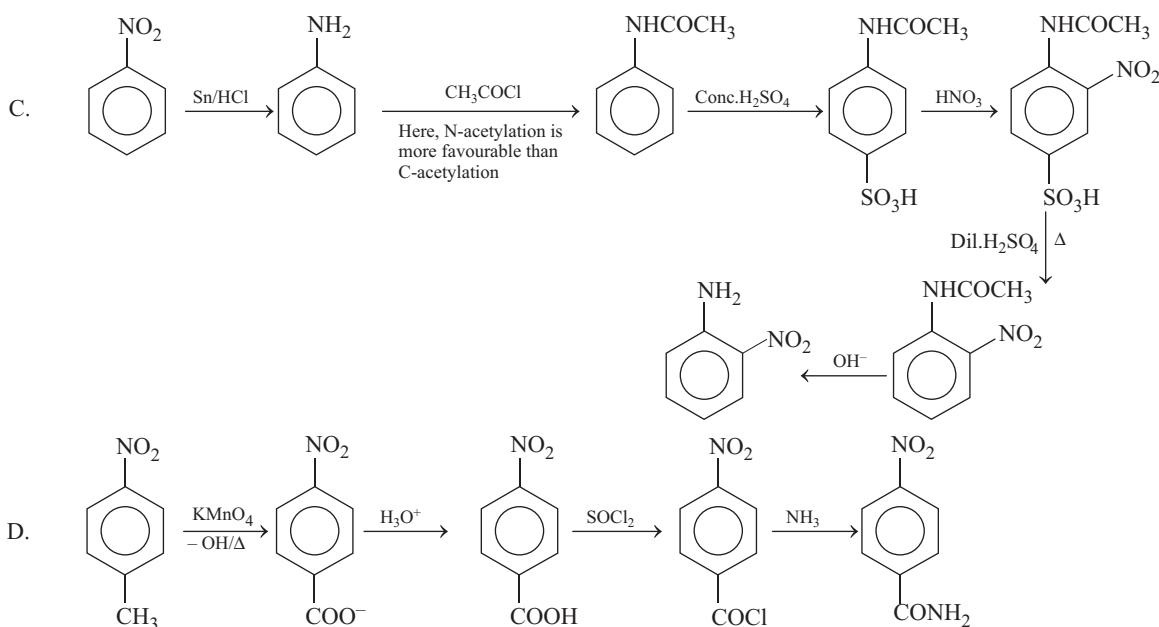
$\Rightarrow$  N-sulphonation is more favourable than C-sulphonation.

$\Rightarrow$  NO<sub>2</sub> is a meta-directing group.

$\Rightarrow$  H<sub>2</sub>S·NH<sub>3</sub> reduces only one NO<sub>2</sub> group selectively in the presence of two NO<sub>2</sub> groups.

Using above concepts the correct sequence of reaction can be written as

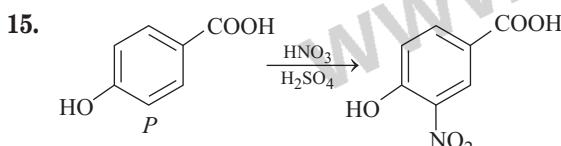
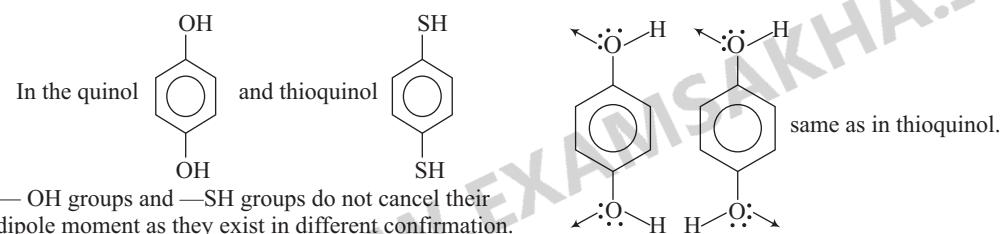




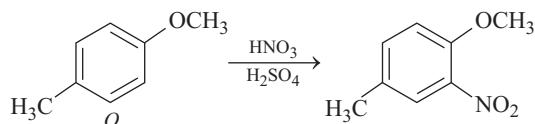
Above reaction proceeds through oxidation, chlorination and amide formation sequentially.

∴ A → r, B → s, C → q, D → p Hence, the correct choice is (c).

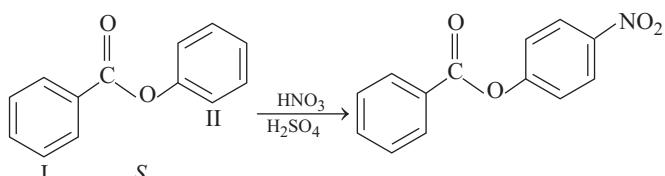
14. Draw the structure of organic compounds indicating net dipole moment which includes lone pair and bond angle also.



— OH is activating while — COOH is deactivating group in  $S_E$ Ar reaction. Therefore, electrophile attack to *ortho* of the activating — OH group.

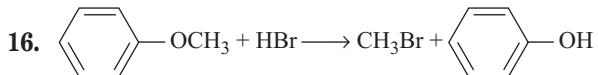


Both — OCH<sub>3</sub> and — CH<sub>3</sub> are activating *ortho/para* directing groups but — OCH<sub>3</sub> is stronger activator, electrophile attack to *ortho* of — OCH<sub>3</sub>.



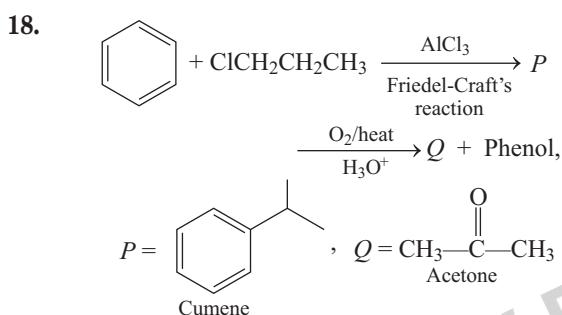
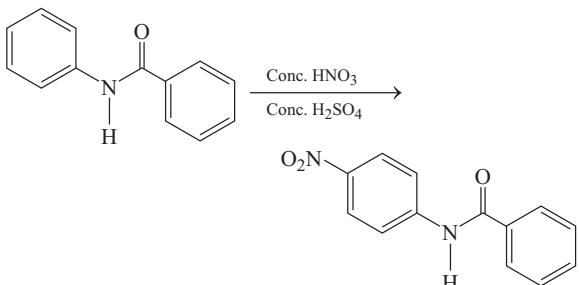
## 434 Benzene and Alkyl Benzene

Ring II is activated while ring I is deactivated in  $S_E$ Ar reaction. Therefore, electrophile attack at *para* to ring-II, the less hindered position.

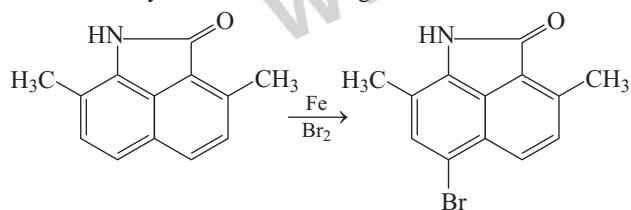


$-\text{OH}$  of phenol is not further substituted by bromide due to resonance with the ring.

17. Ring attached to nitrogen is activated while ring attached to  $\text{C}=\text{O}$  is deactivated. Also, electrophilic substitution occur predominantly at *para* position of the activated ring due to immense steric hindrance at *ortho* position.



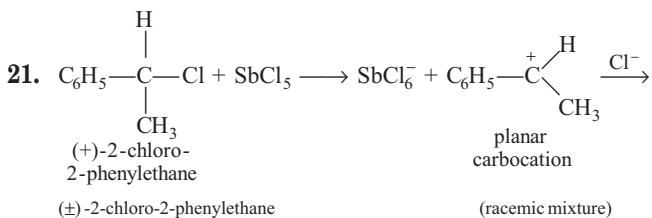
19. Ring attached to nitrogen is activated by electron donating resonance effect while ring attached to carbonyl group is deactivated by electron withdrawing resonance effect :



20. Both chloro and nitro groups are deactivating in electrophilic aromatic substitution reaction. Also nitro group is stronger deactivating group. Methyl group is activator in electrophilic aromatic substitution.

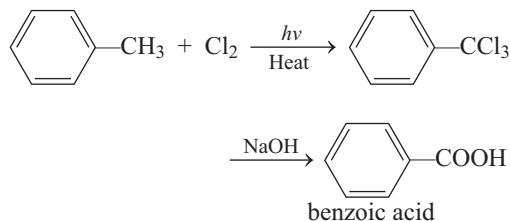
Hence, overall order of reactivity is :

nitrobenzene < chlorobenzene < benzene < toluene

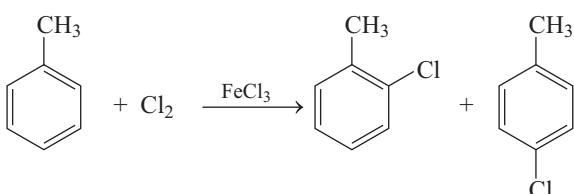


22.  $\text{SO}_2\text{Cl}_2$  brings about free-radical chlorination at  $-\text{CH}_3$  group.

23. Free radical chlorination occurs at  $-\text{CH}_3$ .



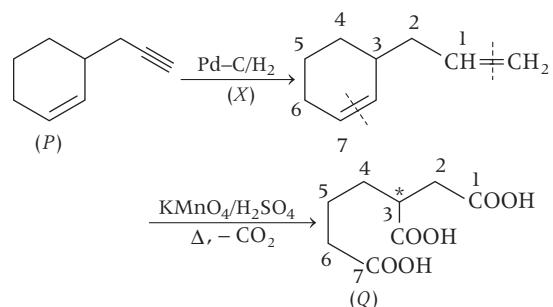
24. The methyl group in toluene is *ortho/para* directing activating group :



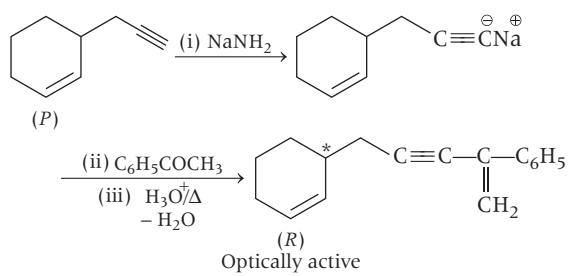
25. Toluene is most reactive among these. Nitro and carboxylic groups are deactivating in aromatic electrophilic substitution reaction.

26. Toluene is most readily sulphonated among these because methyl group is electron donating (+I effect), activates benzene ring for electrophilic aromatic substitution.

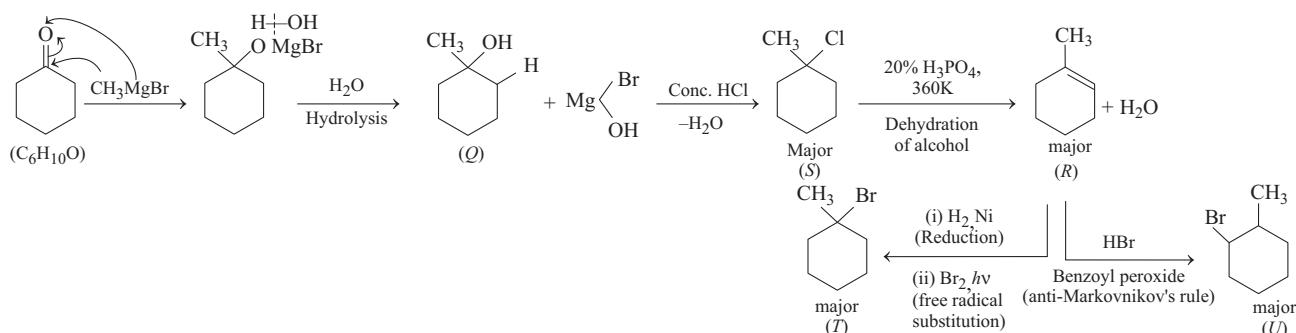
27. Compound (P) on reaction with Lindlar catalyst (X) followed by oxidation in presence of acidified  $\text{KMnO}_4$ , gives an optically active compound (Q) 3-carboxy-heptane-1, 7-dioic acid.



Compound (P) also reacts with strong base ( $\text{NaNH}_2$ ), gives alkaline which on treatment with  $\text{C}_6\text{H}_5\text{COCH}_3 / \text{H}_3\text{O}^+$  /  $\Delta$ , gives an optically active compound (R).

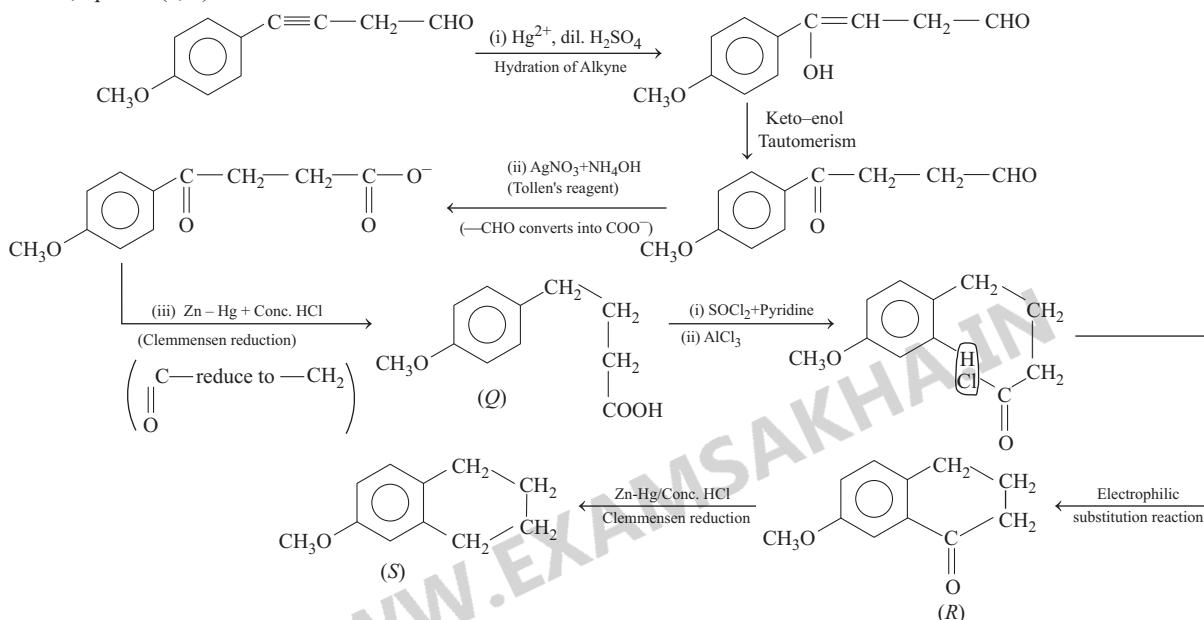


28. The given road map problem is



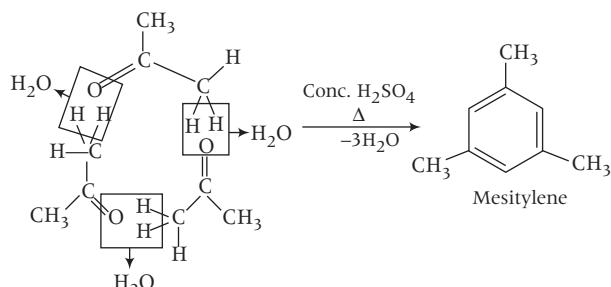
Hence, options (c, d) are correct.

29.



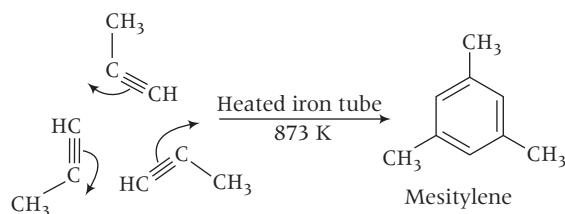
30. Reaction shown in option (a) is aldol condensation in the presence of conc.  $H_2SO_4$  at high temperature.

In summarised way the formation of mesitylene through this can be visualised as



Reaction given in option (b) is simple polymerisation (trimerisation) reaction of alkyne i.e.,

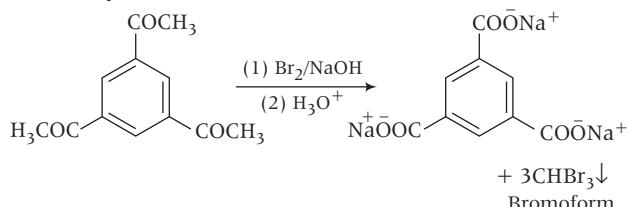
$Me \equiv H$  or  $CH_3-C \equiv CH$  when passed through heated iron tube at  $873K$  then mesitylene is formed as



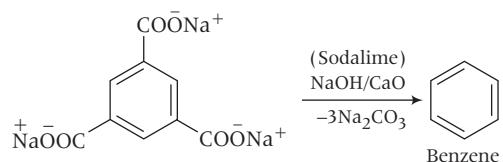
## 436 Benzene and Alkyl Benzene

This reaction is also called aromatisation.

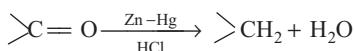
(1) and (2) reactions of option (c) combined to give haloform reaction while (3) reaction given in this option is decarboxylation reaction i.e.,



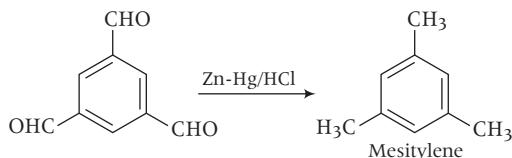
The above product of haloform reaction on decarboxylation gives benzene as



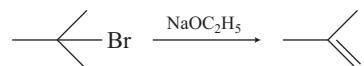
The reaction given in option (d) is Clemmensen reduction i.e.,



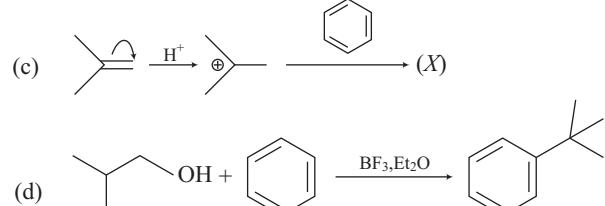
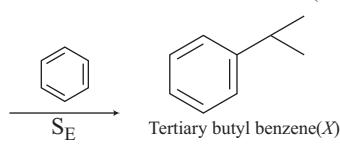
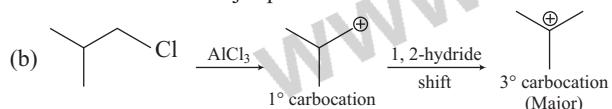
Hence, the final product of this reaction is also mesitylene which can be seen as



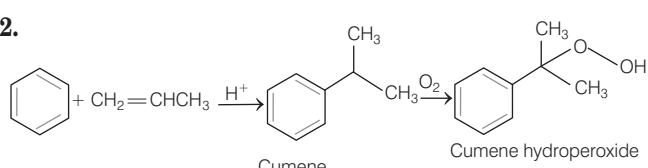
31. (a)



C<sub>2</sub>H<sub>5</sub>O<sup>-</sup> (a strong nucleophile) causes E1 reaction to form isobutene as the major product.

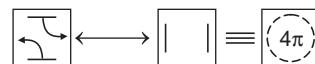


32.

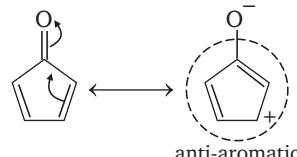


Cumene hydroperoxide formed above is an intermediate in the synthesis of phenol.

33. According to Huckel rule, the compounds which have  $4n$  ( $n = 0, 1, 2, \dots$ ) delocalised  $\pi$ -electrons in a close-loop are anti-aromatic and characteristically unstable. Compound B satisfies the criteria of anti-aromaticity as :

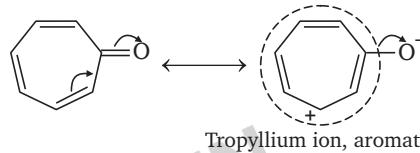


Compound C is anti-aromatic in its resonance form :



Compound A has  $4\pi$ -electrons which are also delocalised but do not constitute close loop, hence non-aromatic.

Compound D is aromatic, characteristically stable.



Order of stability Aromatic > Non-aromatic > Anti-aromatic

34. Aromatic molecule must.

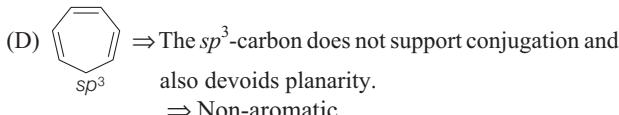
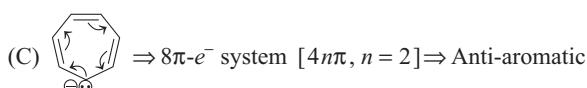
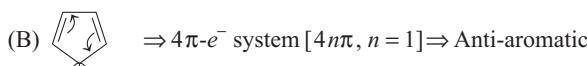
(b) have  $(4n + 2)\pi$  electrons. (c) be planar. (d) be cyclic.

35. A compound is considered to be aromatic, if it follows three rules:

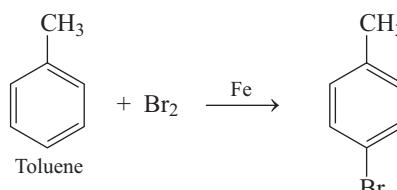
(a) Must be cyclic and planar.

(b) Must have conjugated system in it.

(c) It must follow Huckel rule which states that number of  $\pi$ -electrons =  $(4n + 2)$

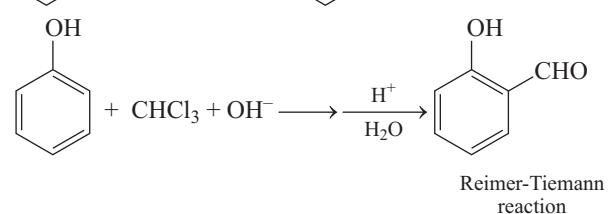
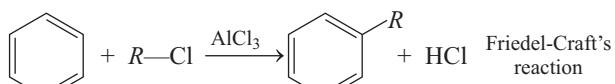


36.

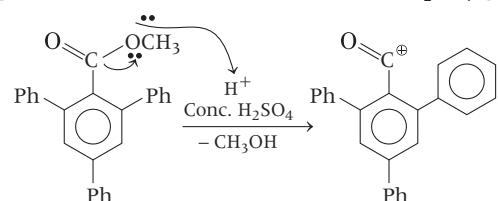


—CH<sub>3</sub> in toluene is *para* directing group. It activates the ring by both inductive and hyperconjugation effect.

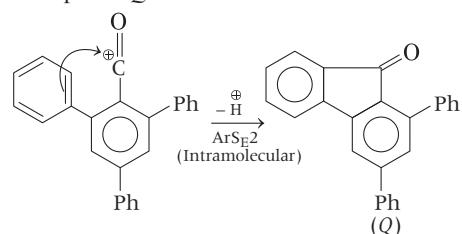
37. In both Friedel-Craft's reaction and Reimer-Tiemann reaction, new carbon-carbon bond is formed :



38. Compound (P) on treatment with concentrated  $\text{H}_2\text{SO}_4$ , gives :



This intermediate compound, on delocalisation, gives a coloured compound Q.

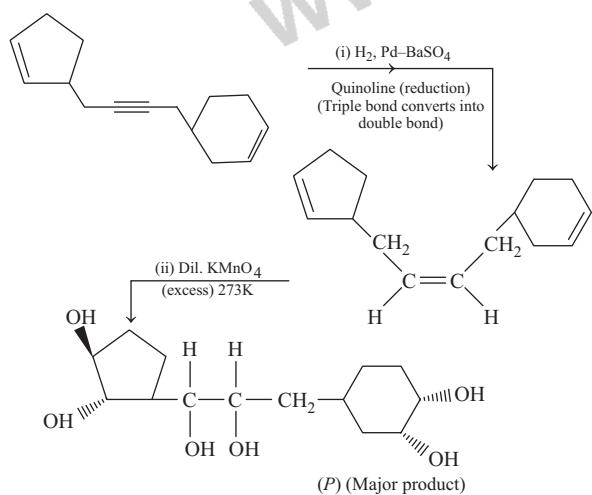


Number of rings = 4 + 1 = 5

Number of  $\pi$ -bonds =  $4 \times 3 + 1 = 13$

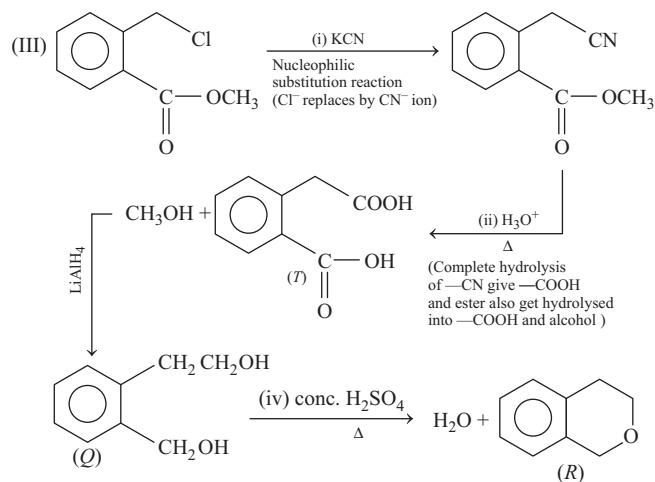
Thus, the degree of unsaturation of Q is 18.

- 39.

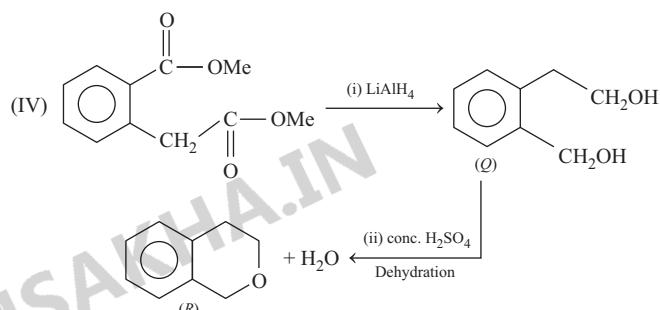


Compound (P) has total number of hydroxyl groups = 6

- 40.



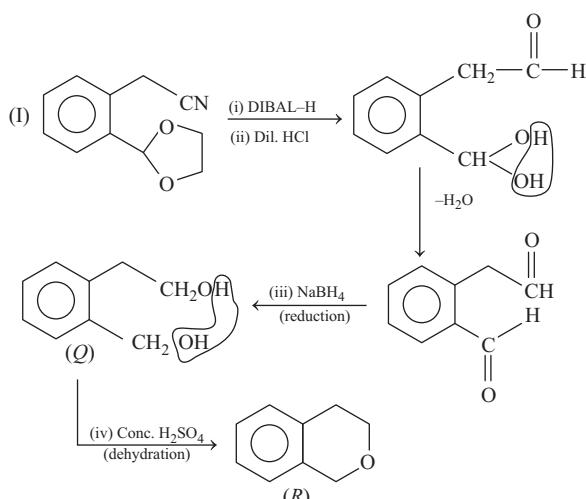
Hence, correct match of (III) are T, Q, R.



Hence, correct match of IV is Q, R.

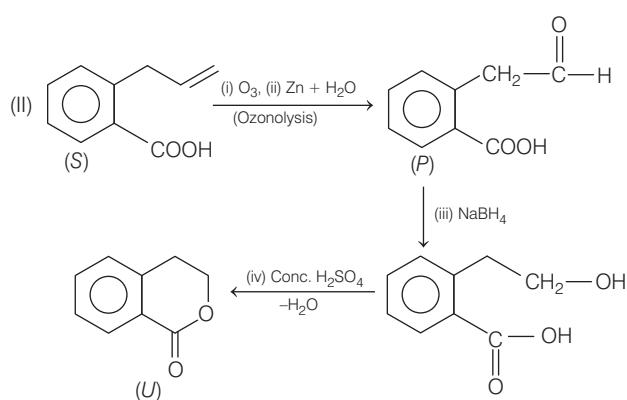
Hence, correct matching from list-I and list II on the basis of given option is (IV), Q, R.

- 41.



Hence, correct match of (I) are (Q, R)

## 438 Benzene and Alkyl Benzene

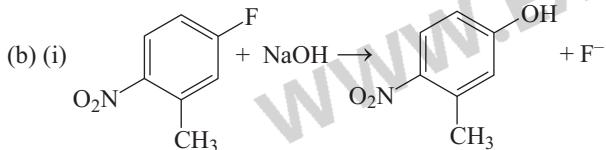
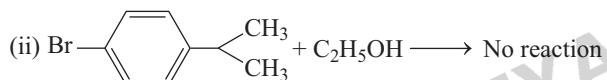
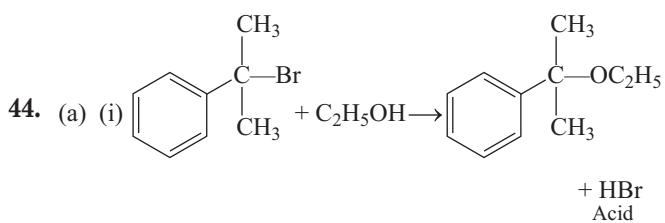


Hence, correct match of II is (P,S,U).

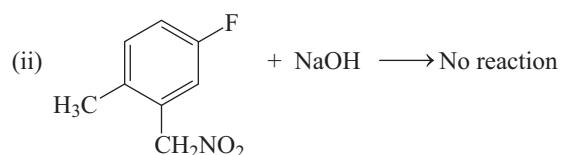
Hence, correct matching from list-I and list-II on the basis of given option is (II), P, S, U.

42. An electron donating substituent in benzene orient *ortho/para* substitution.

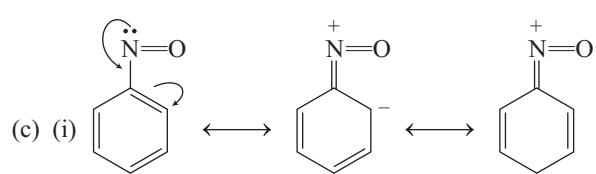
43. In benzene, carbons are  $sp^2$ -hybridised only, hence only two *p*-orbitals are involved in hybridisation.



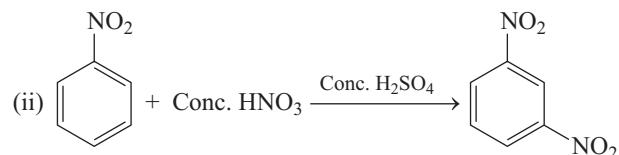
Nitro group from *para* position activate aromatic nucleophilic substitution.



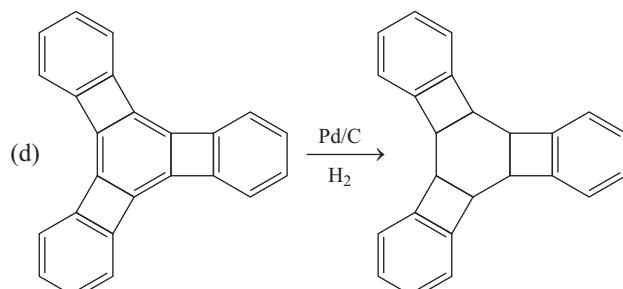
$-\text{NO}_2$  is not in resonance with benzene ring, does not activate the aromatic nucleophilic substitution reaction, hence fluoride is not formed.



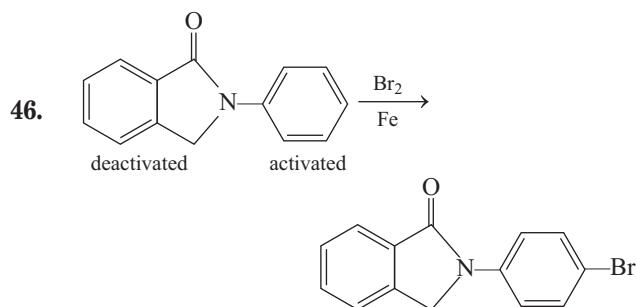
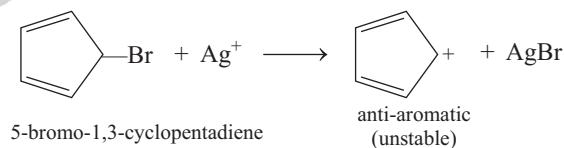
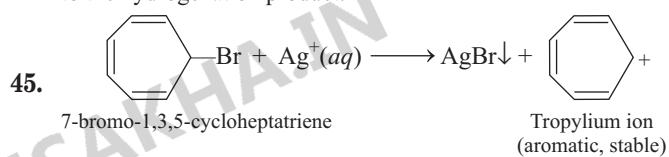
Hence,  $-\text{NO}$  is *ortho/para* directing although deactivating group. Therefore, *ortho/para* nitro derivatives are formed on treatment with mixed acid.



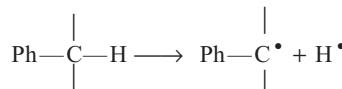
Nitro group is *meta* directing as well as strongly deactivating.



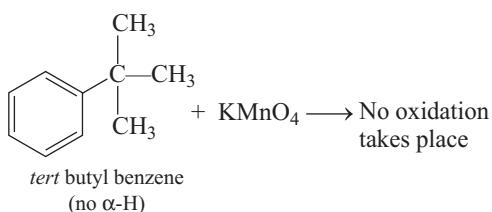
In the above hydrogenation reaction, the anti-aromatic character of three cyclobutadiene rings are relieved that provide stability to the hydrogenation product.



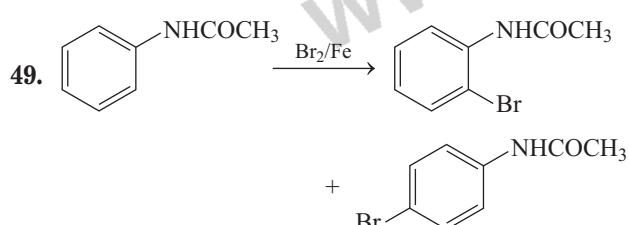
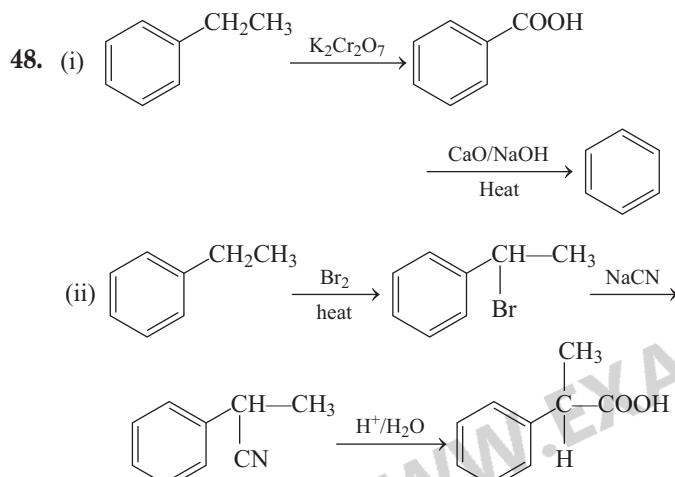
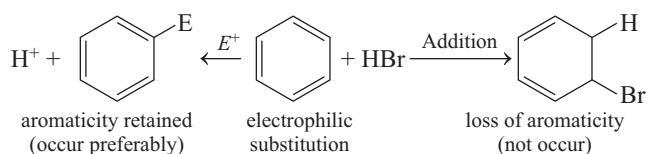
47. (i) Oxidation of side-chain alkyl group of benzene occur through free radical mechanism and it initiates at  $\alpha$ -C as.



In tertiary butyl benzene, there is no  $\alpha$ -H, required to initiate free radical oxidation reaction, hence not oxidised with  $\text{KMnO}_4$ .

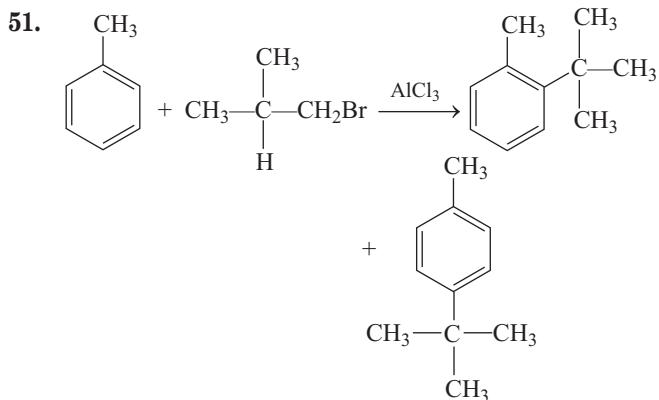


(ii) Pi-electrons of double bonds are involved in aromatic delocalisation (aromaticity), hence electrophilic addition do not occur as it would destroy aromatic stability. However, electrophilic substitution do not destroy aromaticity.

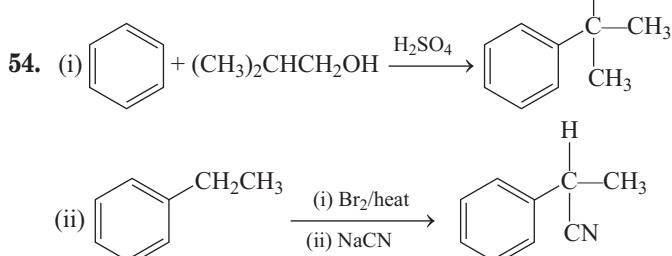
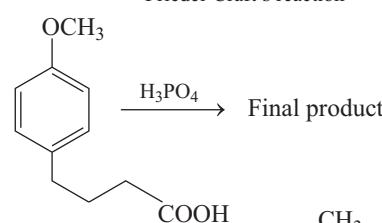
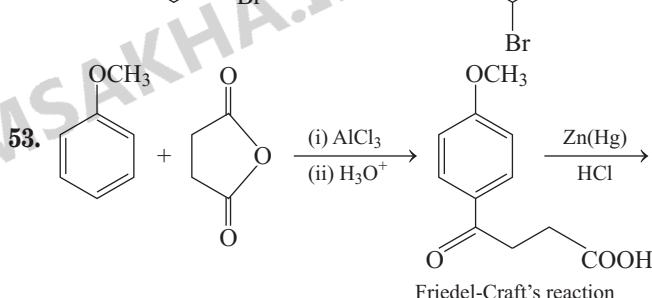
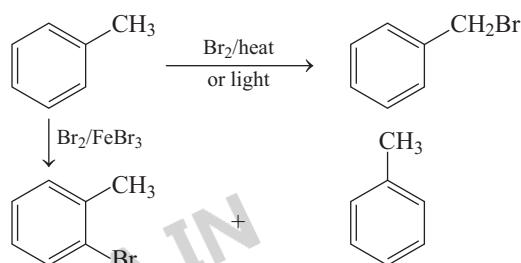


NHCOCH<sub>3</sub> is *ortho/para* directing although deactivating group. Therefore, *Ortho/para* bromoderivatives are formed on treatment.

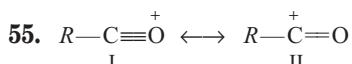
50. Nitro group is a very strong deactivating group, the very slow Friedel-Craft's reaction does not take place in presence of nitro group.



52. In presence of light, free radical reaction takes place at —CH<sub>3</sub> group while in presence of FeBr<sub>3</sub>, electrophilic substitution occur in the ring.



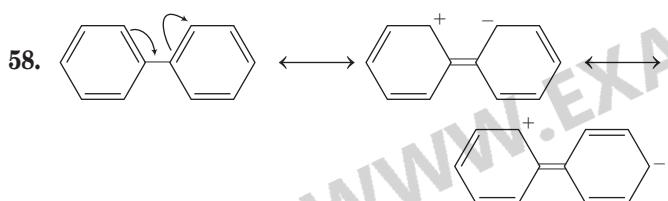
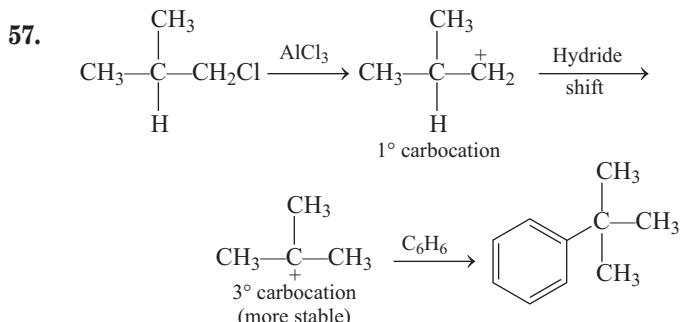
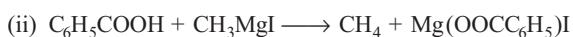
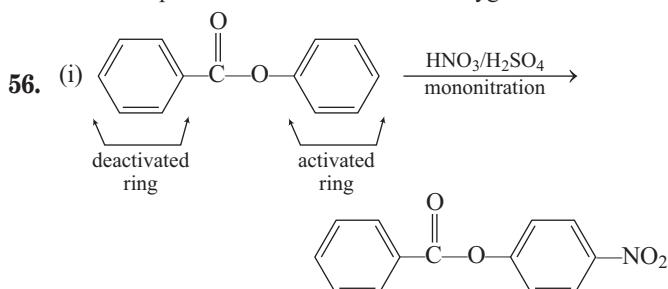
## 440 Benzene and Alkyl Benzene



I is more stable resonance structure of acylium ion than II on the following grounds.

It has more covalent bonds.

It has complete octet of both carbon and oxygen.



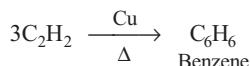
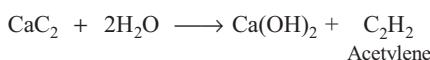
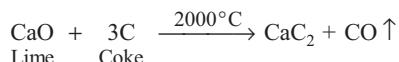
The above resonance activate an aromatic ring for electrophilic substitution reaction.

59. Both  $-CH_3$  and  $-OCH_3$  are activating groups but chloro is deactivating group in electrophilic aromatic substitution reaction.

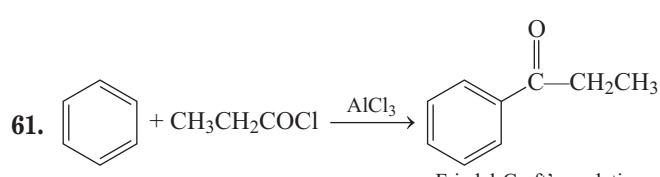
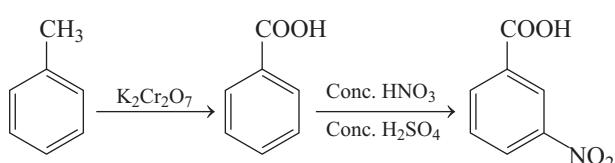
Also  $-OCH_3$  activate more than  $-CH_3$  due to resonance effect by the former group. Therefore, the overall order of reactivity is:

Chlorobenzene < benzene < toluene < methoxy benzene

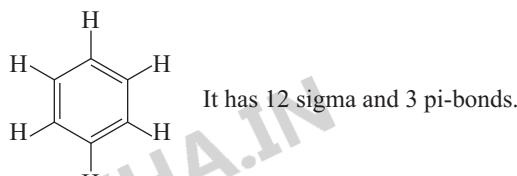
60. (i) Lime is heated with coke at high temperature and then, hydrolysed to form acetylene. This acetylene on passing red hot tube polymerises to form benzene :



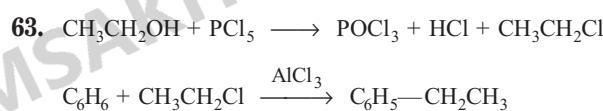
(ii)  $-CH_3$  in toluene is *ortho/para* directing group, first oxidised to  $-COOH$  in order to make it *meta* directing and then nitrated.



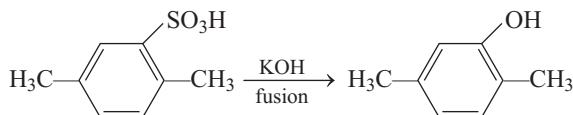
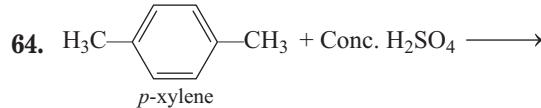
624.



It has 12 sigma and 3 pi-bonds.

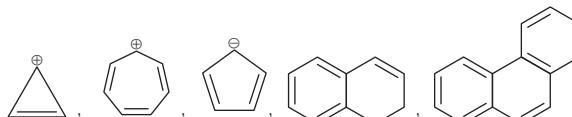


Friedel-Craft's reaction



65. Pi-bonds of benzene are involved in aromaticity, not open for electrophilic addition reaction. Rather, it undergo electrophilic substitution reaction.

66. The aromatic systems are

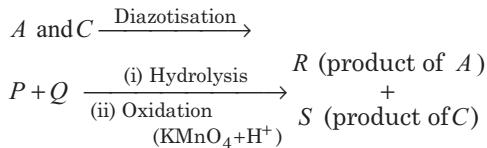


# 29

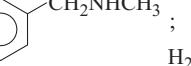
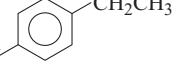
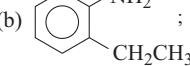
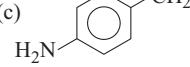
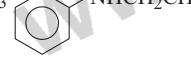
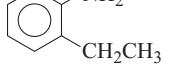
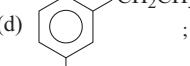
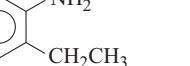
## Aromatic Compounds Containing Nitrogen

### Objective Questions I (Only one correct option)

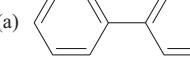
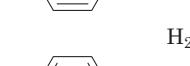
1. Three isomers *A*, *B* and *C* (molecular formula  $C_8H_{11}N$ ) give the following results : (2020 Main, 3 Sep II)



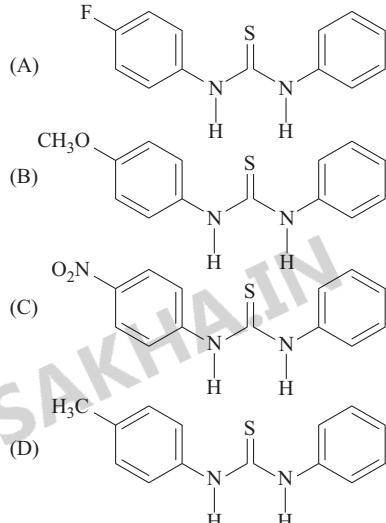
*R* has lower boiling point than *S*. *B*  $\xrightarrow{C_6H_5SO_2Cl}$  alkali-insoluble product *A*, *B* and *C*, respectively are

- (a)  ;  ; 
- (b)  ;  ; 
- (c)  ;  ; 
- (d)  ;  ; 

2. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives (2019 Main, 12 April II)

- (a) 
- (b) 
- (c) 
- (d) 

3. The increasing order of the  $pK_b$  of the following compound is



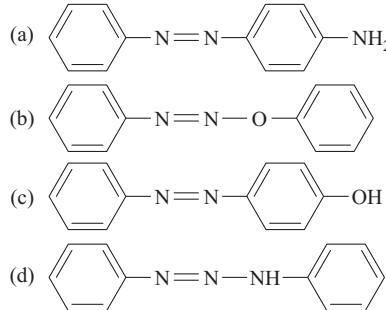
(2019 Main, 12 April I)

- (a) (A) < (C) < (D) < (B)
- (b) (C) < (A) < (D) < (B)
- (c) (B) < (D) < (A) < (C)
- (d) (B) < (D) < (C) < (A)

4. Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene? (2019 Main, 10 April II)

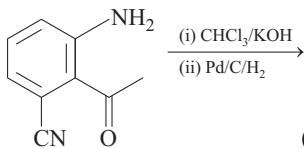
- (a)  $H_2 / Ni$
- (b) (i)  $HCl / H_2O$  (ii)  $NaBH_4$
- (c) (i)  $LiAlH_4$  (ii)  $H_3O^+$
- (d) (i)  $SnCl_2 + HCl$ (gas) (ii)  $NaBH_4$

5. Aniline dissolved in dil.  $HCl$  is reacted with sodium nitrite at  $0^\circ C$ . This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil.  $HCl$ . The structure of the major product is (2019 Main, 9 April I)



## 442 Aromatic Compounds Containing Nitrogen

6. The major product obtained in the following reaction is

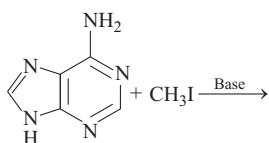


(2019 Main, 8 April II)

- (a) (b)
- (c) (d)

7. The major product in the following reaction is

(2019 Main, 8 April II)

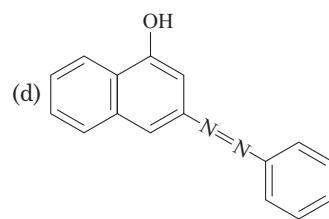
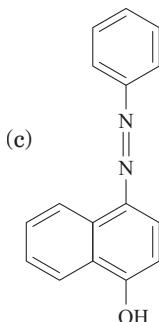


- (a) (b)
- (c) (d)

8. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give

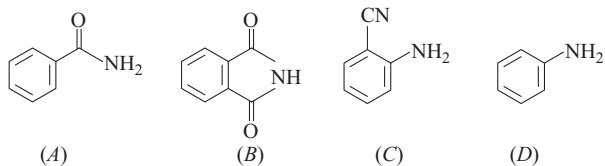
(2019 Main, 8 April I)

- (a) (b)



9. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is

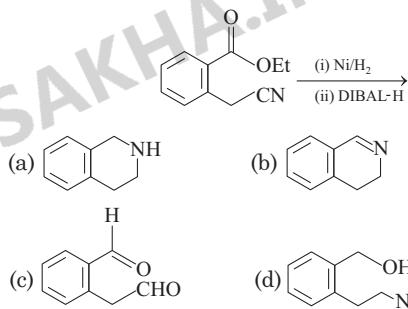
(2019 Main, 12 Jan I)



- (a) (A) < (C) < (D) < (B)  
 (b) (B) < (A) < (C) < (D)  
 (c) (B) < (A) < (D) < (C)  
 (d) (A) < (B) < (C) < (D)

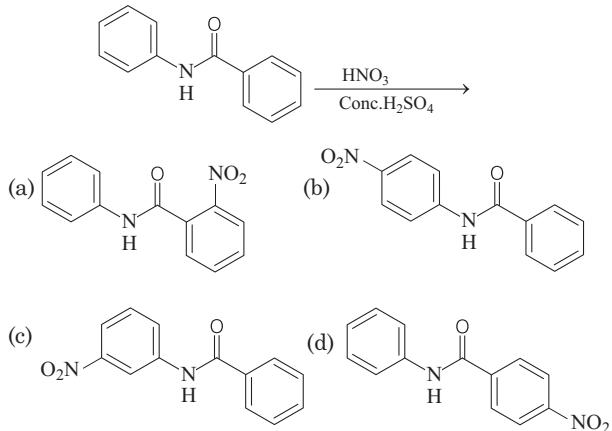
10. The major product of the following reaction is

(2019 Main, 11 Jan I)

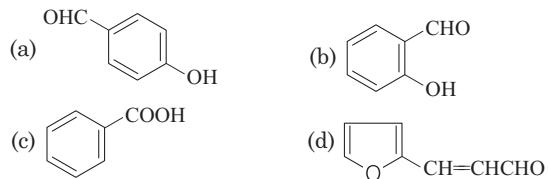


11. What will be the major product in the following mononitration reaction?

(2019 Main, 10 Jan II)



- 12.** An aromatic compound ‘A’ having molecular formula  $C_7H_6O_2$  on treating with aqueous ammonia and heating forms compound ‘B’. The compound ‘B’ on reaction with molecular bromine and potassium hydroxide provides compound ‘C’ having molecular formula  $C_6H_7N$ . The structure of ‘A’ is  
(2019 Main, 10 Jan II)



13. The increasing basicity order of the following compounds is

$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{NH}_2 \end{array}$

(A)  $\begin{array}{c} \text{CH}_3\text{CH}_2\text{NH}_2 \\ | \\ \text{CH}_3 \end{array}$       (B)  $\begin{array}{c} \text{CH}_3\text{CH}_2\text{NH} \\ | \\ \text{CH}_3 \end{array}$

(C)  $\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{CH}_3 \\ | \\ \text{H} \end{array}$       (D)  $\begin{array}{c} \text{Ph}-\text{N}-\text{H} \\ | \\ \text{H} \end{array}$

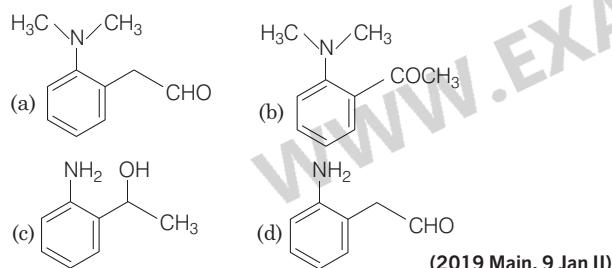
(2019 Main, 9 Jan II)

(a) (D) < (C) < (B) < (A)      (b) (A) < (B) < (C) < (D)  
 (c) (A) < (B) < (D) < (C)      (d) (D) < (C) < (A) < (B)

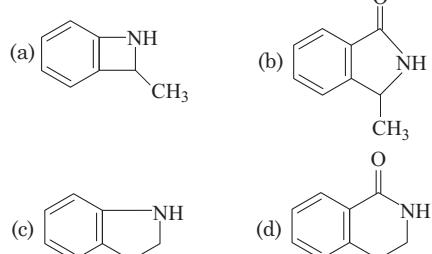
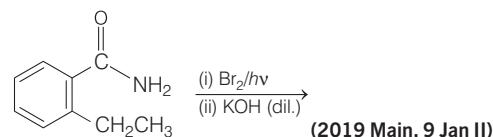
- 14.** The tests performed on compound *X* and their inferences are :

| <b>Test</b>        | <b>Inference</b>     |
|--------------------|----------------------|
| (a) 2, 4- DNP test | Coloured precipitate |
| (b) Iodoform test  | Yellow precipitate   |
| (c) Azo-dye test   | No dye formation     |

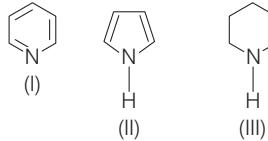
Compound ‘X’ is



- 15.** The major product of the following reaction is



- 16.** Arrange the following amines in the decreasing order of basicity:  
(2019 Main, 9 Jan I)

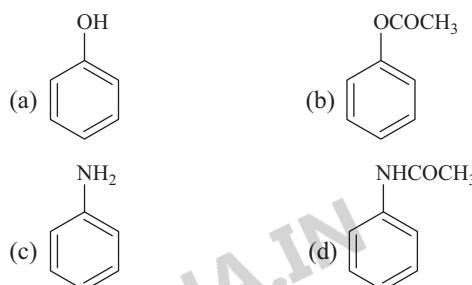




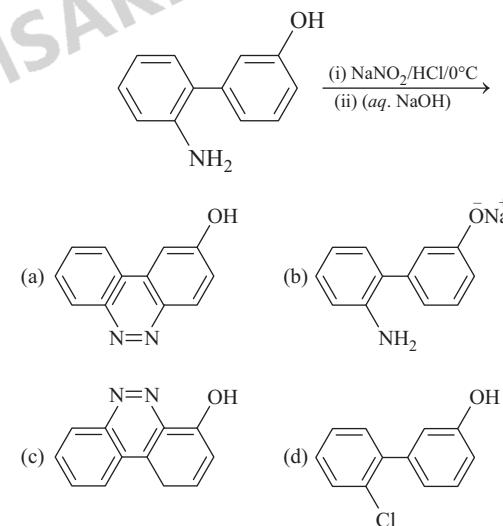
17. The correct decreasing order for acid strength is

- (2019 Main, 9 Jan I)

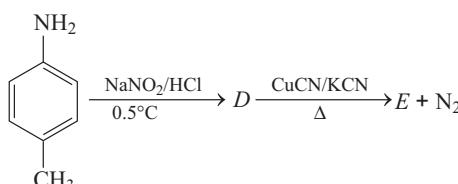
- 18.** Which of the following compounds will give significant amount of *meta*-product during mononitration reaction? (2017 Main)



- 19.** The major product of the following reaction is (2017 Adv.)



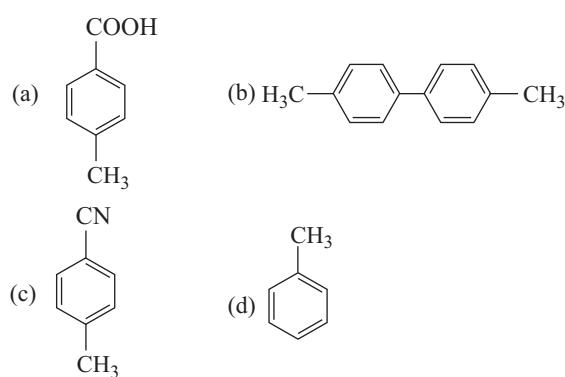
- 20.** In the reaction,



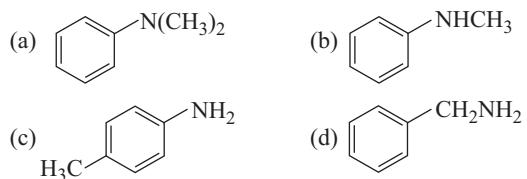
The product  $E$  is

(2015 Main)

## 444 Aromatic Compounds Containing Nitrogen



21. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  followed by addition to an alkaline solution of  $\beta$ -naphthol is

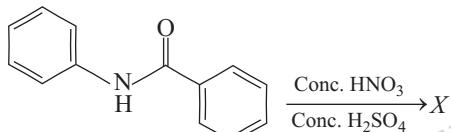


(2011)  
(2010)

22. The species having pyramidal shape is

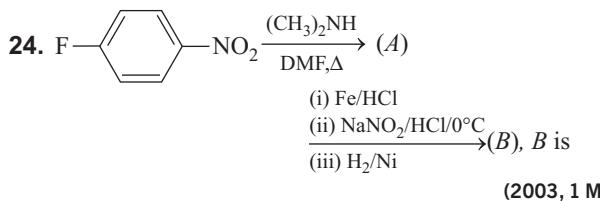
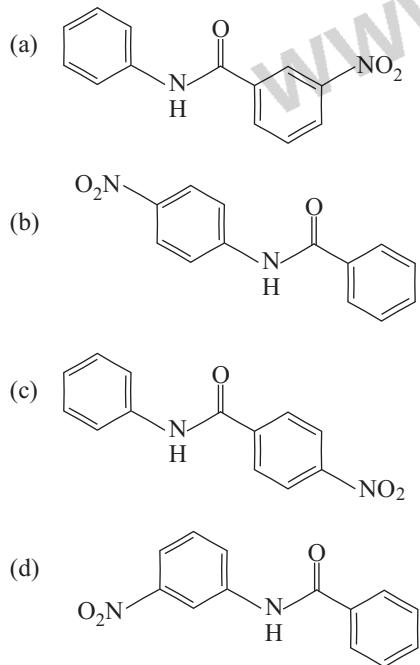


23. In the following reaction,

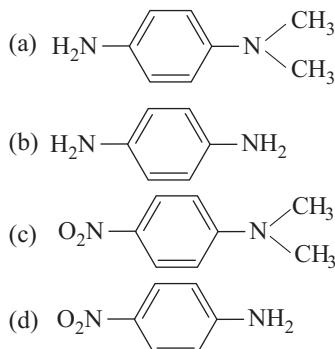


(2007, 3M)

The structure of the major product  $X$  is

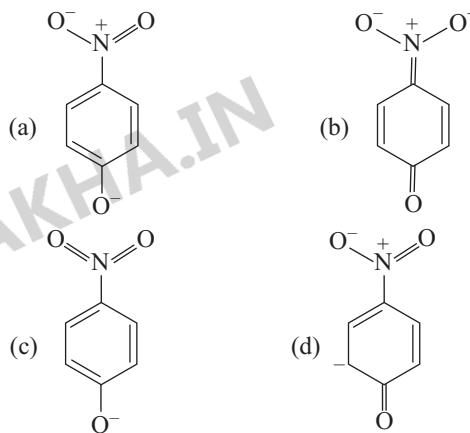


(2003, 1 M)



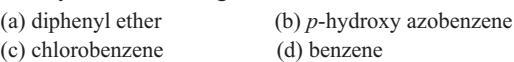
25. The most unlikely representation of resonance structures of  $p$ -nitrophenoxide ion is

(1999, 2M)



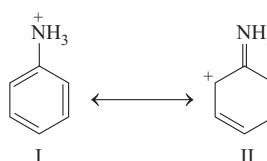
26. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives

(1998, 2M)



27. Examine the following two structures of anilinium ion and choose the correct statement from the ones given below :

(1993, 1M)



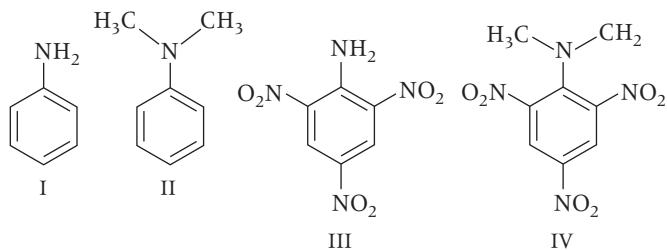
- (a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions  
(b) II is not an acceptable canonical structure because it is non-aromatic  
(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons  
(d) II is an acceptable canonical structure

- 28.** Chlorobenzene can be prepared by reacting aniline with  
 (a) hydrochloric acid (1984, 1M)  
 (b) cuprous chloride  
 (c) chlorine in the presence of anhyd AlCl<sub>3</sub>  
 (d) nitrous acid followed by heating with cuprous chloride

### Objective Questions II

(One or more than one correct option)

- 29.** Consider the following four compounds, I, II, III, and IV.

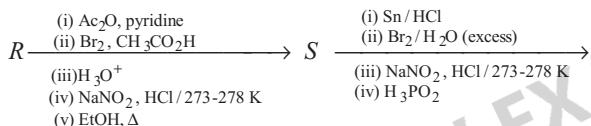


Choose the correct statement(s).

(2020 Adv.)

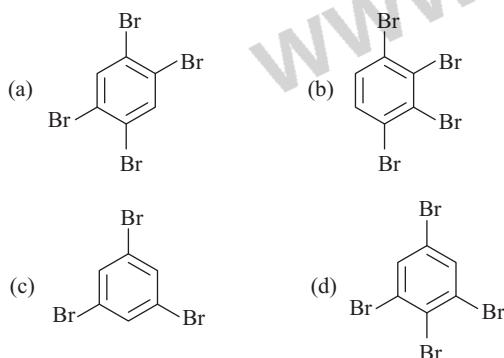
- (a) The order of basicity is II > I > III > IV.  
 (b) The magnitude of pK<sub>b</sub> difference between I and II is more than that between III and IV.  
 (c) Resonance effect is more in III than in IV.  
 (d) Steric effect makes compound IV more basic than III.

- 30.** Aniline reacts with mixed acid (conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>) at 288 K to give P (51%), Q (47%) and R (2%). The major product(s) of the following sequence is (are)

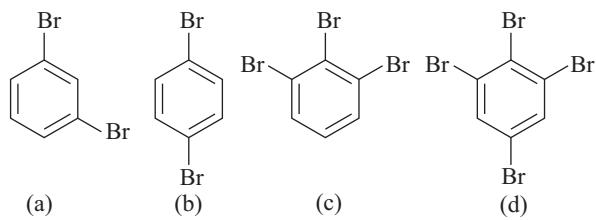
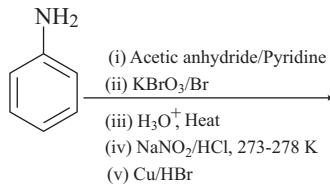


Major product(s)

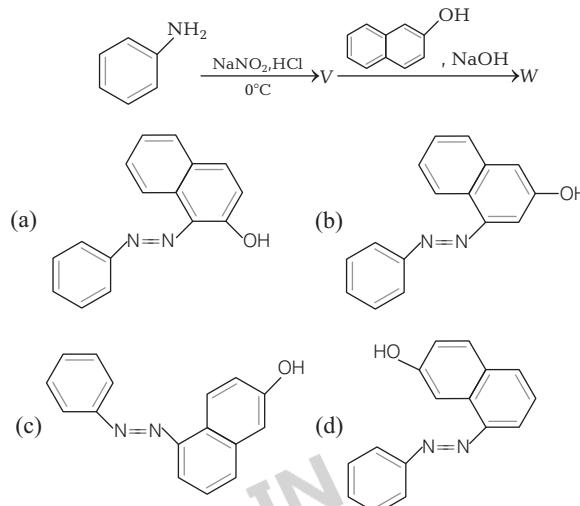
(2018 Adv.)



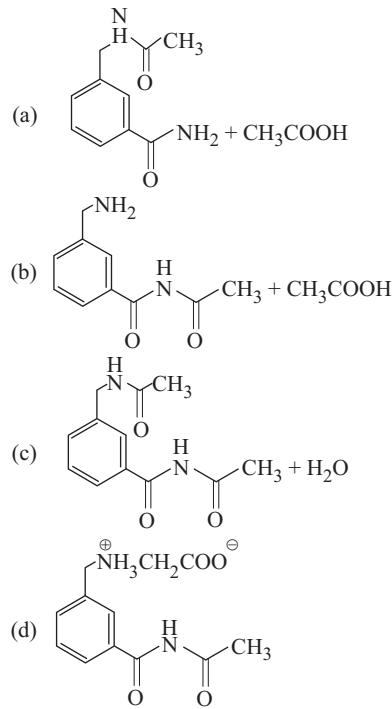
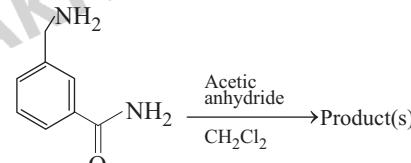
- 31.** The product(s) of the following reaction sequence is (are) (2017, Adv.)



- 32.** In the following reactions, the major product W is (2015 Adv.)



- 33.** In the reaction shown below, the major product(s) formed is/are (2014 Adv.)



## 446 Aromatic Compounds Containing Nitrogen

34. *p*-chloroaniline and anilinium hydrochloride can be distinguished by (1998, 2M)

(a) Sandmeyer reaction      (b)  $\text{NaHCO}_3$   
 (c)  $\text{AgNO}_3$                   (d) Carbylamine test

35. When nitrobenzene is treated with  $\text{Br}_2$  in the presence of  $\text{FeBr}_3$ , the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer, are (1992, 1M)

(a) the electron density on *meta* carbon is more than that on *ortho* and *para* positions  
 (b) the intermediate carbonium ion formed after initial attack of  $\text{Br}^+$  at the *meta* position is less destabilised  
 (c) loss of aromaticity when  $\text{Br}^+$  attacks at the *ortho* and *para* positions and not at *meta* position  
 (d) easier loss of  $\text{H}^+$  to regain aromaticity from *meta* position than from *ortho* and *para* positions

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.  
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.  
 (c) Statement I is correct; Statement II is incorrect.  
 (d) Statement I is incorrect; Statement II is correct.
36. **Statement I** Aniline on reaction with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol gives a dark blue coloured precipitate.

**Statement II** The colour of the compound formed in the reaction of aniline with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol is due to the extended conjugation (2008, 3M)

37. **Statement I** In strongly acidic solution, aniline becomes more reactive towards electrophilic reagents.

**Statement II** The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on nitrogen is no longer available for resonance. (2001, 1M)

### Match the Column

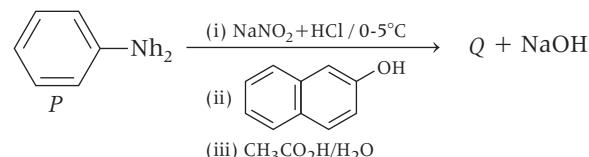
38. Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. (2008, 6M)

| Column I                                                                                                          | Column II                                                                                 |
|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| (A) $\text{H}_2\text{N}-\overset{\oplus}{\text{NH}_3}\overset{\ominus}{\text{Cl}}$                                | (p) Sodium fusion extract of the compound gives Prussian blue colour with $\text{FeSO}_4$ |
| (B) $\text{O}_2\text{N}-\text{C}_6\text{H}_3-\text{NH}-\overset{\oplus}{\text{NH}_3}\overset{\ominus}{\text{Br}}$ | (q) Gives positive $\text{FeCl}_3$ test                                                   |

| Column I | Column II                                                                |
|----------|--------------------------------------------------------------------------|
| (C)      | (r) Gives white precipitate with $\text{AgNO}_3$                         |
| (D)      | (s) Reacts with aldehydes to form the corresponding hydrazone derivative |

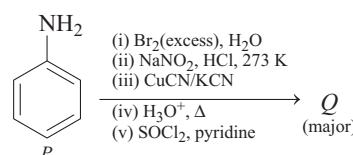
### Numerical Answer Type Questions

39. Consider the reaction sequence from *P* to *Q* shown below. The overall yield of the major product *Q* from *P* is 75%. What is the amount in grams of *Q* obtained from 9.3 mL of *P*? (Use density of *P* =  $1.00 \text{ g mL}^{-1}$ ; Molar mass of C = 12.0, H = 1.0, O = 16.0 and N =  $14.0 \text{ g mol}^{-1}$ ) (2020 Adv.)

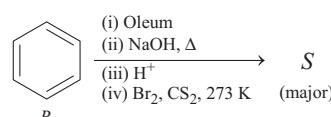


40. Schemes 1 and 2 describe the conversion of *P* to *Q* and *R* to *S*, respectively. Scheme 3 describes the synthesis of *T* from *Q* and *S*. The total number of Br atoms in a molecule of *T* is ..... (2019 Adv.)

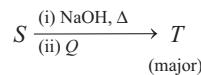
Scheme 1



Scheme 2



Scheme 3

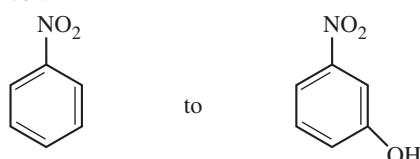


### Fill in the Blanks

41. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its..... structure. (1994, 1M)
42. In an acidic medium, ..... behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981, 1M)

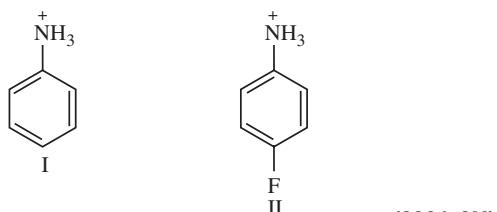
## **Subjective Questions**

**43.** Convert

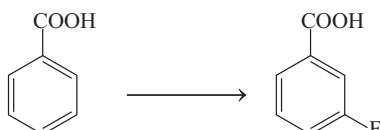


in not more than four steps. Also mention the reaction conditions and temperature. (2004, 4M)

**44.** Which of the following is more acidic and why?

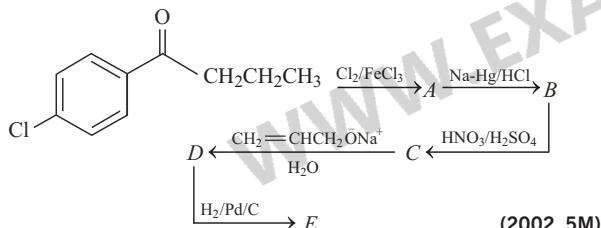


**45.** Convert (in not more than 3 steps) :

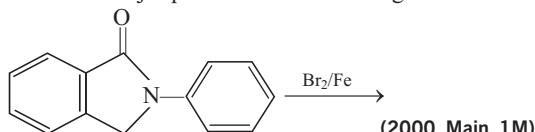


**46.** There is a solution of *p*-hydroxybenzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional group present. (2003, 4M)

**47.** Write structures of the products  $A$ ,  $B$ ,  $C$ ,  $D$  and  $E$  in the following scheme

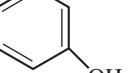


**48.** What would be the major product in the following reaction?



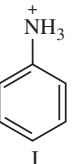
**49.** How would you bring about the following conversion (in 3 steps)?  
Aniline  $\longrightarrow$  Benzylamine (2000, 3M)

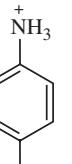
- Subjective Questions**

**43.** Convert  to 

in not more than four steps. Also mention the reaction conditions and temperature. (2004, 4M)

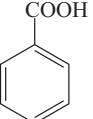
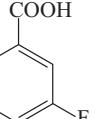
**44.** Which of the following is more acidic and why?

  
I

  
II

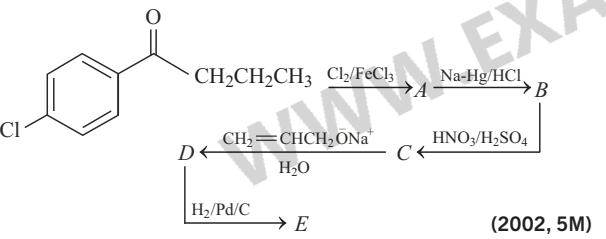
(2004, 2M) (2003, 2M)

**45.** Convert (in not more than 3 steps):

 → 

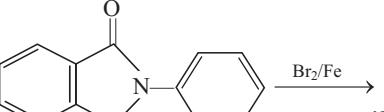
**46.** There is a solution of *p*-hydroxybenzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional group present. (2003, 4M)

**47.** Write structures of the products *A*, *B*, *C*, *D* and *E* in the following scheme



(2002, 5M)

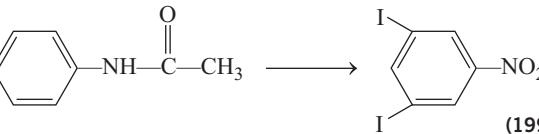
**48.** What would be the major product in the following reaction?



(2000, Main, 1M)

**49.** How would you bring about the following conversion (in 3 steps)?  
Aniline → Benzylamine (2000, 3M)

**50.** Complete the following reactions with appropriate reagents



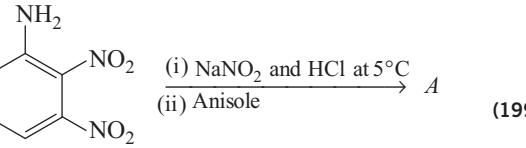
I (1994)

**51.** Following reaction gives two products. Write the structures of the products.

$\text{CH}_3\text{CONHC}_6\text{H}_5 \xrightarrow{\text{Br}_2/\text{Fe}}$  (1998)

**52.** Write the structure of foul smelling compound obtained when aniline is treated with chloroform in the presence of KOH. (1996)

**53.** Complete the following with appropriate structure:



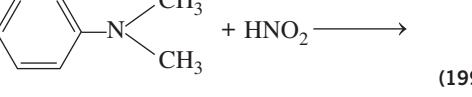
(1995)

**54.** How will you bring about the following conversions?  
“Benzamide from nitrobenzene” (1994)

**55.** How will you bring about the following conversions?  
“4-nitrobenzaldehyde from benzene” (1994)

**56.** Outline a synthesis of *p*-bromonitrobenzene from benzene in three steps. (1993)

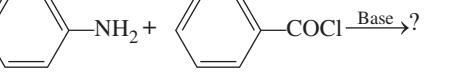
**57.** Write the structure of the major organic product expected in the following reaction.



(1992)

**58.** How will you bring about the following conversion?  
“4-nitro aniline to 1, 2, 3-tribromobenzene.” (1990)

**59.** Complete the following with appropriate structures: (1986)



(1986)

**60.** How would you convert aniline into chlorobenzene? (1985)

**61.** State the conditions under which the following preparation carried out. “Aniline from benzene” (1983)

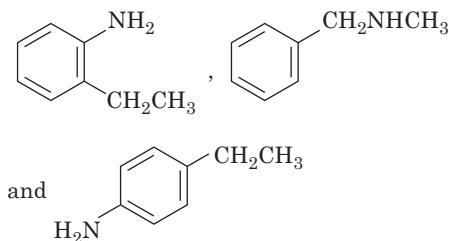
**62.** State the equation for the preparation of following compound  
Chlorobenzene from aniline (in 2 steps). (1982)

## Answers

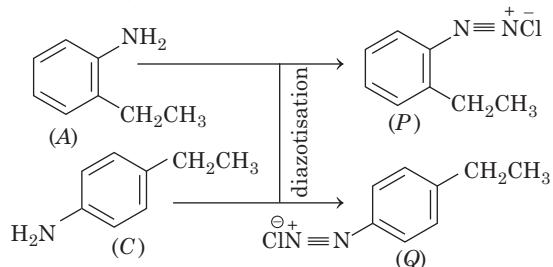
- |                |                |                |                |                      |                                     |                            |                         |                     |
|----------------|----------------|----------------|----------------|----------------------|-------------------------------------|----------------------------|-------------------------|---------------------|
| <b>1.</b> (a)  | <b>2.</b> (c)  | <b>3.</b> (c)  | <b>4.</b> (b)  | <b>25.</b> (c)       | <b>26.</b> (b)                      | <b>27.</b> (c)             | <b>28.</b> (d)          |                     |
| <b>5.</b> (a)  | <b>6.</b> (d)  | <b>7.</b> (*)  | <b>8.</b> (c)  | <b>29.</b> (c,d)     | <b>30.</b> (d)                      | <b>31.</b> (b)             | <b>32.</b> (a)          |                     |
| <b>9.</b> (b)  | <b>10.</b> (b) | <b>11.</b> (b) | <b>12.</b> (c) | <b>33.</b> (a)       | <b>34.</b> (c,d)                    | <b>35.</b> (a,b)           | <b>36.</b> (d)          |                     |
| <b>13.</b> (d) | <b>14.</b> (b) | <b>15.</b> (a) | <b>16.</b> (d) | <b>37.</b> (d)       | <b>38.</b> ( $A \rightarrow r, s$ ) | $B \rightarrow p, q$       | $C \rightarrow p, q, r$ | $D \rightarrow p$ ) |
| <b>17.</b> (c) | <b>18.</b> (c) | <b>19.</b> (a) | <b>20.</b> (c) | <b>39.</b> (18.60)   | <b>40.</b> (4)                      | <b>41.</b> (zwitter ionic) |                         |                     |
| <b>21.</b> (c) | <b>22.</b> (d) | <b>23.</b> (b) | <b>24.</b> (a) | <b>42.</b> (Aniline) |                                     |                            |                         |                     |

# Hints & Solutions

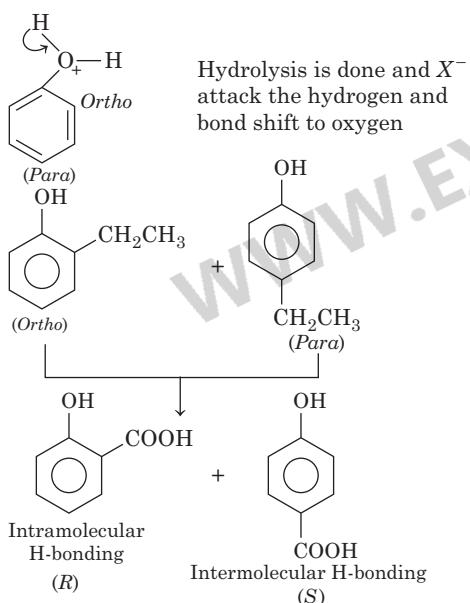
1. A, B and C respectively are



According to the question, A and C undergoes diazotisation to give P and Q. So, amine must be primary aromatic amine.



Which on hydrolysis followed by oxidation gives alcohol derivative.



Given, R has low boiling point than S.

Intramolecular H-bond is weaker than intermolecular H-bond.

It means intramolecular H-bonding show low boiling point and here, R is *ortho* product and S is *para* product.

Given,

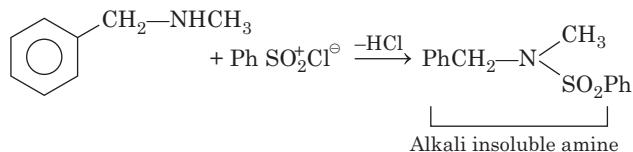


C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl act as electrophile then B must be amine.

Secondary amine act as a nucleophile.

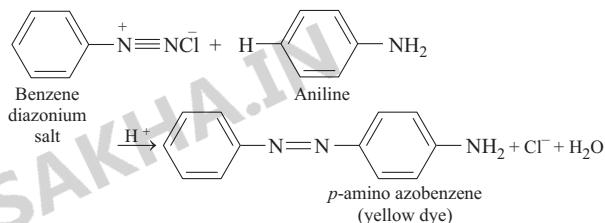
The C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl act as electrophile and displace Cl.

In the given option (b), secondary amine is present in the reaction takes place as follows :



Primary and secondary amine forms poorly soluble ppt. on reaction with PhSO<sub>2</sub>Cl.

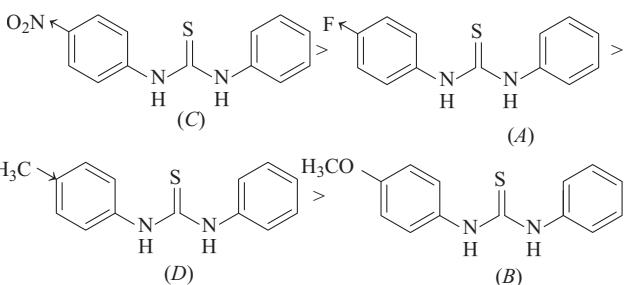
2. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid undergoes coupling reaction and produces *p*-amino azobenzene. In this reaction, benzene diazonium chloride reacts with aniline in which aniline molecule at its *para*-position is coupled with diazonium salt to give *p*-amino azobenzene (yellow dye).



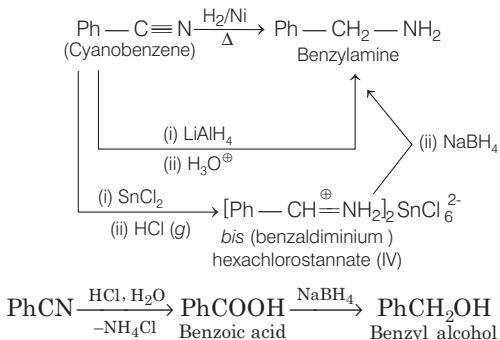
3. **Key Idea**  $pK_b$  value is defined as the minus logarithm of  $K_b$  smaller the value of  $pK_b$  stronger is the base and vice-versa.

In the given options, +R effect is shown by —CH<sub>3</sub> and —OCH<sub>3</sub> group ( $—OCH_3 > —CH_3$ ). These group increases the electron density at *o* and *p*-positions. Groups such as —F and —NO<sub>2</sub> shows —R-effect ( $—NO_2 > —F$ ). These group decreases the electron density at *o* and *p*-positions.

Increase in electron density at *p*-position makes the unshared electron pair of 'N' more available and decrease in electron density at *p*-position makes the unshared electron pair of 'N' less available. Compound containing —OCH<sub>3</sub> group act as strongest base and hence possess lowest value of  $pK_b$ . So, the correct increasing order of  $pK_b$  in the given compound is

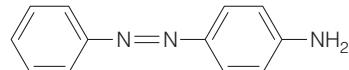


4. The preparation of benzylamine from cyanobenzene using given reagents are as follows :



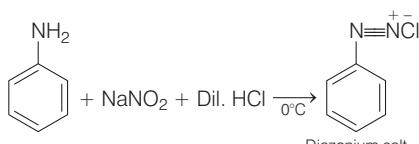
Thus, option (b) is incorrect.

5. Major product of the reaction is

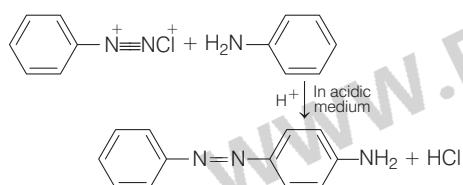


It is obtained by coupling reaction.

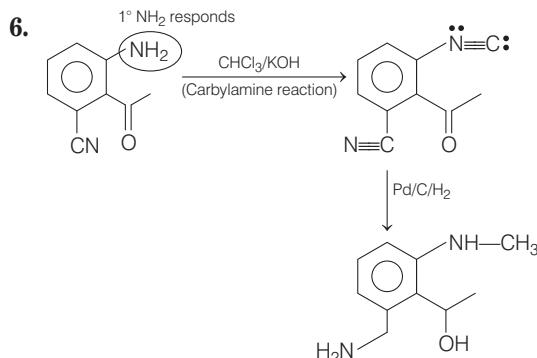
Reaction of aniline with dil. HCl and sodium nitrite at 0°C is shown below :



Diazonium salt formed when added to equimolar mixture of aniline and phenol in dil. HCl then aniline couples with diazonium salt. Reaction is as follows :



For an effective coupling, the solution must be so alkaline that the concentration of diazonium ion is too low. It must not be so acidic that the concentration of free amine or phenoxide ion is too low. That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

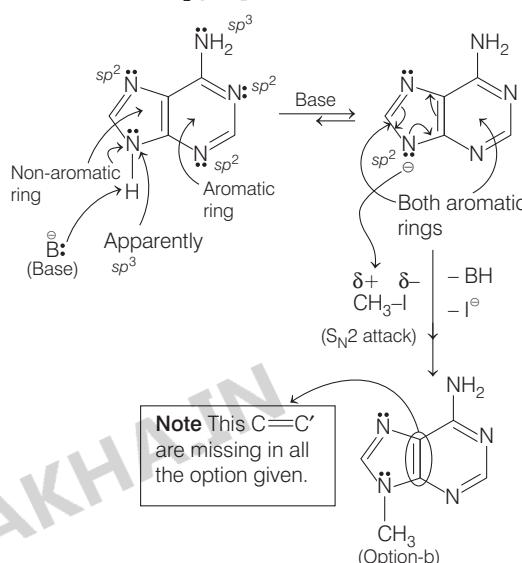


In step (i), 1° amine is converted into isocyanide, when reacts with  $\text{CHCl}_3 / \text{KOH}$ . This reaction is known as carbylamine reaction. This reaction is used to detect primary amine in a compound.

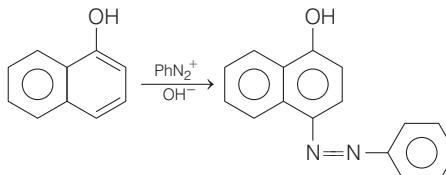
In step (ii), isocyanide is reduced to secondary amine and cyanide is reduced to primary amine, and carbonyl group to alcoholic group when treated with  $\text{Pd/C/H}_2$ .

7. N is more electronegative than 'C'. So, H of  $\text{N}-\text{H}$  bond is more acidic than that of  $\text{C}-\text{H}$  bond in the ring.

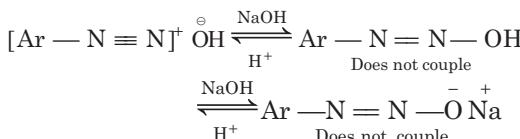
Again,  $sp^2$ -N is more electronegative ( $s\% = 33.3$ ) than  $sp^3$ -N ( $s\% = 25$ ) of the  $-\text{NH}_2$  group.



8. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give the following coupling reaction.



In the presence of  $\text{OH}^-$  ion,  $\text{ArN}_2^+$  exists in equilibrium with an unionised compound ( $\text{Ar}-\text{N}=\text{N}-\text{OH}$ ) and salts  $[\text{ArN}=\text{N}^+] \text{---} \text{OH}^-$  derived from it, which do not couple.

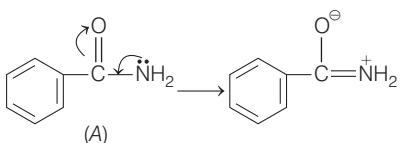


Following conditions are very useful for coupling reaction to take place.

- (a) The solution must be so alkaline that the concentration of diazonium ion is too low.
- (b) It must not be so acidic that the concentration of free phenoxide ion is too low.

9. The reaction of alkyl halide with amine or amides is a nucleophilic substitution reaction. More nucleophilic nitrogen is more reactive with alkyl halide. Compound (A) is benzamide and lone pair of 'N' of it, is not available in this compound.

## 450 Aromatic Compounds Containing Nitrogen

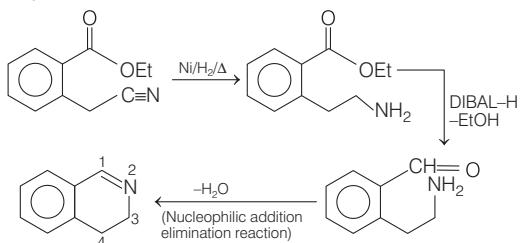


In compound (D), lone pair of 'N' are available but in compound (C), the lone pair of 'N' are not readily available due to the presence of electron withdrawing group ( $\text{—CN}$ ) attach to benzene ring.

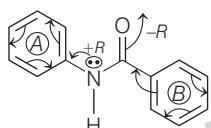
In compound (B), i.e. phthalimide, 'N' is not nucleophilic due to the presence of two polar groups attached to it that pulls lone pair towards them. Hence, the correct order is:



10. Ni/H<sub>2</sub> can reduce  $\text{—C}\equiv\text{N}$  into  $\text{—CH}_2\text{—NH}_2$  ( $1^\circ$ -amine) but cannot reduce an ester group ( $\text{—CO}_2\text{Et}$ ) whereas DIBAL-H, di-isobutylaluminium hydride,  $[(\text{CH}_3)_2\text{CH}]_2\text{AlH}$  reduces the ester group ( $\text{—CO}_2\text{Et}$ ) into  $\text{—CHO}$  (an aldehyde) and  $\text{C}_2\text{H}_5\text{OH}$ .

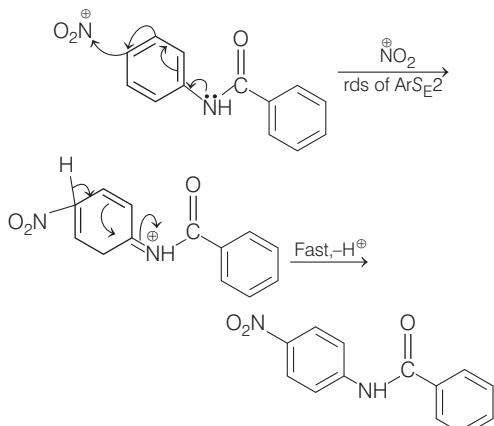


11. Here, in mononitration the electrophile produced from mixed acid ( $\text{HNO}_3 + \text{conc. H}_2\text{SO}_4$ ) is  $\text{NO}_2^+$ .

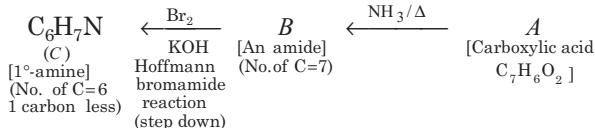


Ring-(A) is activated, i.e. becomes more nucleophilic by the  $+R$  effect of the  $\text{—NH}_2$  group and it becomes *o* / *p*-directing towards the electrophile,  $\text{NO}_2^+$  in the  $\text{ArS}_E^2$  reaction. For mononitration,  $\text{NO}_2^+$  will preferably come at *p*-position, whereas

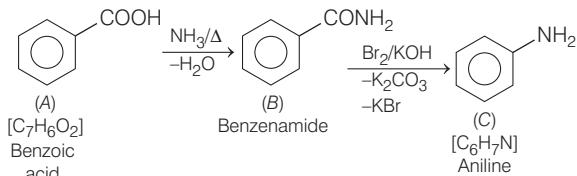
the ring-(B) gets deactivated by  $-R$ -effect of the  $\text{—C}\equiv\text{O}$  group,



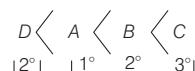
12. Using retro-synthesis, to get the required compounds, *A*, *B* and *C*.



So, the reactions can be shown as:



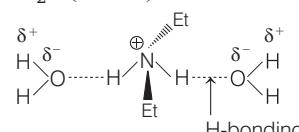
13. If we consider Lewis basicity (basicity in aprotic solvents or in vapour phase), the order of basicity will be.



But, this order does not match with the options given. So, it has been asked on basicity of the amines in aqueous solution. When no phase is given, then basicity of amine is considered in aqueous solution as they are liquids. In aqueous solution, basicity of  $2^\circ$ -amines (aliphatic) is maximum because, of the thermodynamic stability of its conjugate acid.



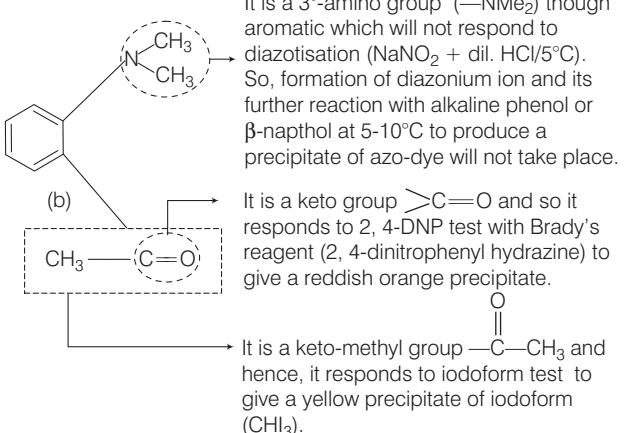
$\text{Et}_2\text{NH}_2^-$  is a sterically symmetric tetrahedral ion as it contains equal number (two) of bulkier Et-group and small size H-atoms. Here, two H-atoms give additional stability through hydrogen bonding with  $\text{H}_2\text{O}$  (solvent) molecules.



Aromatic amines (*D*) are always weaker bases than aliphatic amines, because of the conjugation of  $l_p$  of electrons of N ( $+R$ -effect) with the benzene ring.

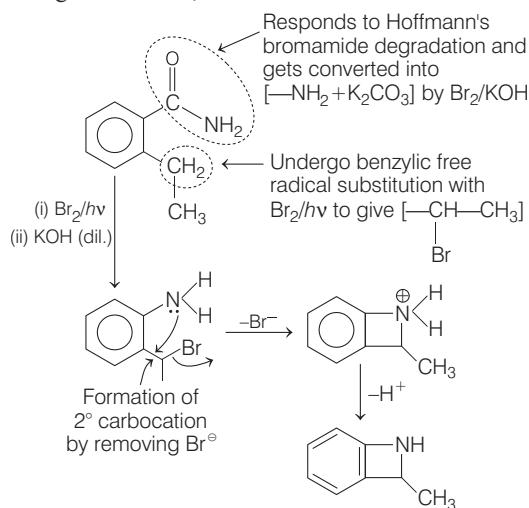
So, the correct order is  $(D) < (C) < (A) < (B)$ .

- 14.



Compound (c) is an alcohol and does not give positive 2, 4-DNP test. Hence, eliminated (a) and (d) does not have  $\text{—CH}_3\text{CO}$  group and does not give iodoform test. Hence, eliminated.

15. In the given reaction,

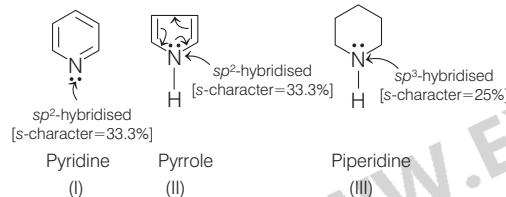


### 16. Key Idea

Basicity  $\propto$  Ease of donation of lone pair of electrons

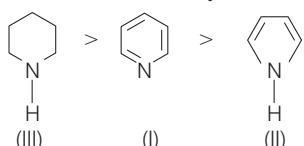
$$\propto \frac{1}{\% \text{ of } s\text{-character of } N} \propto \frac{1}{\text{Electronegativity of } N}$$

The % of *s*-character in the given amines are as follows:



Therefore, piperidine (III) having minimum

% *s*-character is most basic. Among the rest, pyridine (I) and pyrrole (II) the lone pair of electrons of N in pyrrole (II) is involved in delocalisation and follows  $(4n + 2)\pi$  aromatic ( $n = 1$ ) system. So, the N-atom of pyrrole (II) will show least basicity. Thus, the order of basicity is as follows:

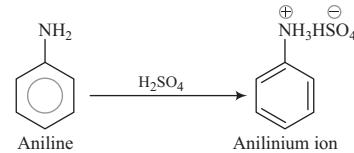


17. All the given compounds are  $\alpha$ -monosubstituted acetic acid derivatives and the  $\alpha$ -substitutions have been made by strong-*I* groups/atoms. More powerful the  $—I$  group, stronger will be the acid.

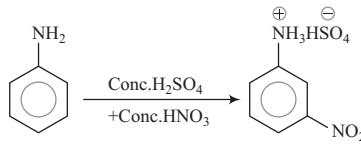
$—I$  power of different groups is as follows :  
 $—\text{NO}_2 > —\text{CN} > —\text{F} > —\text{Cl}$

Thus, the correct decreasing order for acid strength is:  
 $\text{NO}_2\text{CH}_2\text{COOH} > \text{NCCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$ .

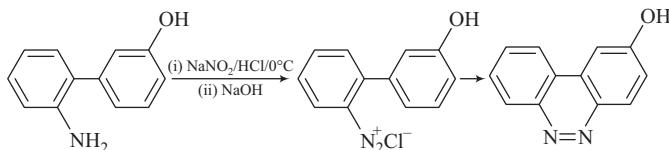
18. Aniline in presence of nitrating mixture (conc.  $\text{HNO}_3 + \text{conc. H}_2\text{SO}_4$ ) gives significant amount ( $\approx 47\%$ ) of meta-product because in presence of  $\text{H}_2\text{SO}_4$  its protonation takes place and anilinium ion is formed.



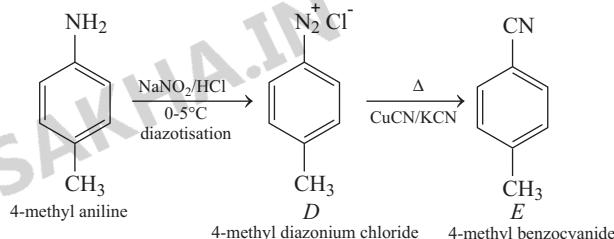
Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



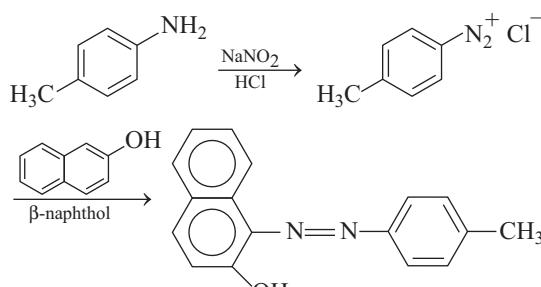
19. Diazo coupling occurs at *para*-position of phenol.



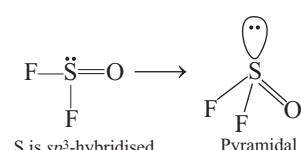
- 20.



21. As we know, benzenediazonium salt forms brilliant coloured dye with  $\beta$ -naphthol, the compound under consideration must be *p*-toluidine (c) as it is a primary aromatic amine. Primary aromatic amine, on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  forms the corresponding diazonium chloride salt.

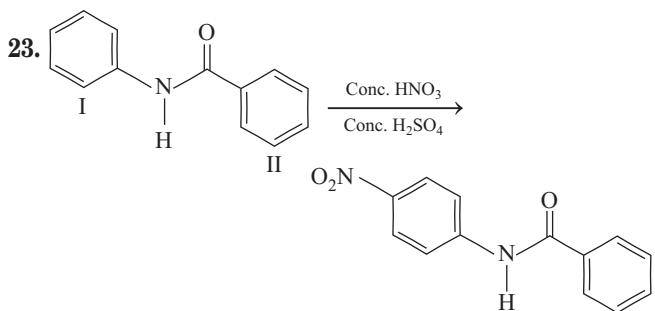


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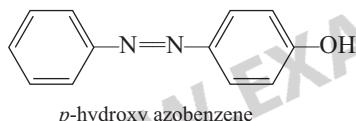
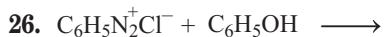
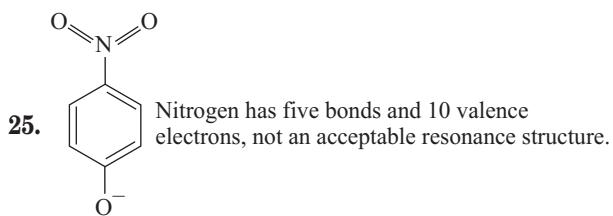
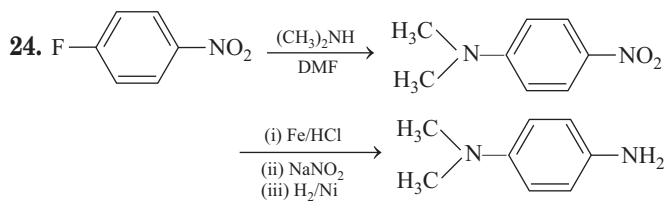


$\text{SO}_3$  is planar (S is  $sp^2$ -hybridised),  $\text{BrF}_3$  is T-shaped and  $\text{SiO}_3^{2-}$  is planar (Si is  $sp^2$ -hybridised).

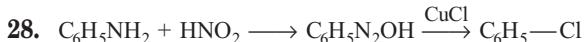
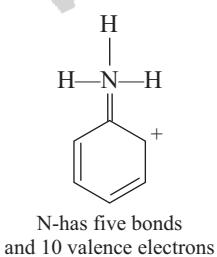
## 452 Aromatic Compounds Containing Nitrogen



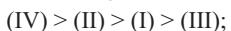
Ring-I is activated while ring-II is deactivated towards electrophilic aromatic substitution reaction.



27. In structure II, nitrogen is associated with five bonds and 10 valence electrons, hence not acceptable.



29. (a) The correct basic strength order is



(IV) is strongest base due to steric inhibition to resonance effect.

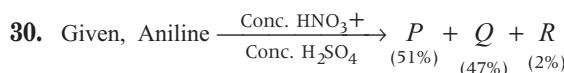
(III) is weakest base due to *M* group of three nitro groups present at *ortho* and *para* positions.

(II) is stronger than (I) since (III) is tertiary and (I) primary aromatic amine.

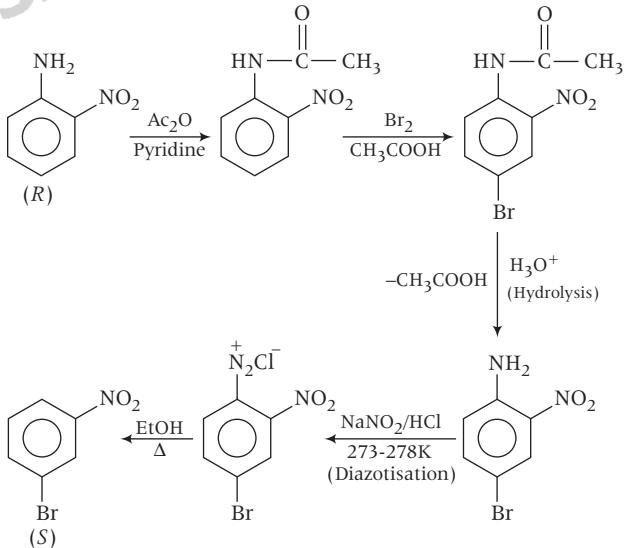
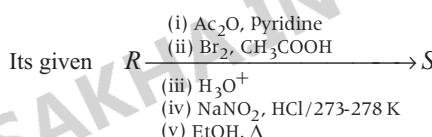
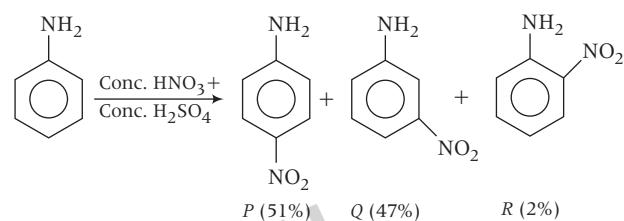
So, option (a) is incorrect.

(b)  $pK_b$  different between I and II is 0.53 and that of III and IV is 4.6. So, option (b) is incorrect.

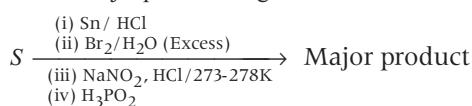
(c) and (d) In 2, 4, 6-trinitro aniline (III) due to strong *-R* effect of  $-\text{NO}_2$  groups, the lone pair of  $-\text{NH}_2$  is more involved with benzene ring hence it has least basic strength. Whereas (IV) N, N-dimethyl 2, 4, 6-trinitro aniline, due to steric inhibition to resonance (SIR) effect; the lone pair of nitrogen is not in the plane of benzene, hence makes it lone pair more free to protonate.

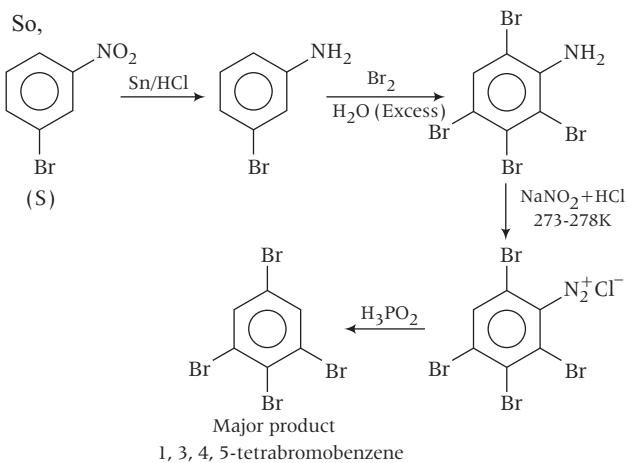


Then P, Q and R will be

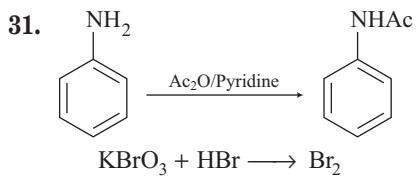


Now from S to major products its given.

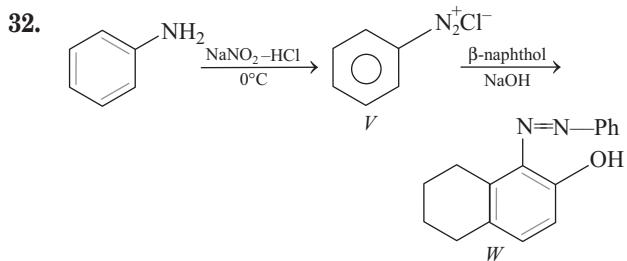
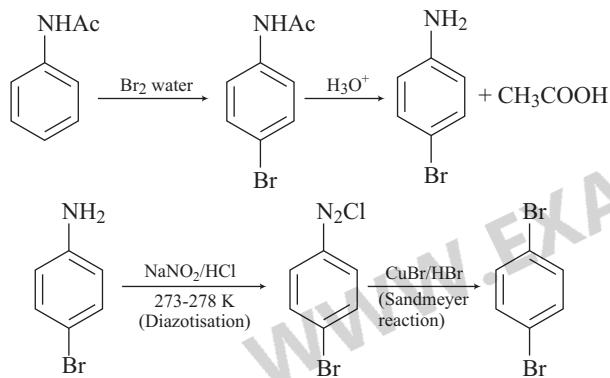




Hence, only (d) is the correct answer.

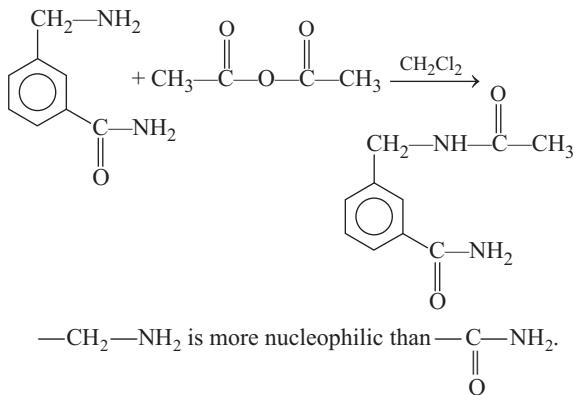


Ac is  $\text{CH}_3\text{CO}$  (acetyl), it protects  $-\text{NH}_2$  group from being oxidised.



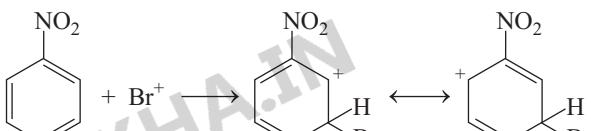
33. **PLAN** This problem includes concept of acylation reaction and regioselectivity of chemical reaction.

Regioselectivity means which group will react selectively in the presence of two or more than two functional groups. Here, among two functional group  $-\text{NH}_2$  and  $-\text{CONH}_2$ ,  $\text{NH}_2$  is more nucleophilic, hence  $\text{NH}_2$  group will undergo reaction faster than  $\text{CONH}_2$ .

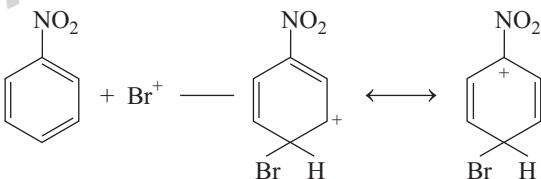


Hence, correct choice is (a).

34.  $(\text{C}_6\text{H}_5\text{NH}_3^{\text{+}}\text{Cl}^-) + \text{AgNO}_3 \xrightarrow{+} \text{AgCl} \downarrow$   
anilinium hydrochloride precipitate  
No such precipitate is formed with *p*-chloroaniline.  
Also, carbylamine test will not be given by anilinium hydrochloride but *p*-chloroaniline give this test.
35. Nitro group withdraws electrons more from *ortho/para* position than from *meta* position. Also the  $\sigma$ -complex formed from *meta* attack is less destabilised than from *ortho/para* positions.



Nitro group not destabilising the positive charge by resonance.

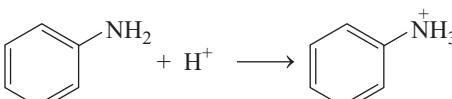


Nitro group destabilises the positive charge directly by resonance, less stable  $\sigma$ -complex.

Similar phenomenon is observed with *ortho* attack.

36.  $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 / \text{HCl} \xrightarrow{0^\circ\text{C}} \text{C}_6\text{H}_5\text{N}_2^{\text{+}}\text{Cl}^-$
- $\xrightarrow{\beta\text{-naphthol}}$
- 
- coloured dye

37. In strongly acidic medium, aniline is fully protonated, becomes deactivated for  $S_E\text{Ar}$  reaction.

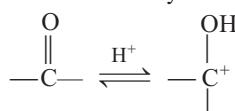


Lone pair on nitrogen is not available for resonance. Positive charge makes the group strongly electron withdrawing.

## 454 Aromatic Compounds Containing Nitrogen

38. Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both present in the compound. Phenolic group and salt of carboxylic acid gives  $\text{FeCl}_3$  test.

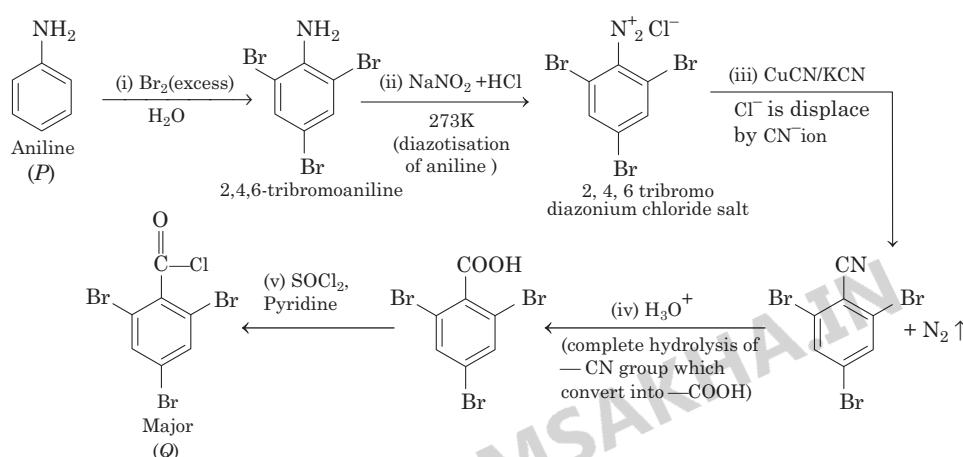
Chloride salt gives white precipitate of  $\text{AgCl}$  on treatment with  $\text{AgNO}_3$ . Hydrazone formation occurs effectively at  $\text{pH} = 4.5$ . The reaction proceeds in that condition only when  $\text{H}^+$  concentration is just sufficient to activate the following enolisation.



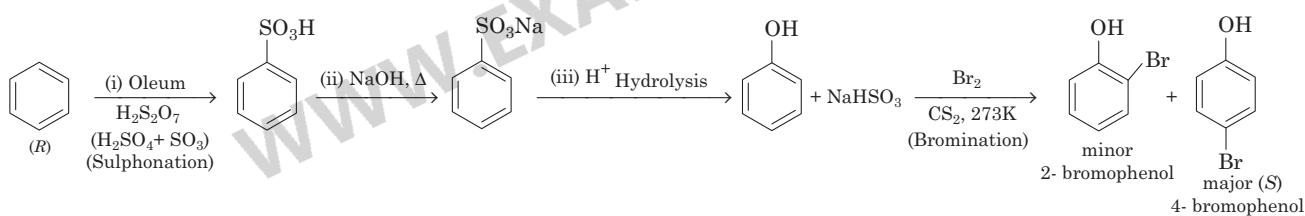
As  $\text{H}^+$  concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazinium ion which is not nucleophilic and reaction becomes impossible. Further low concentration of  $\text{H}^+$  (in the case of 2,4-dinitrophenyl hydrazinium bromide) is not effective to proceed elimination.

39. Aniline (*P*) is treated with  $\text{NaNO}_2$  and  $\text{HCl}$  in cold condition to form benzene diazonium chloride. The process of conversion of primary aromatic amines into its diazonium salt is called diazotisation.

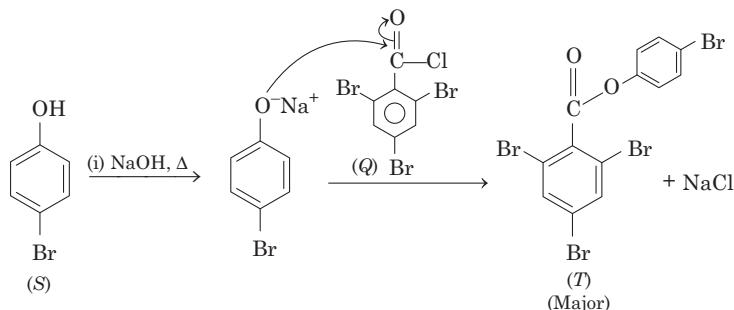
### 40. Scheme -1



Scheme-2

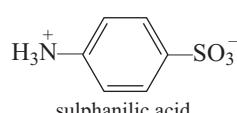


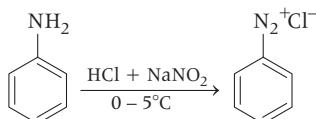
Scheme-3



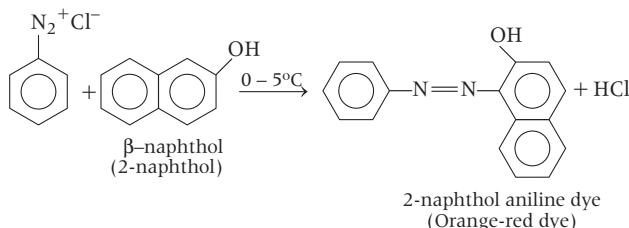
*T* compound has total number of Br atom = 4

### 41. Zwitter ionic





$\beta$ -naphthol couples with phenyldiazonium electrophile to produce an intense orange-red dye ( $Q$ ) as major product.



Given that, volume of aniline ( $P$ ) = 9.3 mL

(density of  $P$  = 1.00 g/mL)

So, mass of aniline = 9.3 g

Molecular mass of aniline ( $\text{C}_6\text{H}_7\text{N}$ ) = 93 g/mol

Therefore, moles of aniline =  $9.3 / 93 = 0.1$  mol of  $P$ .

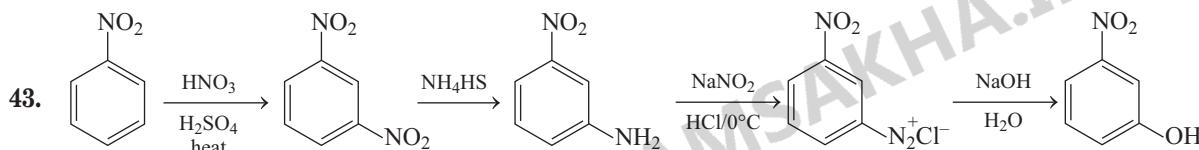
Molecular mass of 2 naphthol aniline orange dye ( $Q$ ) = 248 g/mol

$\Rightarrow 0.1$  mol of aniline ( $P$ ) will produce 0.1 mol of compound ( $Q$ ).

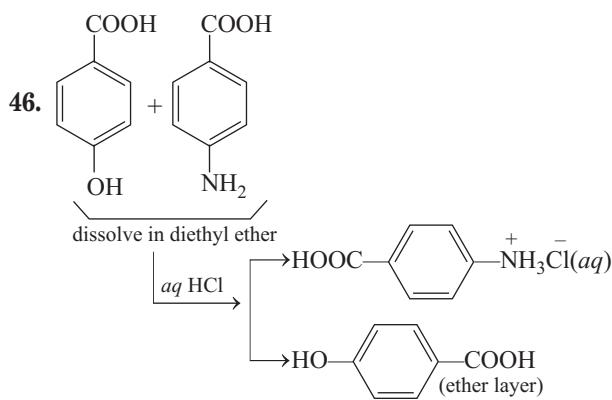
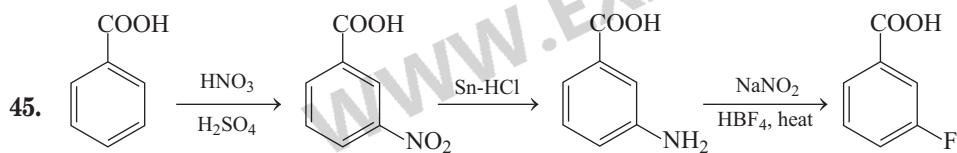
But, according to the question the major product  $Q$  from  $P$  is 75%.

Therefore, mass of ' $Q$ ' produced =  $(0.1 \times 248 \times 0.75)$  g = 18.60 g

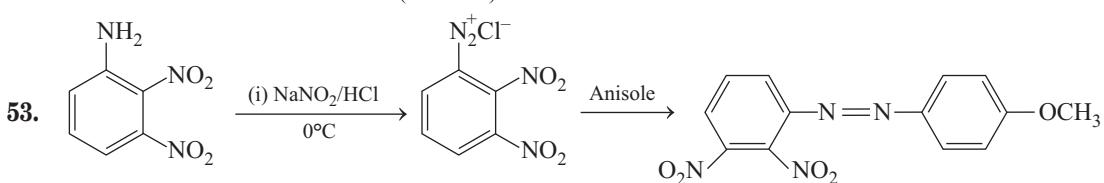
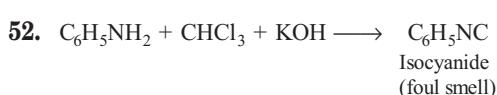
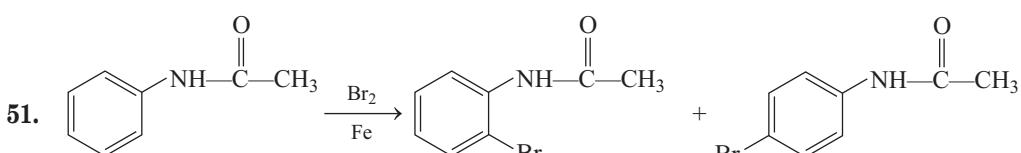
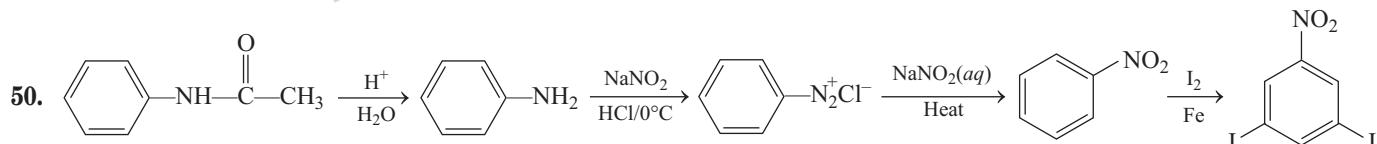
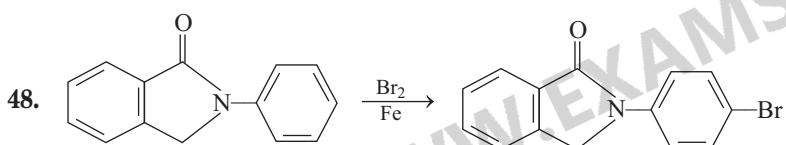
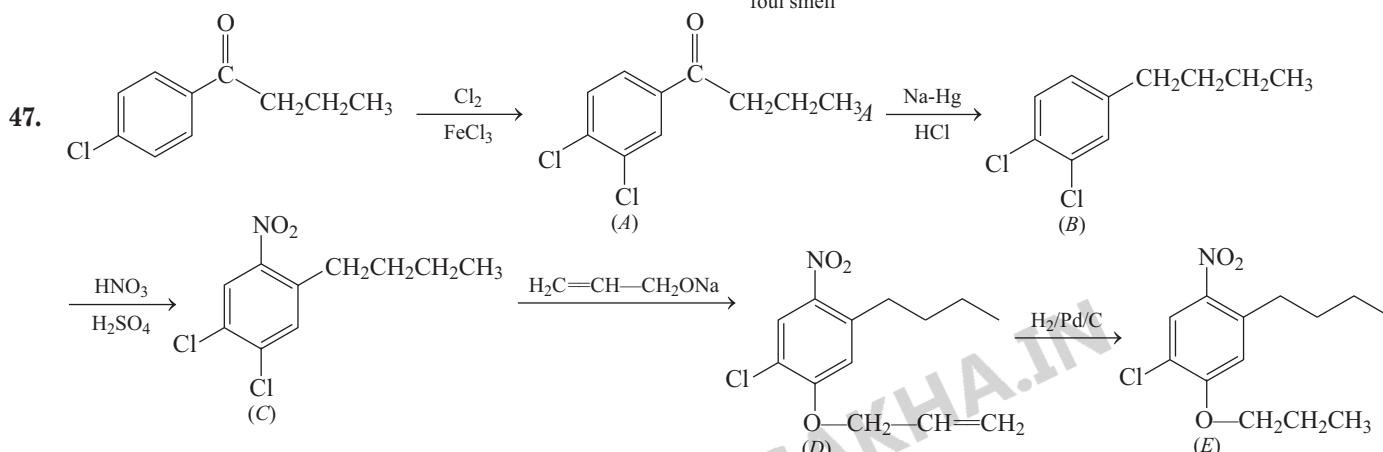
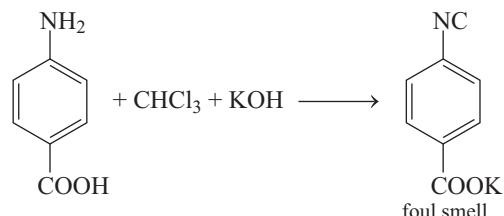
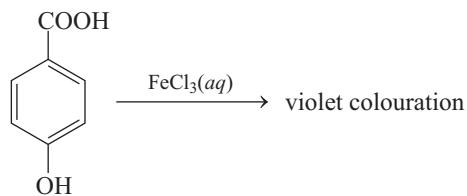
- 42. Aniline** It is a stronger base than either phenol or nitrobenzene.

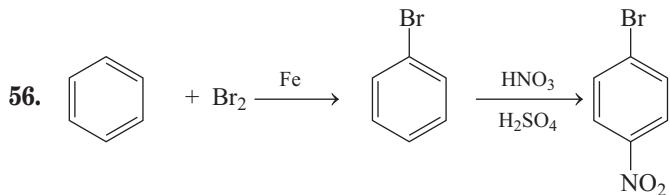
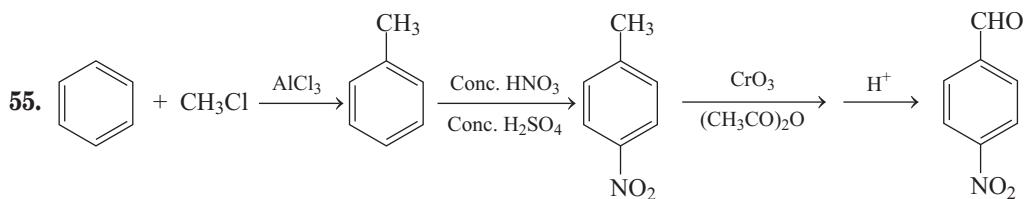
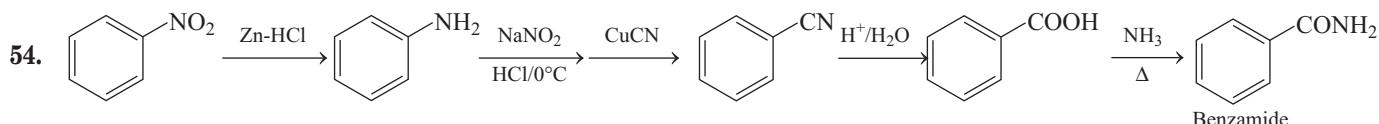


44. II is more acidic due to  $-I$  effect of F.

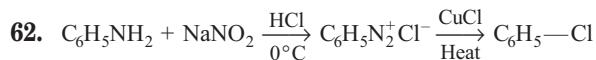
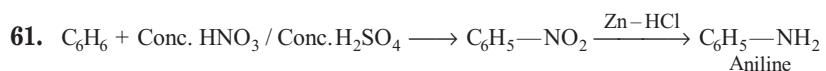
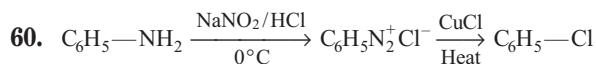
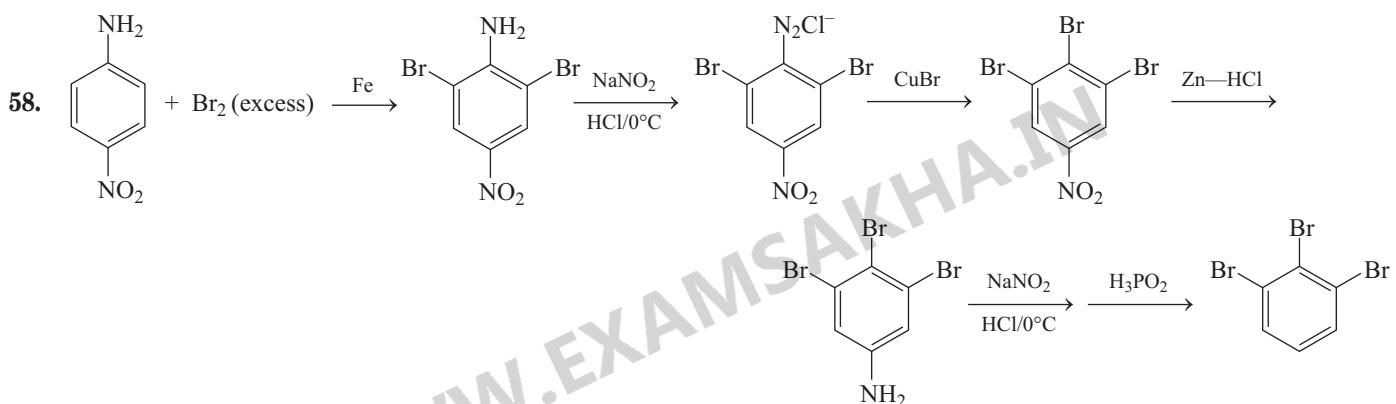


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57. No reaction. Tertiary amine does not react with nitrous acid.

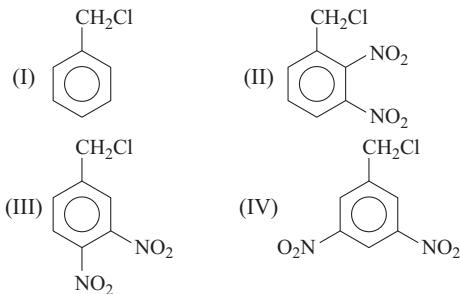


# 30

# Aryl Halides and Phenols

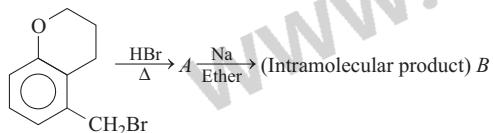
## Objective Questions I (Only one correct option)

1. The decreasing order of reactivity of the following compounds towards nucleophilic substitution ( $S_N2$ ) is (2020 Main, 3 Sep II)



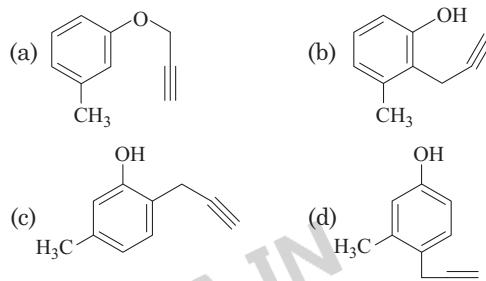
- (a) (II) > (III) > (IV) > (I)  
 (b) (IV) > (II) > (III) > (I)  
 (c) (III) > (II) > (IV) > (I)  
 (d) (II) > (III) > (I) > (IV)

2. In the following reaction sequence, structures of *A* and *B*, respectively will be (2020 Main, 7 Jan II)

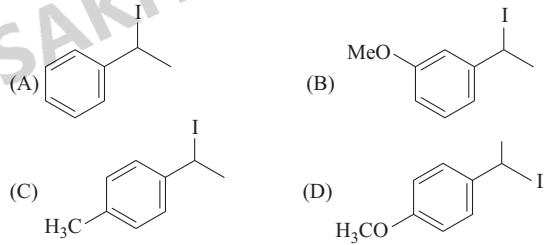


- (a) and   
 (b) and   
 (c) and   
 (d) and

3. What will be the major product when *m*-cresol is reacted with propargyl bromide ( $\text{HC}\equiv\text{C}-\text{CH}_2\text{Br}$ ) in presence of  $\text{K}_2\text{CO}_3$  in acetone? (2019 Main, 12 April II)

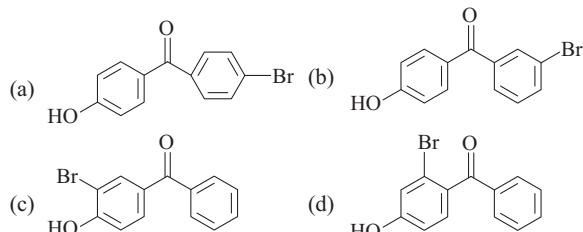


4. Increasing rate of  $S_N1$  reaction in the following compounds is



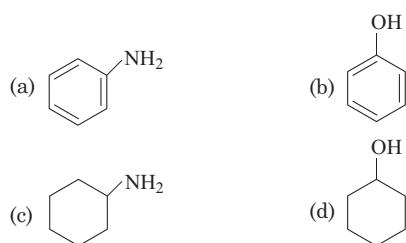
- (a) (A) < (B) < (C) < (D)  
 (b) (B) < (A) < (C) < (D)  
 (c) (A) < (B) < (D) < (C)  
 (d) (B) < (A) < (D) < (C)

5. *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives (2019 Main, 9 April II)

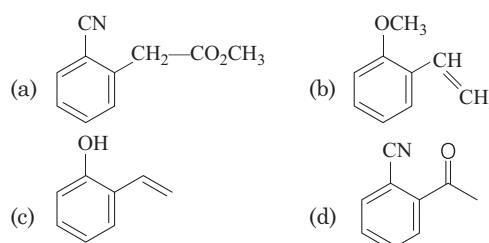


6. The organic compound that gives following qualitative analysis is (2019 Main, 9 April II)

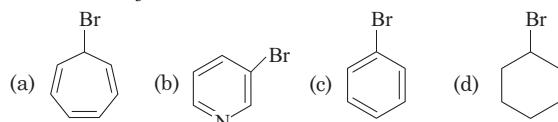
| Test                        | Inference       |
|-----------------------------|-----------------|
| (i) Dil. $\text{HCl}$       | Insoluble       |
| (ii) $\text{NaOH}$ solution | Soluble         |
| (iii) $\text{Br}_2$ /water  | Decolourisation |



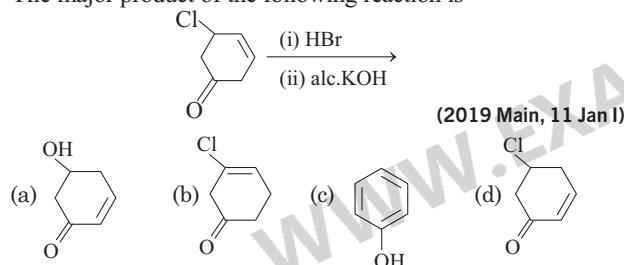
7. Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution  
(2019 Main, 11 Jan II)



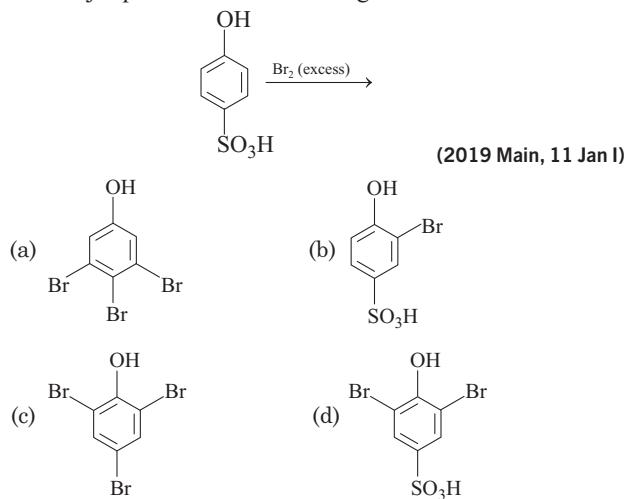
8. Which of the following compounds will produce a precipitate with  $\text{AgNO}_3$ ?  
(2019 Main, 11 Jan I)



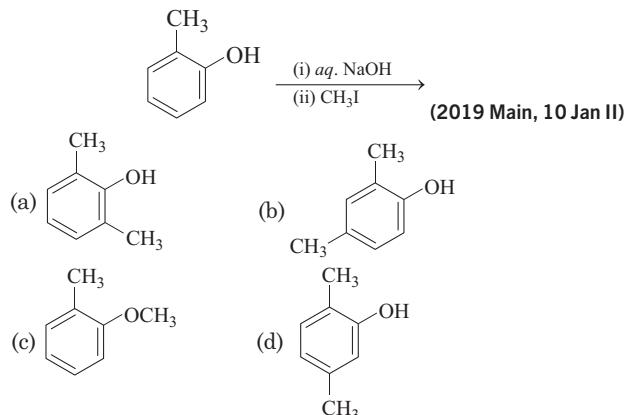
9. The major product of the following reaction is



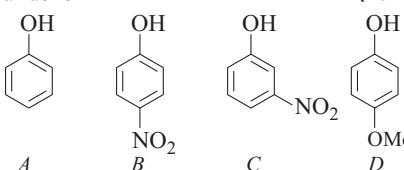
10. The major product of the following reaction is



11. The major product of the following reaction is

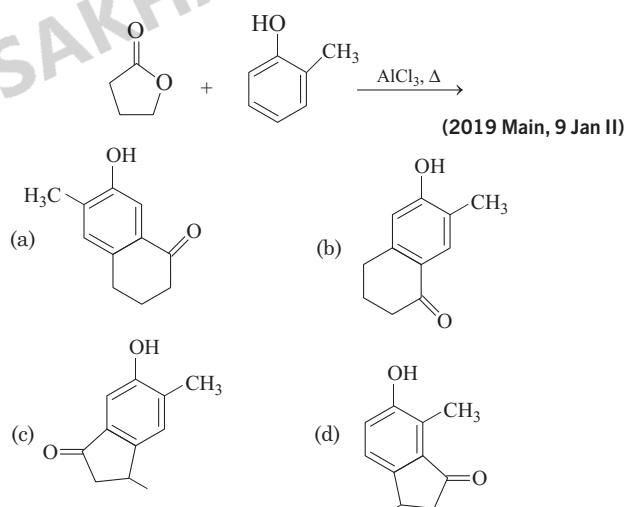


12. The increasing order of the  $pK_a$  values of the following compounds is  
(2019 Main, 10 Jan I)

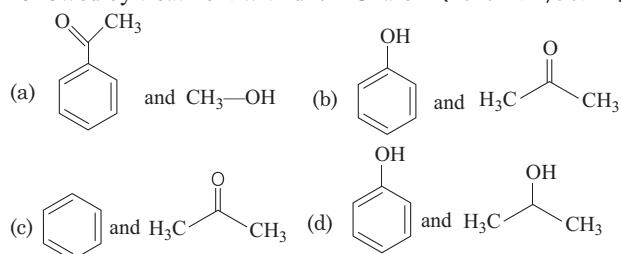


- (a)  $D < A < C < B$    (b)  $B < C < A < D$   
(c)  $C < B < A < D$    (d)  $B < C < D < A$

13. The major product of the following reaction is

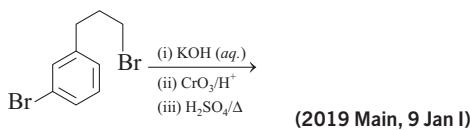


14. The products formed in the reaction of cumene with  $\text{O}_2$  followed by treatment with dil.  $\text{HCl}$  are  
(2019 Main, 9 Jan II)

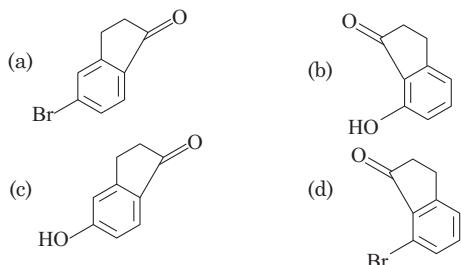


## 460 Aryl Halides and Phenols

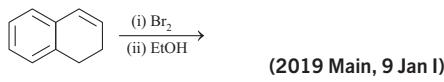
15. The major product of the following reaction is



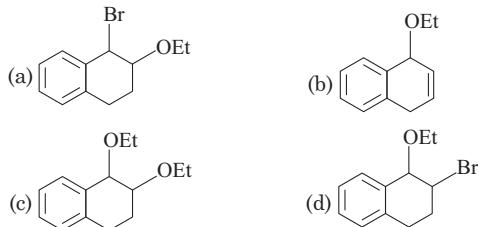
(2019 Main, 9 Jan I)



16. The major product of the following reaction is

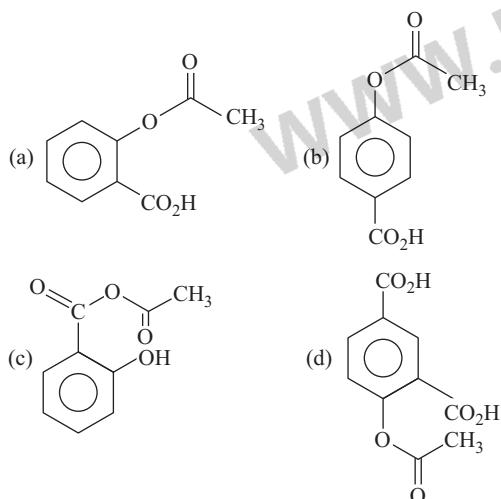


(2019 Main, 9 Jan I)



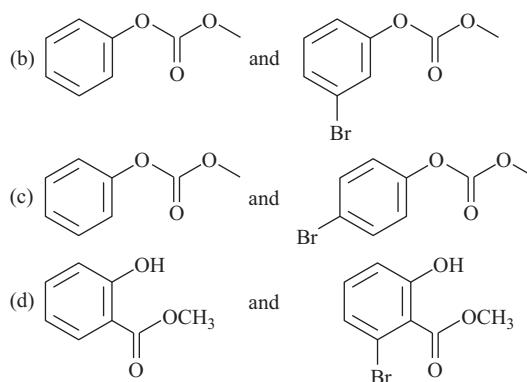
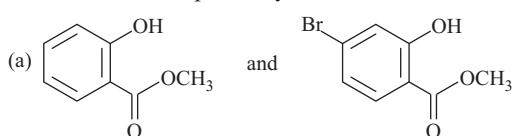
17. Phenol on treatment with  $\text{CO}_2$  in the presence of  $\text{NaOH}$  followed by acidification produces compound  $X$  as the major product.  $X$  on treatment with  $(\text{CH}_3\text{CO})_2\text{O}$  in the presence of catalytic amount of  $\text{H}_2\text{SO}_4$  produces:

(2018 Main)



18. Phenol reacts with methyl chloroformate in the presence of  $\text{NaOH}$  to form product  $A$ .  $A$  reacts with  $\text{Br}_2$  to form product  $B$ .  $A$  and  $B$  are respectively

(2018 Main)

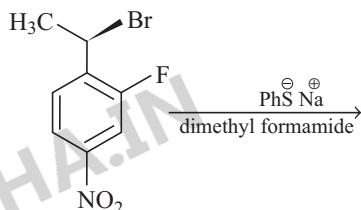


19. For the identification of  $\beta$ -naphthol using dye test, it is necessary to use

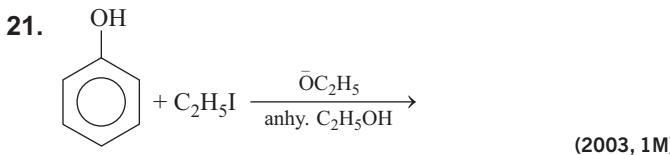
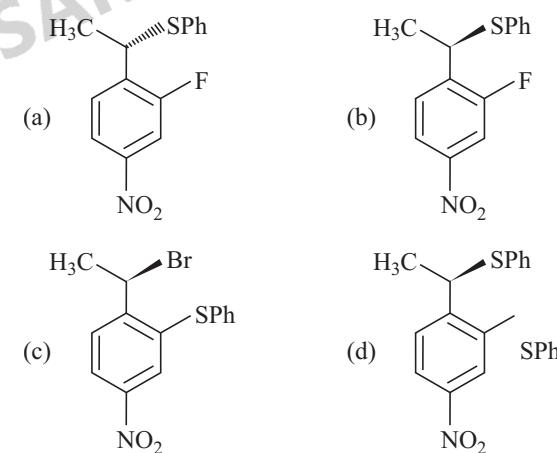
(2014 Adv.)

- (a) dichloromethane solution of  $\beta$ -naphthol
- (b) acidic solution of  $\beta$ -naphthol
- (c) neutral solution of  $\beta$ -naphthol
- (d) alkaline solution of  $\beta$ -naphthol

20. The major product of the following reaction is



(2008, 3M)



(2003, 1M)

- (a)  $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$
- (b)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
- (c)  $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$
- (d)  $\text{C}_6\text{H}_5\text{I}$

22. In the reaction of  $p$ -chlorotoluene with  $\text{KNH}_2$  in liq.  $\text{NH}_3$ , the major product is

(1997, 1M)

- (a)  $o$ -toluidine
- (b)  $m$ -toluidine
- (c)  $p$ -toluidine
- (d)  $p$ -chloroaniline

23. Phenol reacts with bromine in carbon disulphide at low temperature to give (1988, 1M)

(a) *m*-bromophenol      (b) *o*- and *p*-bromophenol  
 (c) *p*-bromophenol      (d) 2, 4, 6-tribromophenol

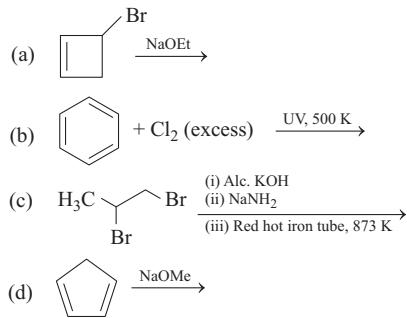
24. When phenol is treated with excess of bromine water, it gives (1984, 1M)

(a) *m*-bromophenol      (b) *o*- and *p*-bromophenol  
 (c) 2, 4-dibromophenol      (d) 2, 4, 6-tribromophenol

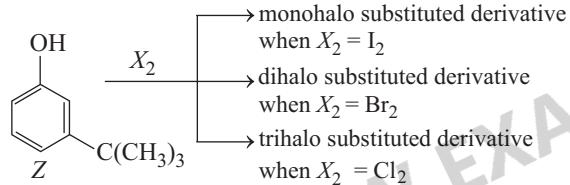
### Objective Questions II

(One or more than one correct option)

25. Choose the correct option(s) that give(s) an aromatic compound as the major product. (2019 Adv.)



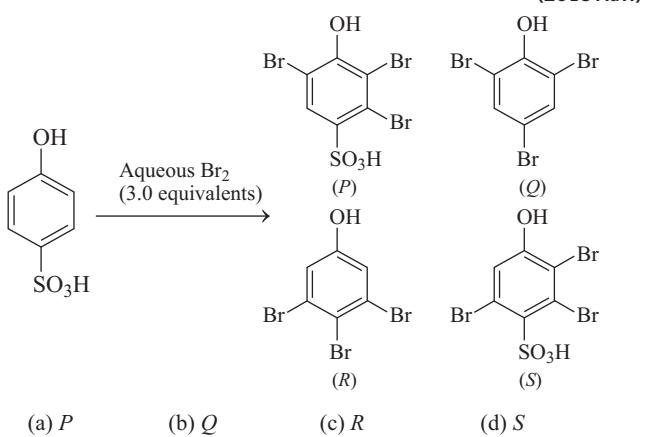
26. The reactivity of compound Z with different halogens under appropriate conditions is given below



The observed pattern of electrophilic substitution can be explained by

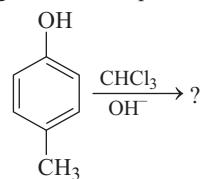
- (a) the steric effect on the halogen  
 (b) the steric effect of the *tert*-butyl group  
 (c) the electronic effect of the phenolic group  
 (d) the electronic effect of the *tert*-butyl group

27. The major product(s) of the following reaction is/are (2013 Adv.)

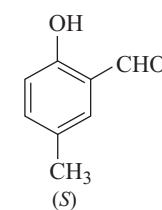
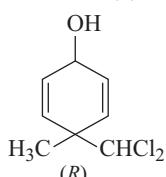
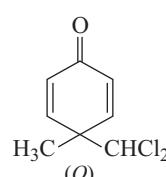
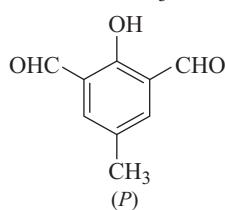


- (a) *P*      (b) *Q*      (c) *R*      (d) *S*

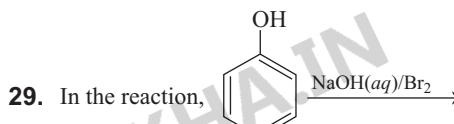
28. In the following reaction, the product (s) formed is/are



(2013 Adv.)

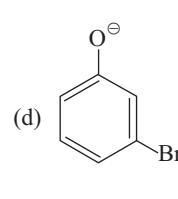
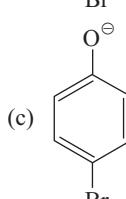
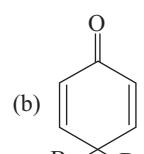
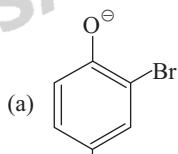


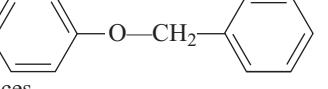
- (a) *P* (major)  
 (b) *Q* (minor)  
 (c) *R* (minor)  
 (d) *S* (major)

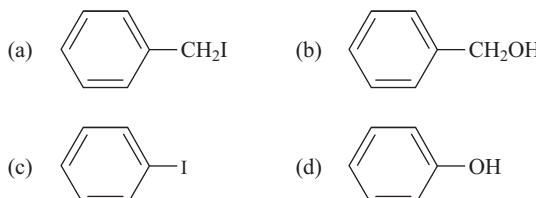


(2010)

the intermediate(s) is/are

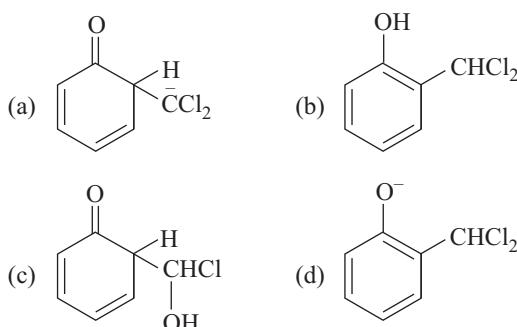


30. The ether  , when treated with HI produces (1999, 3M)



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31. When phenol is reacted with  $\text{CHCl}_3$  and  $\text{NaOH}$  followed by acidification, salicylaldehyde is formed. Which of the following species are involved in the above mentioned reaction as intermediates ? (1995, 2M)



32. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to (1990, 1M)
- the formation of less stable carbonium ion
  - resonance stabilisation
  - longer carbon halogen bond
  - $sp^2$ -hybridised carbon bonded to halogen

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct  
Statement II is the correct explanation of Statement I
- (b) Statement I is correct; Statement II is correct  
Statement II is not the correct explanation of Statement I
- (c) Statement I is correct; Statement II is incorrect
- (d) Statement I is incorrect; Statement II is correct
33. **Statement I** Bromobenzene, upon reaction with  $\text{Br}_2/\text{Fe}$  gives 1,4-dibromobenzene as the major product.

**Statement II** In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. (2008, 3M)

34. **Statement I** Phenol is more reactive than benzene towards electrophilic substitution reaction.

**Statement II** In the case of phenol, the intermediate carbocation is more resonance stabilised. (2000, M)

35. **Statement I** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

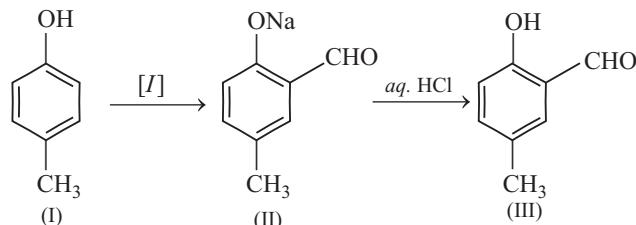
**Statement II** Cyanide ( $\text{CN}^-$ ) is a strong nucleophile. (1998, 2M)

36. **Statement I** Aryl halides undergo nucleophilic substitution with ease.

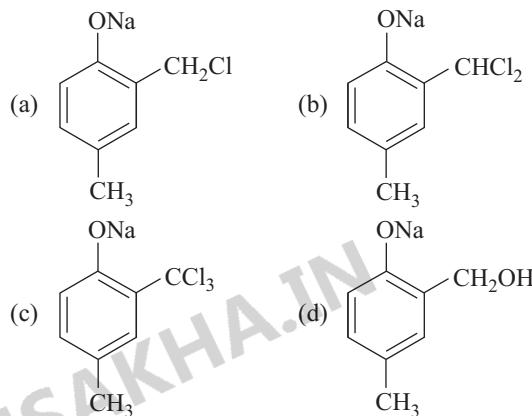
**Statement II** The carbon halogen bond in aryl halides has partial double bond character. (1991, 2M)

### Passage Based Problems

Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



37. The structure of the intermediate I is



38. The electrophile in this reaction is



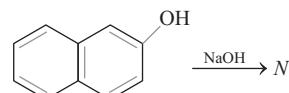
39. Which one of the following reagents is used in the above reaction ?



### Integer Answer Type Questions

40. An organic compound ( $\text{C}_8\text{H}_{10}\text{O}_2$ ) rotates plane-polarised light. It produces pink color with neutral  $\text{FeCl}_3$  solution. What is the total number of all the possible isomers for this compound? (2020 Adv.)

41. The number of resonance structures for N is (2015, Adv.)



### Fill in the Blanks

42. Amongst the three isomers of nitrophenol, the one that is least soluble in water is ..... (1992, 1M)

43. Phenol is acidic due to resonance stabilisation of its conjugate base, namely ..... (1990, 1M)

44. Formation of phenol from chlorobenzene is an example of ..... aromatic substitution. (1989, 1M)

45. The acidity of phenol is due to the ..... of its anion. (1984, 1M)

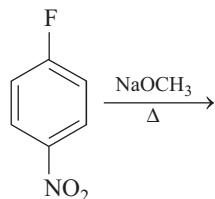
**Subjective Questions**

46. Carry out the following conversions.

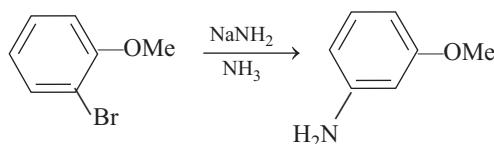
- (i) Phenol to aspirin
- (ii) Benzoic acid to *meta*-fluorobenzoic acid in not more than three steps. (2003)

47. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. (2001, 5M)

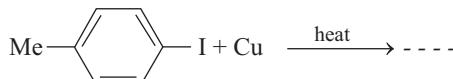
48. What would be the major product in the following reaction?



49. Explain briefly the formation of the products giving the structures of the intermediates.



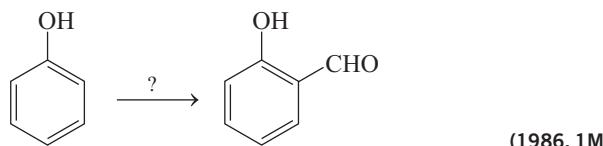
50. Complete the following, giving the structures of the principal organic products



51. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps)? (1996, 2M)

52. Explain the following in one or two sentences only : "Phenol is an acid, but it does not react with sodium bicarbonate." (1987, 1M)

53. Complete the following with appropriate structures :



54. A compound of molecular formula C<sub>7</sub>H<sub>8</sub>O is insoluble in water and dilute sodium bicarbonate but dissolve in dilute NaOH solution and gives a characteristic colour with FeCl<sub>3</sub>. On treatment with bromine water, it readily gives a precipitate of C<sub>7</sub>H<sub>5</sub>OBr<sub>3</sub>. Write down the structure of the compound. (1985, 2M)

55. Give reason in one or two sentences for the following : "*o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not." (1985, 1M)

**Answers**

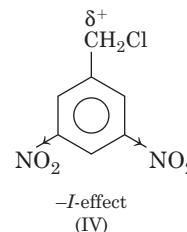
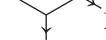
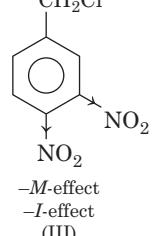
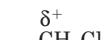
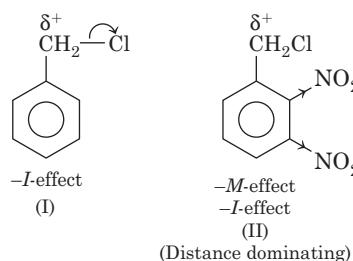
- |           |             |         |           |
|-----------|-------------|---------|-----------|
| 1. (a)    | 2. (d)      | 3. (a)  | 4. (b)    |
| 5. (c)    | 6. (b)      | 7. (c)  | 8. (a)    |
| 9. (c)    | 10. (c)     | 11. (c) | 12. (b)   |
| 13. (c)   | 14. (b)     | 15. (a) | 16. (d)   |
| 17. (a)   | 18. (c)     | 19. (d) | 20. (a)   |
| 21. (a)   | 22. (b)     | 23. (c) | 24. (d)   |
| 25. (c,d) | 26. (a,b,c) | 27. (b) | 28. (b,d) |

- |                     |                                  |                    |           |
|---------------------|----------------------------------|--------------------|-----------|
| 29. (b,c)           | 30. (a, d)                       | 31. (a,d)          | 32. (b,d) |
| 33. (c)             | 34. (a)                          | 35. (d)            | 36. (d)   |
| 37. (b)             | 38. (c)                          | 39. (c)            | 40. (6)   |
| 41. (9)             | 42. ( <i>ortho</i> -nitrophenol) |                    |           |
| 43. (phenoxide ion) | 44. (nucleophilic)               | 45.(phenoxide ion) |           |

**Hints & Solutions**

1. Rate of S<sub>N</sub>2 reaction  $\propto \frac{1}{\text{Stability of carbocation}}$

Stability of carbocation  $\propto \frac{1}{-I / -M}$  (effective group)

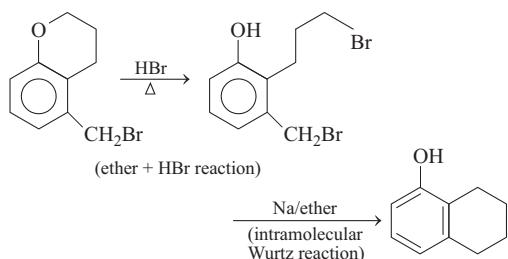


So, the decreasing order of reactivity of the given compounds toward S<sub>N</sub>2 reaction is

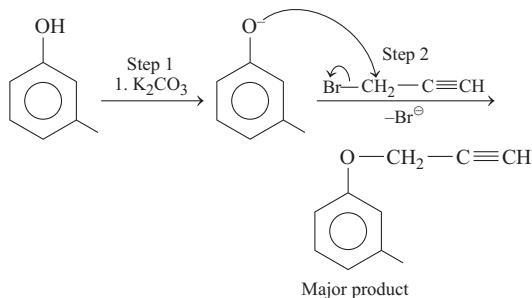
(II) > (III) > (IV) > (I)

## 464 Aryl Halides and Phenols

2. The given reaction can be completed as follows :



3. The major product when *m*-cresol reacts with propargyl bromide ( $\text{HC}\equiv\text{C}-\text{CH}_2\text{Br}$ ) in presence of  $\text{K}_2\text{CO}_3$  in acetone is given in the following reaction:

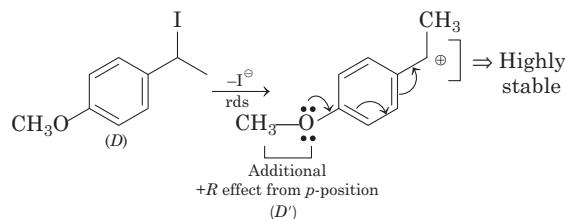
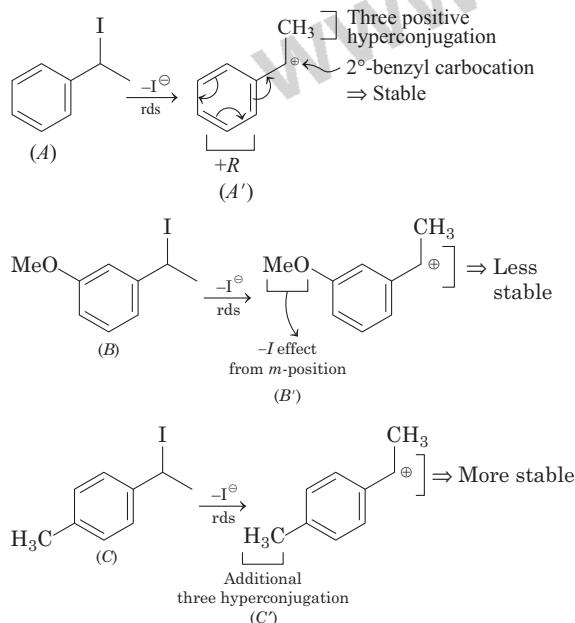


In **step 1**  $\text{K}_2\text{CO}_3$  act as a base and abstract H-atom from  $-\text{OH}$  group. This leads to the formation of substituted phenoxide ion (highly stable).

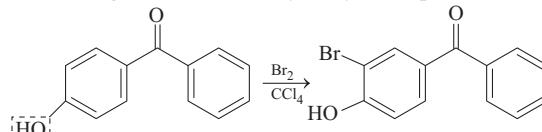
In **step 2** substituted phenoxide ion on reaction with  $\text{Br}-\text{CH}_2-\text{C}\equiv\text{CH}$  gives the required product.

4. More stable the carbocation intermediate, higher will be the rate of  $\text{S}_{\text{N}}1$  reaction.

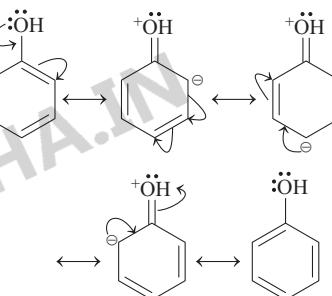
The reaction involving carbocation intermediate formation for the given compounds are as follows:



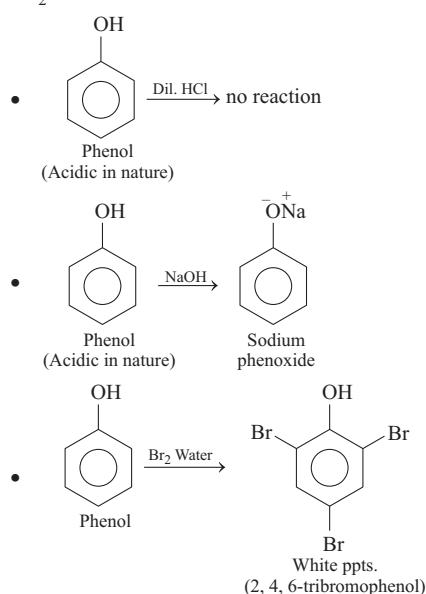
5. *p*-hydroxy benzophenone upon reaction with bromine in carbon tetrachloride gives 3-bromo-4-hydroxy benzophenone.



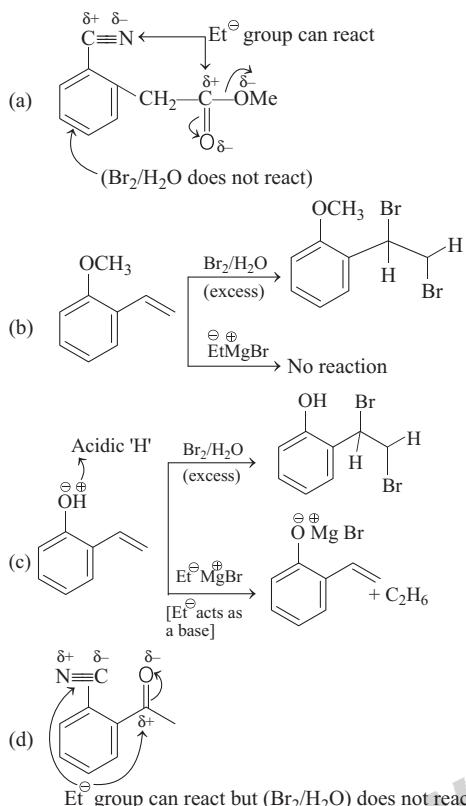
$-\text{OH}$  group attached on the benzene ring direct the incoming group at *ortho* and *para*-positions due to increase in electron density at *o* and *p*-positions.  $-\text{OH}$  group also exhibit  $-\text{I}$  group that reduces the electron density to some extent at *o* and *p*-positions. But overall electron density increases at these positions of the ring due to resonance. Hence, attack of  $-\text{Br}$  occur at *ortho* position. Resonating structures are as follows:



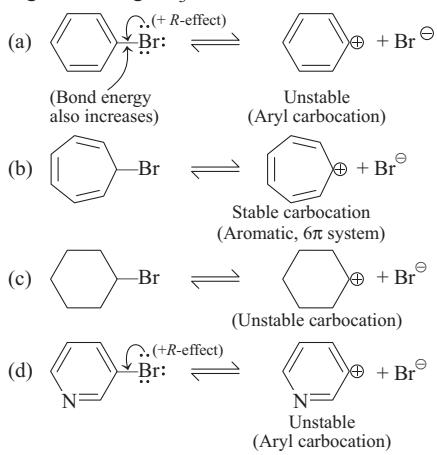
6. Phenol ( $\text{ArOH}$ ) is insoluble in dil.  $\text{HCl}$  and readily soluble in  $\text{NaOH}$  solution. It reacts with  $\text{Br}_2/\text{water}$  to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of  $\text{Br}_2$  water. Reactions involved are as follows :

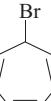


7. Ethyl magnesium bromide is a Grignard reagent (GR), it constitutes  $C_2H_5^+ [C_2H_5^- MgBr]$  in ether/aprotic medium] which can act as nucleophile as well as strong base. Bromine water ( $Br_2/H_2O$ , red) gets decolourised with phenol derivatives (option, c), anisole derivatives (option, b) etc., as  $>C=C<$  is present outside the ring (aliphatic, not aromatic).

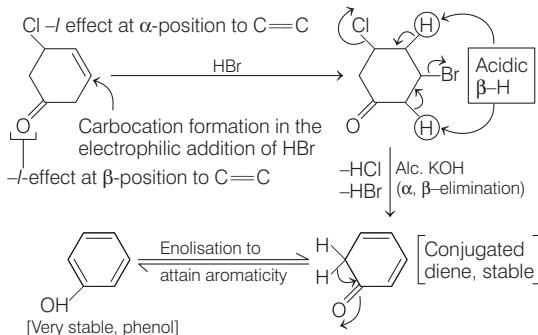


8. Only ionic halides ( $X^-$ ) give precipitate of  $\text{AgX}$  with  $\text{AgNO}_3$  solution. So, an organic bromide able to produce  $R^\oplus$  (stable carbocation) and  $\text{Br}^-$  in aqueous solution will give precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$ .

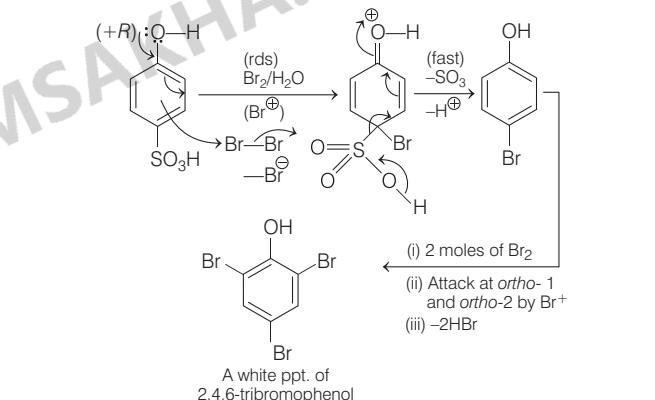


So, only  produces a precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$  solution.

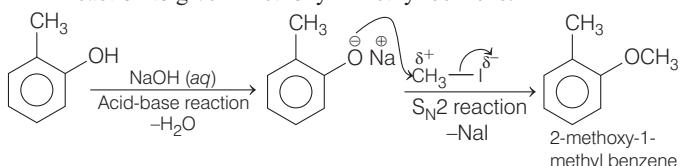
9. In presence of  $\text{HBr}$ , reactant containing  $>C=C<$  undergoes electrophilic addition reaction and give substituted alkyl halide. On further reaction with alc.  $\text{KOH}$ ,  $\alpha,\beta$ -elimination takes place that give corresponding diene. The diene undergoes enolisation to give stable product (phenol).



10. In  ipso-substitution takes place with the carbon bearing  $-\text{SO}_3\text{H}$  group. After the attack of the electrophilic  $\text{Br}^+$  in the rate determining step (rds) of the  $\text{ArS}_{\text{E}2}$  pathway desulphonation ( $-\text{SO}_3$ ) takes place with a faster rate.



11. Substituted phenols react with *aq.*  $\text{NaOH}$  to form sodium phenoxides which on reaction with  $\text{CH}_3\text{I}$  undergoes  $\text{S}_{\text{N}}2$  reaction to give 2-methoxy-1-methyl benzene.



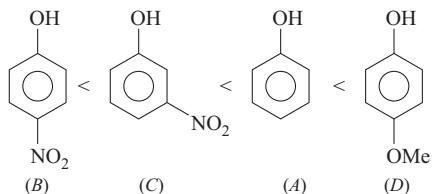
12. Acidic strength is inversely proportional to  $pK_a$  value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol. Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol. Electron withdrawing groups ( $-\text{NO}_2$ ) increases the acidic strength of phenol whereas electron donating group ( $-\text{OCH}_3$ ) decreases the acidic strength of phenol. In case of  $-\text{NO}_2$  group attached to

## 466 Aryl Halides and Phenols

phenol, the dispersal of negative charge is more pronounced at *o*- and *p*-position than at *m*-position.

Thus, order of acidic strength of nitrophenol is:

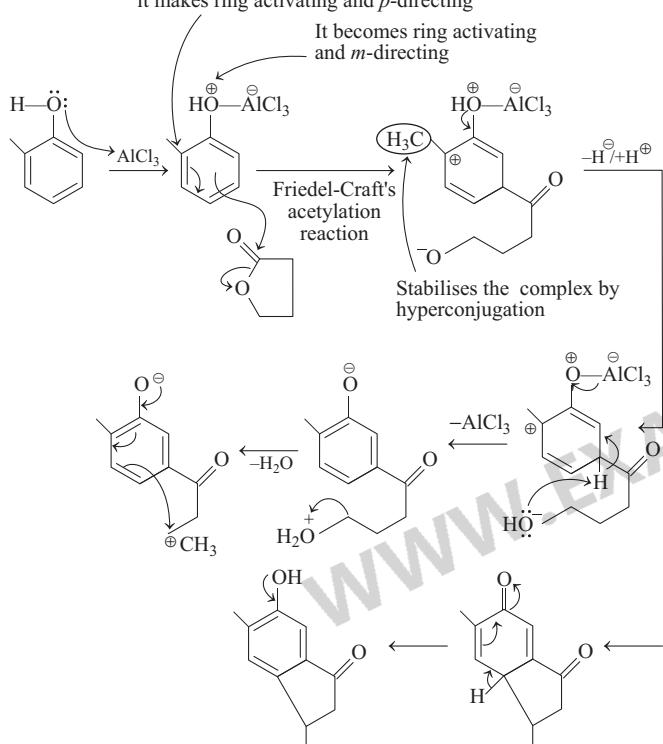
*p*-nitrophenol > *o*-nitrophenol and the correct order of the  $pK_a$  values of given option is



13. It is an aromatic electrophilic substitution reaction ( $\text{ArS}_{\text{E}}2$ ).

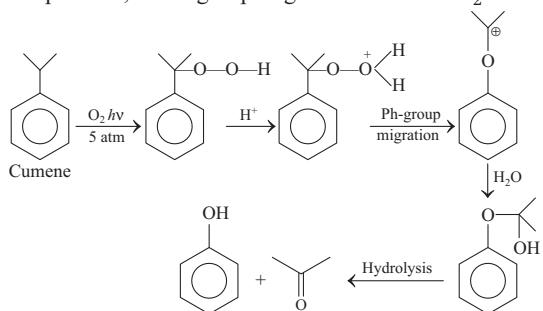
The reaction follows  $\text{Ar S}_{\text{E}}2$  (Aromatic electrophilic substitution pathway) as shown below :

it makes ring activating and *p*-directing



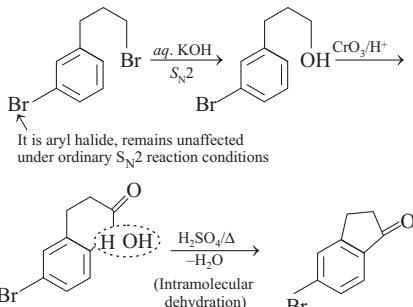
14. The given process is cumene process (Hock process) to synthesise phenol and acetone industrially.

In Hock process, Ph — group migrate and release  $\text{H}_2\text{O}$ .

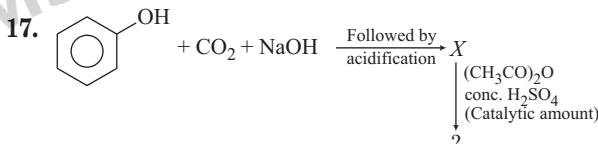
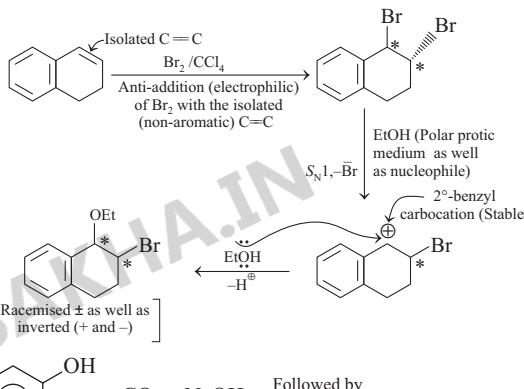


15. **Key Idea** The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is that, the Br group attached directly to aromatic ring will not undergo substitution in step 1.

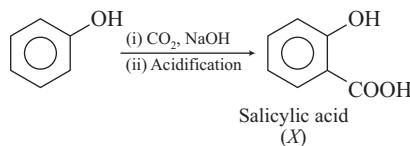
The road map of the given reaction is as follows:



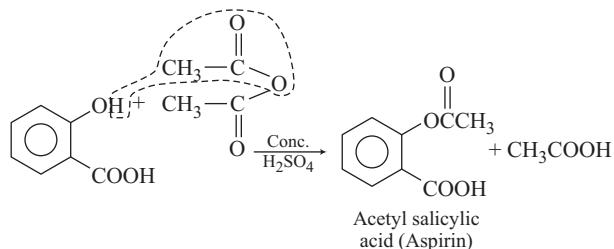
16. The road map of the given reaction is :



The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as

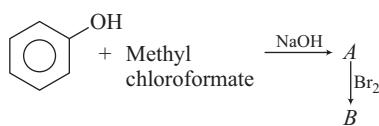


The salicylic acid with acetic anhydride [ $(\text{CH}_3\text{CO})_2\text{O}$ ] in the presence of catalytic amount of conc.  $\text{H}_2\text{SO}_4$  undergoes acylation to produce aspirin as



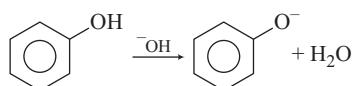
Aspirin is a non-narcotic analgesic (Pain killer).

18. Given,

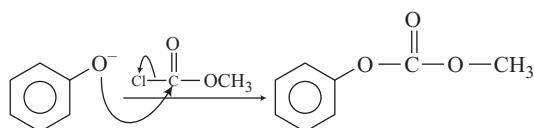


In the above road map, first reaction appears as acid base reaction followed by  $S_NAE$  (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

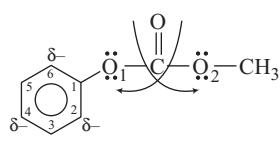
(i) Acid base reaction



(ii)  $S_NAE$

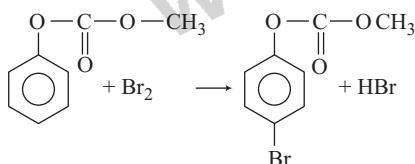


In the product of  $S_NAE$  the attached group is *ortho* and *para*-directing due to following cross conjugation



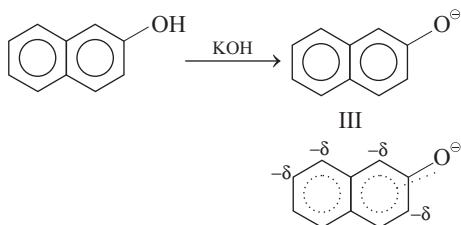
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group  $\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$  is bulky.

Hence, on further bromination of  $S_NAE$  product *para* bromo derivative will be the preferred product i.e.

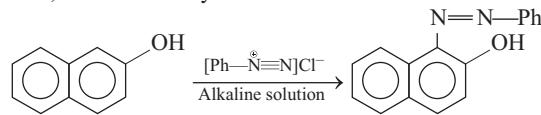


19. PLAN This problem can be solved by using the concept of synthesis of dye using electrophilic aromatic substitution reaction.

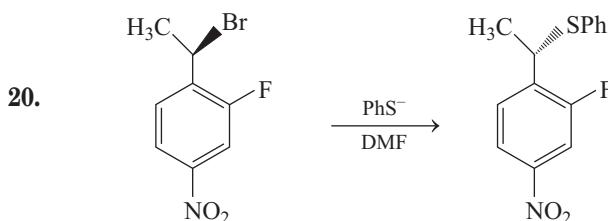
In basic (alkaline) solution naphthol exists as naphthoxide ion which is a strong *o*, *p*-directing group.



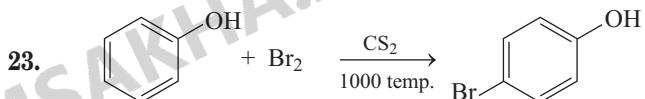
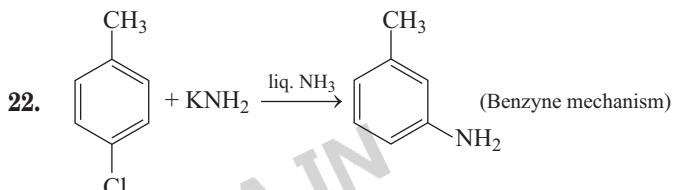
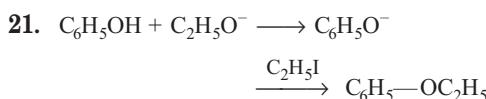
Thus, formation of dye can be shown as



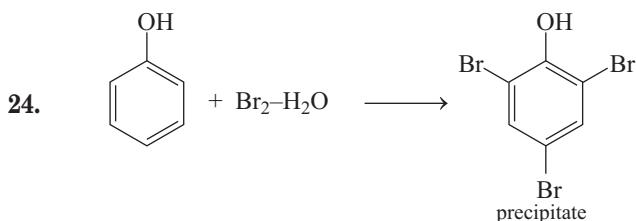
Thus, (d) is the correct choice.



$S_N2$  reaction bring about inversion of configuration.

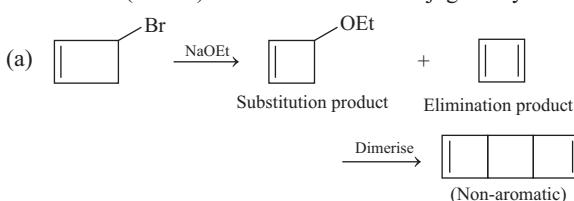


In carbon disulphide, no phenoxide ion exist, therefore only monobromination takes place.



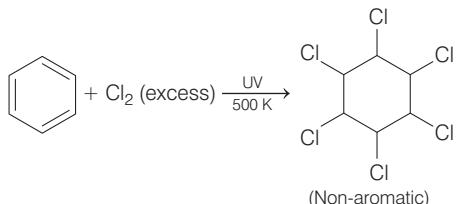
It is a reversible reaction, but equilibrium is significantly shifted to left, also indicated as  $\text{Br}_2(aq)$ .

25. Key Idea An aromatic compound must be cyclic and planar. It must follow  $(4n+2)e^-$  rule and have the conjugated system in it.



## 468 Aryl Halides and Phenols

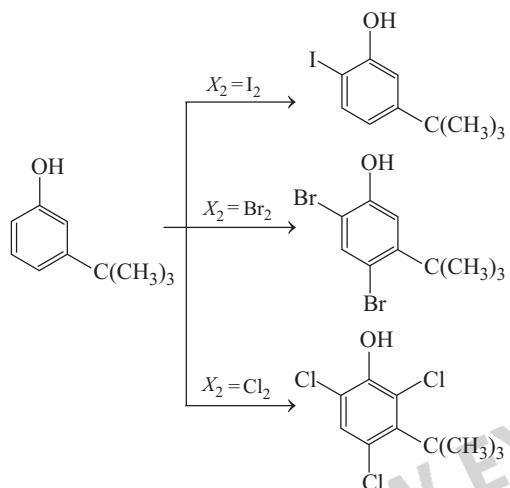
- (b) Benzene reacts with  $\text{Cl}_2$  (excess) in presence of UV light and 500 K of temperature to form benzene hexachloride (non-aromatic).



- 26. PLAN** This problem includes concept of effect of steric and electronic effect on reactivity of organic compounds.

Steric effect of halogens are as follows  $\text{Cl}_2 < \text{Br}_2 < \text{I}_2$

Electronic effect of phenolic group directs the approaching electrophile towards *ortho* and *para* positions. Tertiary butyl group has large size so it causes steric effect around aromatic nucleus. On the basis of above factors the products of the given reactions are as follows:



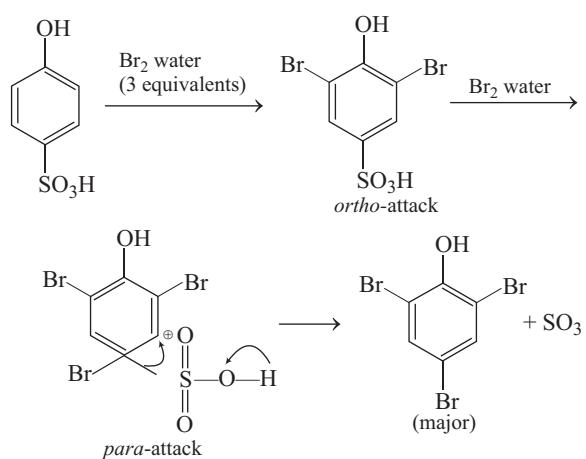
Hence, orientation in electrophilic substitution reaction is decided by

- (a) The steric effect of the halogen
- (b) The steric effect of the *tert*-butyl group
- (c) The electronic effect of the phenolic group

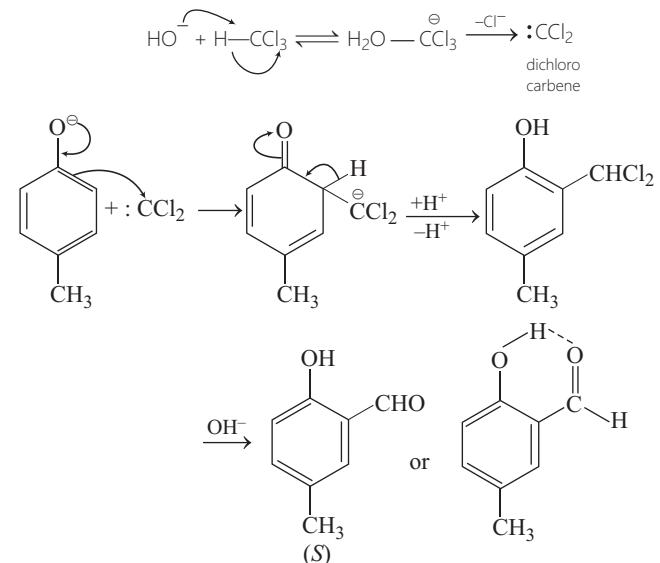
So, (a), (b) and (c) are correct choices.

- 27. PLAN** —OH group is activating group and is *o*- and *p*-directing.

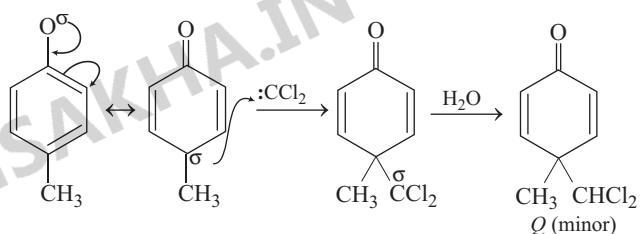
Also, —SO<sub>3</sub>H is a better leaving group and is knocked out by Br<sup>-</sup>.



- 28. PLAN** Phenolic compounds in alkaline solution react with chloroform ( $\text{CHCl}_3$ ) at a temperature lower than that of  $\text{CHCl}_3$  to form *ortho*-isomer as the major product (due to greater stability resulting from intramolecular hydrogen bonding).

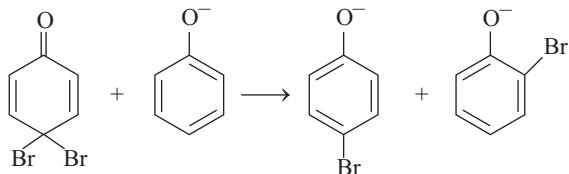
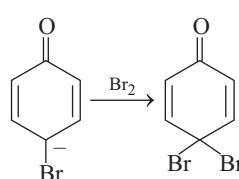
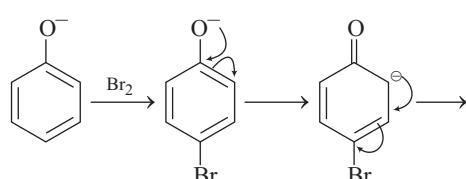


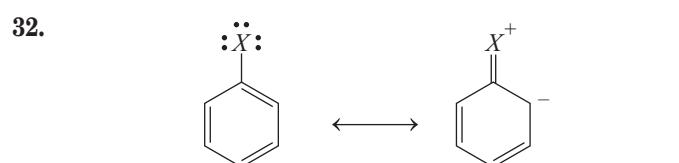
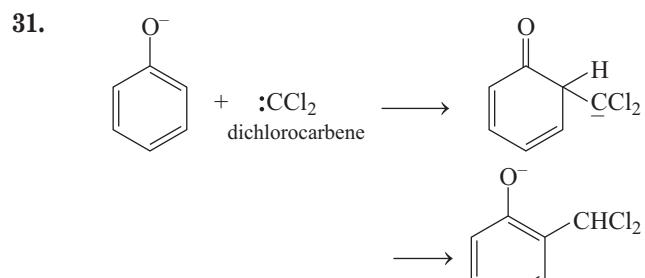
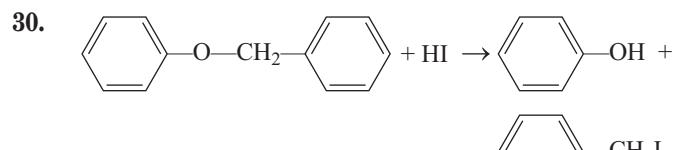
Major as stable due to intramolecular H-bonding.



Thus, (b) and (d) are correct.

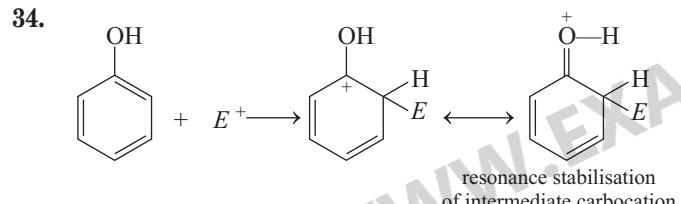
- 29.** —OH in phenol is *ortho/para* directing group.





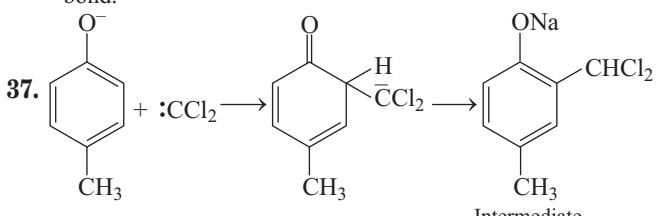
Above resonance makes  $\text{X}^-$  a poor leaving group. Also, the carbon bearing  $\text{X}$  is  $sp^2$ -hybridised.

33. Bromo group is deactivating due to dominance of inductive effect over resonance effect. However, orientation is determined by mesomeric effect of  $-\text{Br}$ .

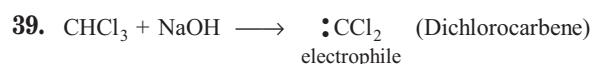


35. Statement I is incorrect, aryl halides do not undergo nucleophilic substitution reaction with ease. Cyanide ion ( $\text{CN}^-$ ) is a strong nucleophile.

36. Statement I is incorrect, aryl halides do not usually undergo nucleophilic substitution with ease. Statement II is correct, resonance introduces partial double bond character to  $\text{C}-\text{X}$  bond.



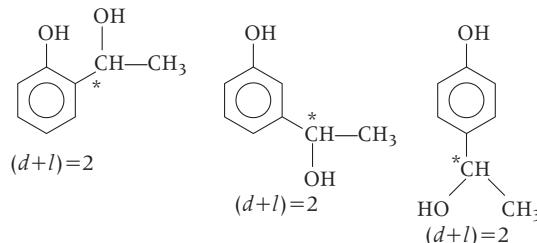
38. Dichlorocarbene is the electrophile as shown above.



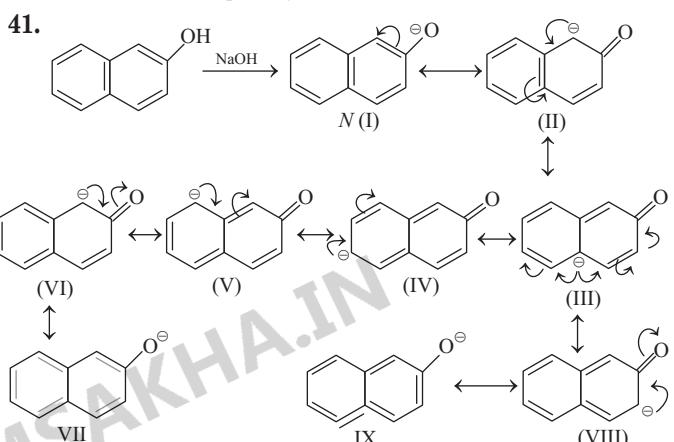
40. Phenolic ( $-\text{OH}$ ) group gives positive test with neutral  $\text{FeCl}_3$  solution, means organic compound ( $\text{C}_8\text{H}_{10}\text{O}_2$ ) is a phenol derivative.

Compound ( $\text{C}_8\text{H}_{10}\text{O}_2$ ) also rotates plane polarised light means compound is an optically active and chiral carbon atom is present.

So, the possible structures which are optically active and have phenolic group are as followed:

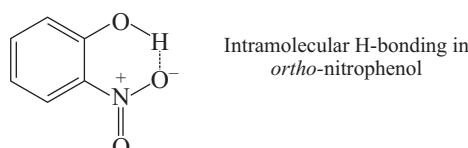


Therefore, total optically active isomers will be 6.



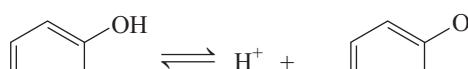
All the above shown nine resonance structures are different.

42. *Ortho-nitrophenol* : Due to intramolecular H-bonding.

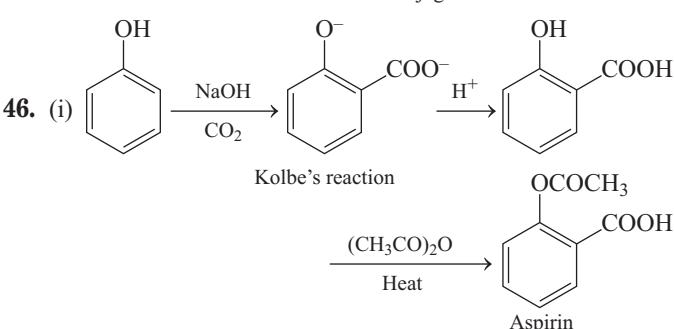


43. Phenoxide ion

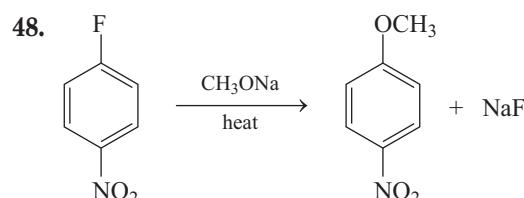
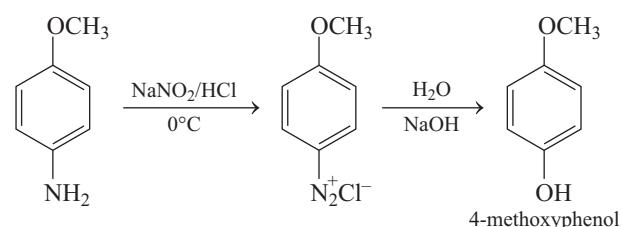
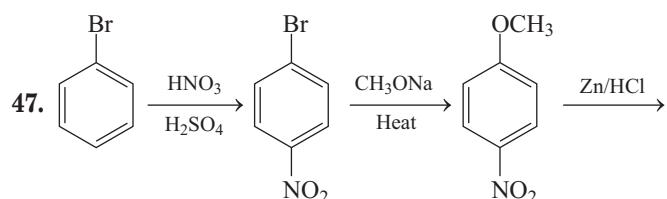
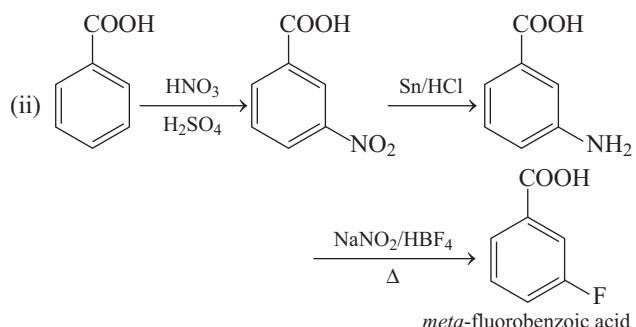
45. Phenoxide ion :



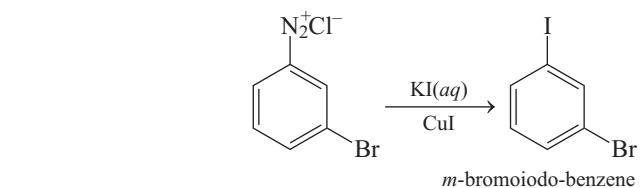
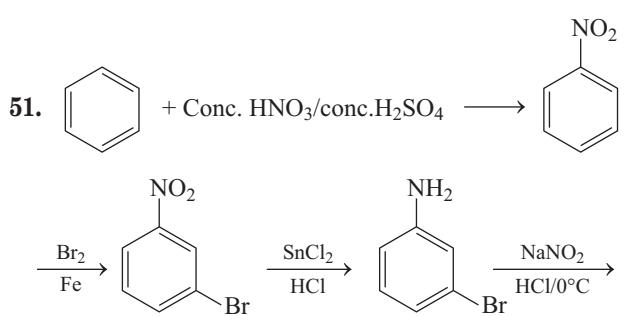
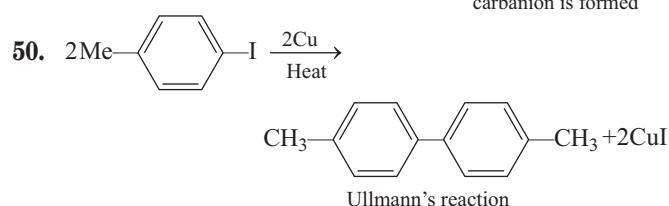
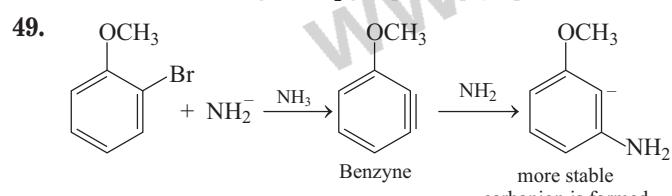
Resonance stabilised conjugate base



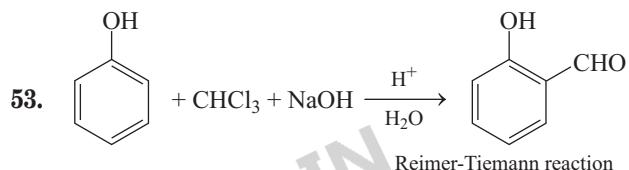
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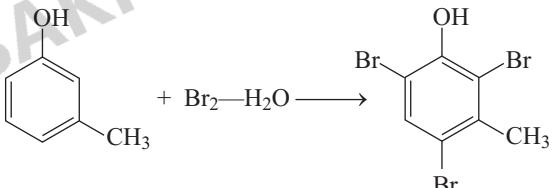
Nucleophilic aromatic substitution occur which is assisted by electron withdrawing  $-\text{NO}_2$  group from para position.



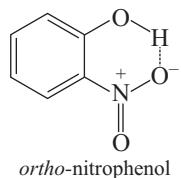
52. Phenol is weaker acid than carbonic acid.



54. The compound must contain a hydroxy group on the ring with all three *ortho/para* positions vacant :



55. Intramolecular H-bonding in *ortho*-nitrophenol lowers its boiling point. No such intramolecular H-bonding is possible with *p*-nitrophenol and rather it is associated together by intermolecular H-bonding which increases the boiling point.



# 31

## Aromatic Aldehydes, Ketones and Acids

### Objective Questions I (Only one correct option)

1. The correct electronic configuration and spin-only magnetic moment (BM) of  $\text{Gd}^{3+}$  ( $Z = 64$ ), respectively, are

(2020 Main, 5 Sep I)  
 (a)  $[\text{Xe}] 4f^7$  and 7.9      (b)  $[\text{Xe}] 5f^7$  and 7.9  
 (c)  $[\text{Xe}] 5f^7$  and 8.9      (d)  $[\text{Xe}] 4f^7$  and 8.9

2. The correct match between Item-I (starting material) and Item-II (reagent) for the preparation of benzaldehyde is

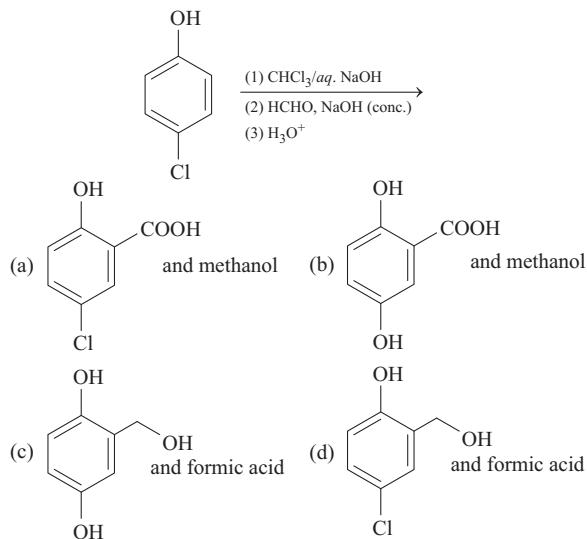
(2020 Main, 6 Sep II)

| Item - I             | Item - II                                                     |
|----------------------|---------------------------------------------------------------|
| I Benzene            | (P) $\text{HCl}$ and $\text{SnCl}_2$ , $\text{H}_3\text{O}^+$ |
| II Benzonitrile      | (Q) $\text{H}_2$ , $\text{Pd-BaSO}_4$ , S and quinoline       |
| III Benzoyl chloride | (R) $\text{CO}$ , $\text{HCl}$ and $\text{AlCl}_3$            |

- (a) (I) - (Q), (II) - (R) and (III) - (P)  
 (b) (I) - (P), (II) - (Q) and (III) - (R)  
 (c) (I) - (R), (II) - (P) and (III) - (Q)  
 (d) (I) - (R), (II) - (Q) and (III) - (P)

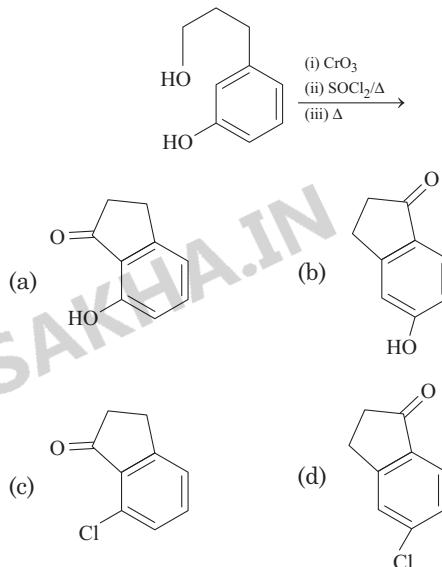
3. The major products of the following reaction are

(2019 Main, 12 April I)



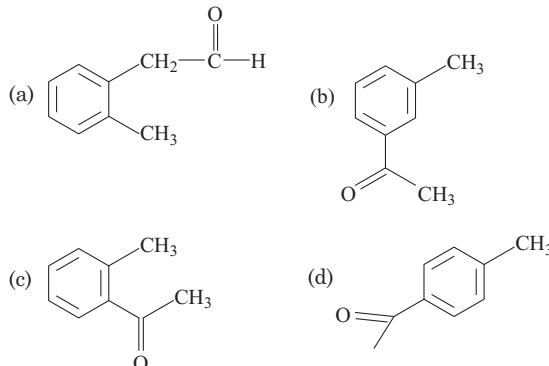
4. The major product of the following reaction is

(2019 Main, 12 April I)



5. Compound A ( $\text{C}_9\text{H}_{10}\text{O}$ ) shows positive iodoform test. Oxidation of A with  $\text{KMnO}_4/\text{KOH}$  gives acid B ( $\text{C}_8\text{H}_6\text{O}_4$ ). Anhydride of B is used for the preparation of phenolphthalein. Compound A is

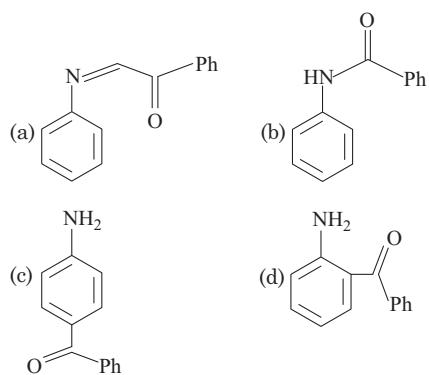
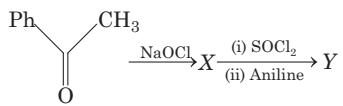
(2019 Main, 10 April II)



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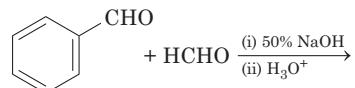
6. The major product  $Y$  in the following reaction is

(2019 Main, 10 April II)



7. Major products of the following reaction are

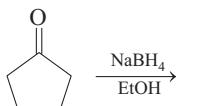
(2019 Main, 10 April I)



- (a)  $\text{CH}_3\text{OH}$  and  $\text{HCO}_2\text{H}$   
 (b)  $\text{CH}_3\text{OH}$  and   
 (c)  $\text{HCOOH}$  and   
 (d) and

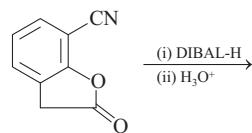
8. The major product of the following reaction is

(2019 Main, 12 Jan II)



- (a)   
 (b)   
 (c)   
 (d)

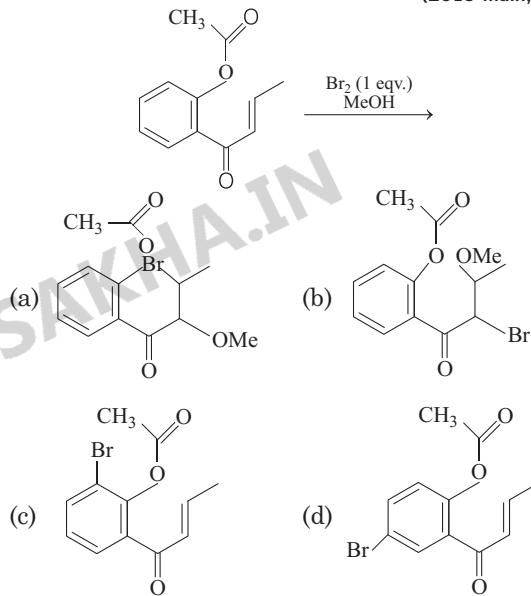
9. The major product of the following reaction is



- (a)   
 (b)   
 (c)   
 (d)

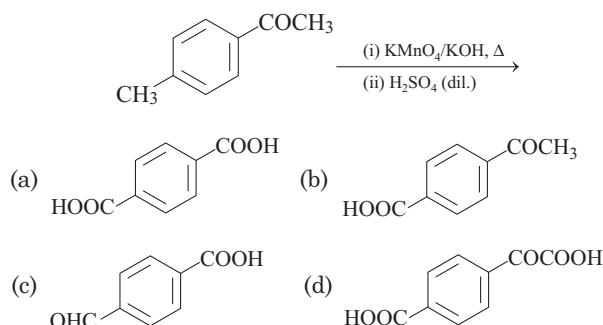
10. The major product obtained in the following conversion is

(2019 Main, 11 Jan II)

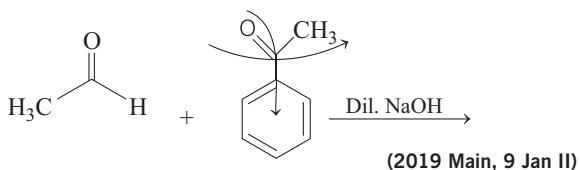


11. The major product of the following reaction is

(2019 Main, 11 Jan I)

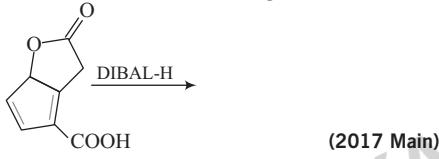


12. The major product formed in the following reaction is



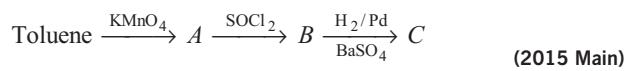
- (a)
- (b)
- (c)
- (d)

13. The major product obtained in the following reaction is



- (a)
- (b)
- (c)
- (d)

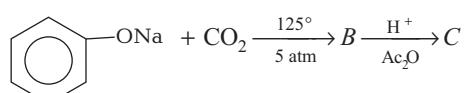
14. In the following sequence of reaction,



The product *C* is

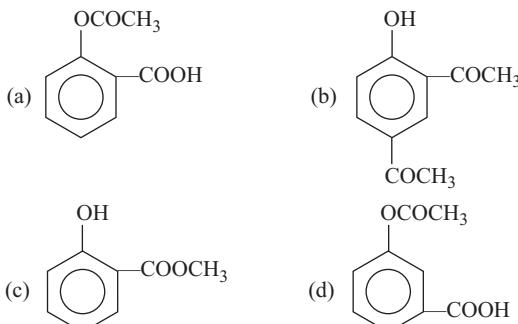
- (a)  $\text{C}_6\text{H}_5\text{COOH}$
- (b)  $\text{C}_6\text{H}_5\text{CH}_3$
- (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- (d)  $\text{C}_6\text{H}_5\text{CHO}$

15. Sodium phenoxide when heated with  $\text{CO}_2$  under pressure at  $125^\circ\text{C}$  yields a product which on acetylation produces *C*.

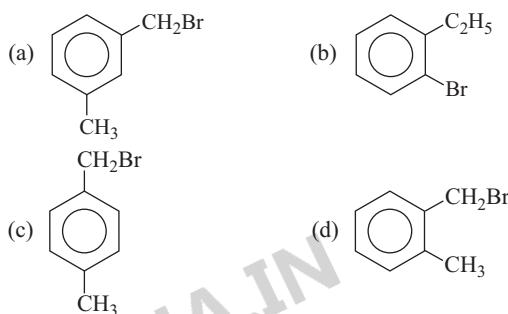


The major product *C* would be

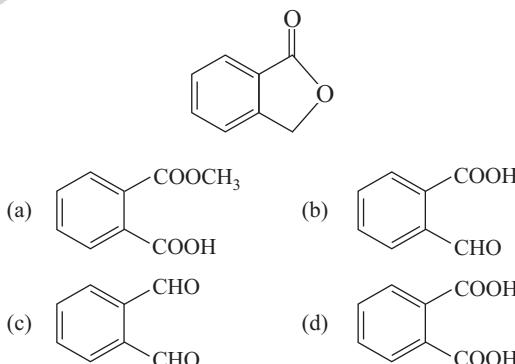
(2014 Main)



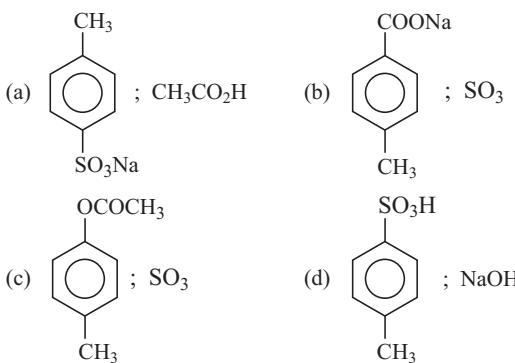
16. Compound (*A*),  $\text{C}_8\text{H}_9\text{Br}$  gives a white precipitate when warmed with alcoholic  $\text{AgNO}_3$ . Oxidation of (*A*) gives an acid (*B*),  $\text{C}_8\text{H}_6\text{O}_4$ . (*B*) easily forms anhydride on heating. Identify the compound (*A*). (2013 Main)



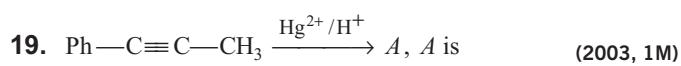
17. Which of the following reactants on reaction with conc.  $\text{NaOH}$  followed by acidification gives following lactone as the main product ? (2006, 5M)



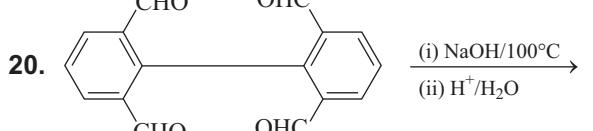
18. 4-methyl benzene sulphonic acid reacts with sodium acetate to give (2005, 1M)



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- (a) (b)   
 (c) (d)



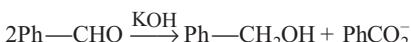
Major product (2003, 1M)

- (a)   
 (b)   
 (c)   
 (d)

21. In Cannizzaro's reaction, the intermediate which is the best hydride donor is (1997)

- (a)   
 (b)   
 (c)   
 (d)

22. In the Cannizzaro's reaction given below :



The slowest step is

(1996, 1M)

- (a) the attack of  $-\text{OH}$  at the carbonyl group  
 (b) the transfer of hydride to the carbonyl group  
 (c) the abstraction of proton from the carboxylic acid  
 (d) the deprotonation of  $\text{Ph}-\text{CH}_2\text{OH}$

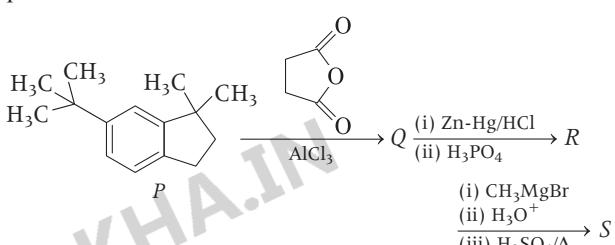
23. *m*-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives (1991, 1M)

- (a) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol  
 (b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol  
 (c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol  
 (d) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde

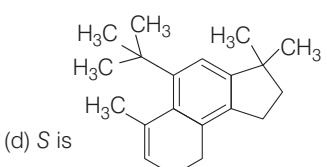
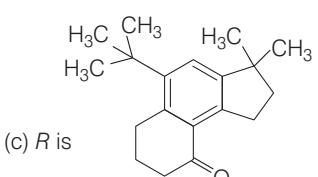
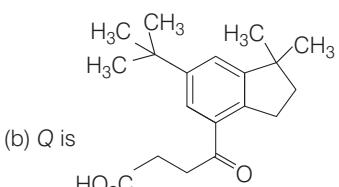
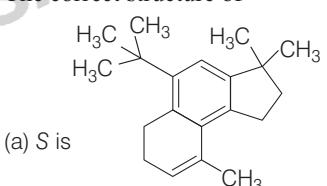
### Objective Questions II

(One or more than one correct option)

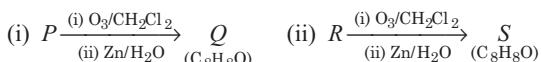
24. In the reaction scheme shown below *Q*, *R* and *S* are the major products. (2020 Adv.)



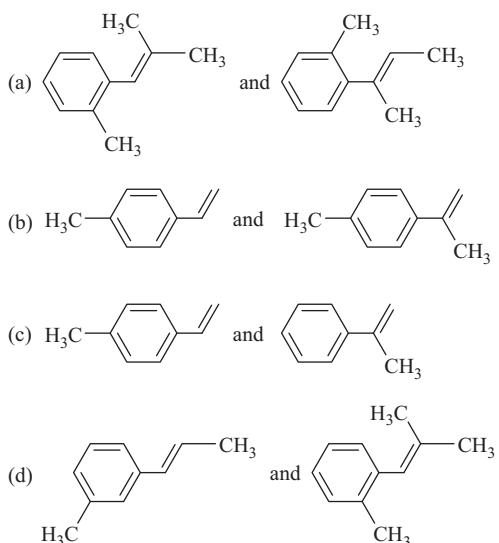
The correct structure of



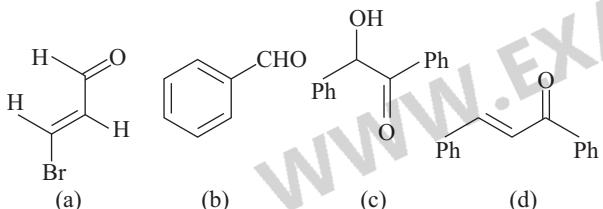
- 25.** Compound *P* and *R* upon ozonolysis produce *Q* and *S*, respectively. The molecular formula of *Q* and *S* is  $C_8H_8O$ . *Q* undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction. **(2017 Adv.)**



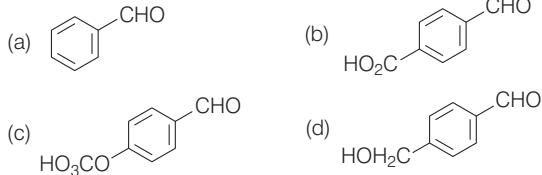
The option(s) with suitable combination of *P* and *R*, respectively, is(are)



- 26.** Positive Tollen's test is observed for



- 27.** The aldehydes which will not form Grignard product with one equivalent Grignard reagents are **(2019 Main 12 Jan II)**

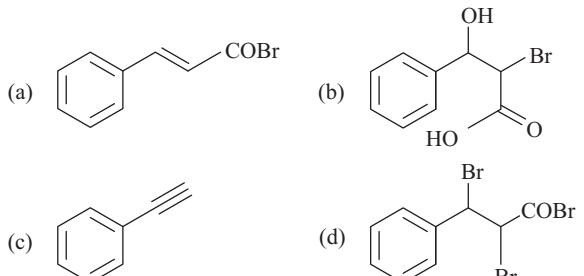


### Passage Based Questions

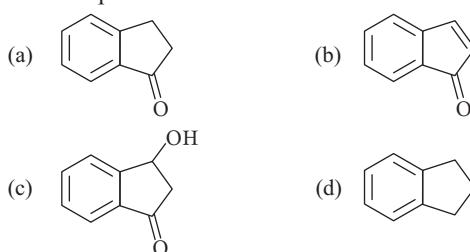
#### Passage 1

Treatment of benzene with  $CO/HCl$  in the presence of anhydrous  $AlCl_3/CuCl$  followed by reaction with  $Ac_2O/NaOAc$  gives compound *X* as the major product. Compound *X* upon reaction with  $Br_2/Na_2CO_3$  followed by heating at 473 K with moist KOH furnishes *Y* as the major product. Reaction of *X* with  $H_2/Pd-C$ , followed by  $H_3PO_4$  treatment gives *Z* as the major product.

- 28.** The compound *Y* is **(2018 Adv.)**

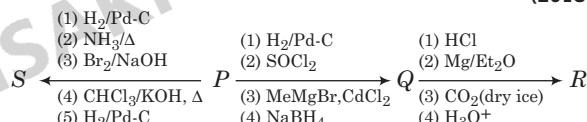


- 29.** The compound *Z* is

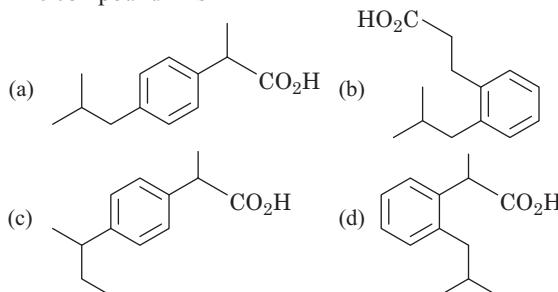


### Passage 2

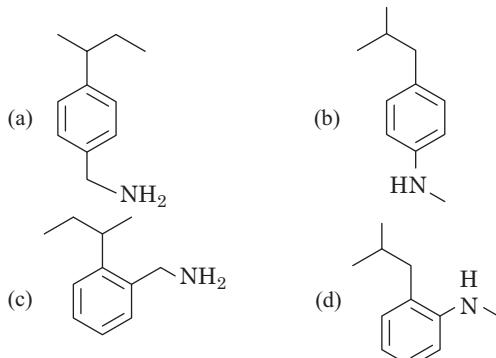
An organic acid *P* ( $C_{11}H_{12}O_2$ ) can easily be oxidised to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, *P* gives an aliphatic ketone as one of the products. *P* undergoes the following reaction sequences to furnish *R* via *Q*. The compound *P* also undergoes another set of reactions to produce *S*. **(2018 Adv.)**



- 30.** The compound *R* is



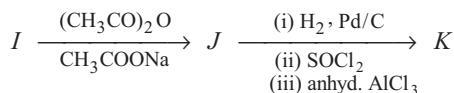
- 31.** The compound *S* is



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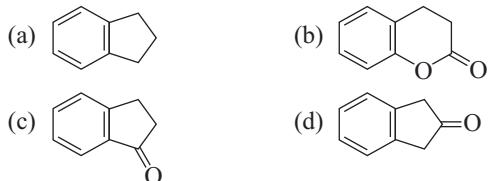
### Passage 3

In the following reactions sequence, the compound *J* is an intermediate.

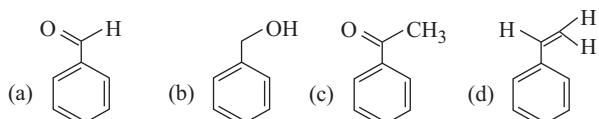


*J* ( $\text{C}_9\text{H}_8\text{O}_2$ ) gives effervescence on treatment with  $\text{NaHCO}_3$  and positive Baeyer's test. (2012)

32. The compound *K*, is



33. The compound *I*, is



### Fill in the Blank

34. The structure of the intermediate product formed by the oxidation of toluene with  $\text{CrO}_3$  and acetic anhydride, whose hydrolysis gives benzaldehyde is ..... (1992, 2M)

### True/False

35. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982, 1M)

### Subjective Questions

36. Five isomeric *para*-disubstituted aromatic compounds *A* to *E* with molecular formula  $\text{C}_8\text{H}_8\text{O}_2$  were given for identification. Based on the following observations, give structures of the compounds : (2002, Main, 5M)

- (i) Both *A* and *B* form a silver mirror with Tollen's reagent; also, *B* gives a positive test with  $\text{FeCl}_3$  solution.
- (ii) *C* gives positive iodoform test .
- (iii) *D* is readily extracted in aqueous  $\text{NaHCO}_3$  solution.
- (iv) *E* on acid hydrolysis gives 1, 4-dihydroxy benzene.

37. An organic compound *A*,  $\text{C}_8\text{H}_4\text{O}_3$ , in dry benzene in the presence of anhydrous  $\text{AlCl}_3$  gives compound *B*. The compound *B* on treatment with  $\text{PCl}_5$ , followed by reaction with  $\text{H}_2/\text{Pd}/\text{BaSO}_4$  gives compound *C*, which on reaction

with hydrazine gives a cyclised compound *D* ( $\text{C}_{14}\text{H}_{10}\text{N}_2$ ). Identify *A*, *B*, *C* and *D*. Explain the formation of *D* from *C*. (2000, 5M)

38. Explain, why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid? (1999, 2M)

### Match the Columns

Answer Q. 39, Q. 40 and Q. 41 by appropriately matching the information given in the three columns of the following table.

Column 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively. (2017 Adv.)

| Column 1           | Column 2                                                        | Column 3          |
|--------------------|-----------------------------------------------------------------|-------------------|
| (I) Toluene        | (i) $\text{NaOH}/\text{Br}_2$                                   | (P) Condensation  |
| (II) Acetophenone  | (ii) $\text{Br}_2/\text{h}\nu$                                  | (Q) Carboxylation |
| (III) Benzaldehyde | (iii) $(\text{CH}_3\text{CO})_2\text{O}/\text{CH}_3\text{COOK}$ | (R) Substitution  |
| (IV) Phenol        | (iv) $\text{NaOH}/\text{CO}_2$                                  | (S) Haloform      |

39. The only **CORRECT** combination in which the reaction proceeds through radical mechanism is

- (a) (IV) (i) (Q)
- (b) (III) (ii) (P)
- (c) (II) (iii) (R)
- (d) (I) (ii) (R)

40. For the synthesis of benzoic acid, the only **CORRECT** combination is

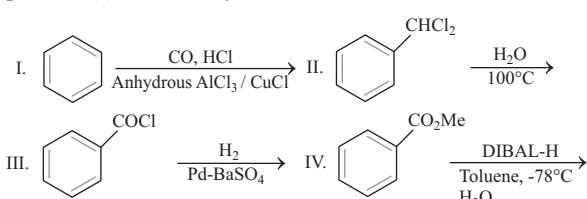
- (a) (II) (i) (S)
- (b) (I) (iv) (Q)
- (c) (IV) (ii) (P)
- (d) (III) (iv) (R)

41. The only **CORRECT** combination that gives two different carboxylic acids is

- (a) (IV) (iii) (Q)
- (b) (II) (iv) (R)
- (c) (I) (i) (S)
- (d) (III) (iii) (P)

### Integer Answer Type Question

42. Among the following the number of reaction(s) that produce(s) benzaldehyde is (2015 Adv.)



### Answers

- |         |         |         |           |
|---------|---------|---------|-----------|
| 1. (a)  | 2. (c)  | 3. (d)  | 4. (b)    |
| 5. (c)  | 6. (b)  | 7. (c)  | 8. (a)    |
| 9. (d)  | 10. (b) | 11. (a) | 12. (c)   |
| 13. (a) | 14. (d) | 15. (a) | 16. (d)   |
| 17. (c) | 18. (a) | 19. (a) | 20. (b)   |
| 21. (d) | 22. (b) | 23. (a) | 24. (b,d) |

- |           |                                                    |           |         |
|-----------|----------------------------------------------------|-----------|---------|
| 25. (b,c) | 26. (a,b,c)                                        | 27. (b,d) | 28. (c) |
| 29. (a)   | 30. (a)                                            | 31. (b)   | 32. (c) |
| 33. (a)   | 34. $\text{C}_6\text{H}_5-\text{CH}(\text{OAc})_2$ | 35. False |         |
| 39. (a)   | 40. (d)                                            | 41. (b)   | 42. (4) |

# Hints & Solutions

1. Electronic configuration of  $\text{Gd}^{3+}$  is



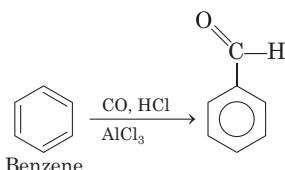
$\text{Gd}^{3+}$  having 7 unpaired electrons.

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM}$$

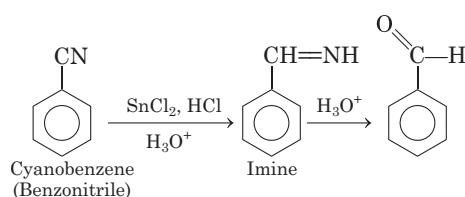
$$\Rightarrow \mu = \sqrt{7(7+2)} \text{ BM} = 7.9 \text{ BM}$$

where,  $n$  = number of unpaired electrons.

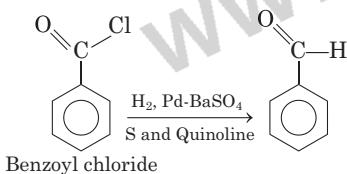
2. (I) Given, reaction is Gattermann - Koch reaction involves the formation of an aryl aldehyde using CO and HCl as reactants. The reaction catalysed by  $\text{AlCl}_3$ .



- (II) Given, reaction is Stephen reduction reaction involves the preparation of aldehydes from nitriles using tin (II) chloride, hydrochloric acid and quenching the resulting minimum salt with water.



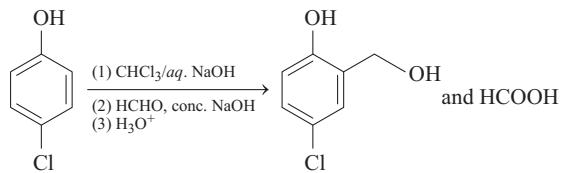
- (III) Given, reaction is Rosenmund reduction is a hydrogenation process in which an acyl chloride is selectively reduced to an aldehyde.



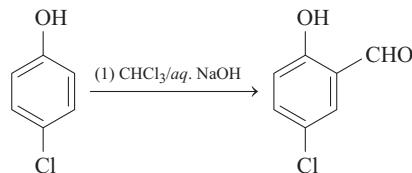
Correct match of Item-I and Item-II will be

(I) - (R), (II) - (P) and (III) - (Q).

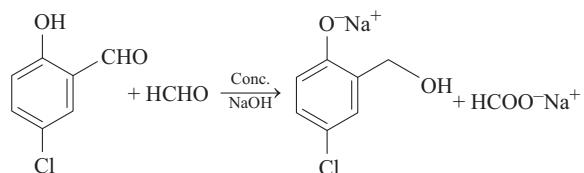
3. The major products of the given reaction are as follows:



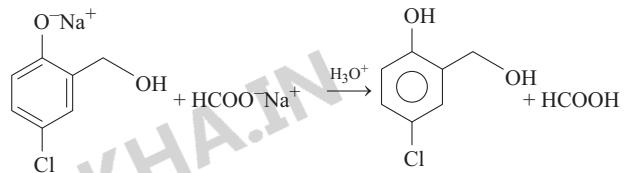
In step-I, substituted phenol undergoes Reimer-Tiemann reaction in presence of  $\text{CHCl}_3 / \text{aq. NaOH}$



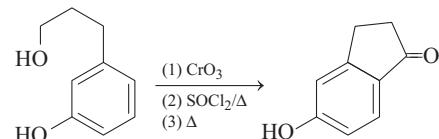
The aldehyde obtained in above equation does not possess  $\alpha$ -hydrogen. In presence of formaldehyde and conc. NaOH it undergoes Cannizzaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



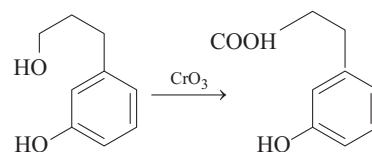
Upon hydrolysis, following reaction takes place



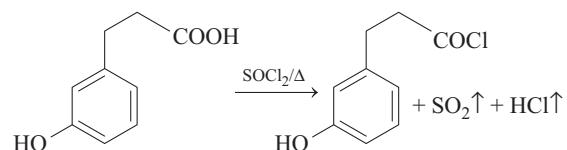
4. The major product formed in the reaction is as follows :



Primary alcohol readily oxidised to corresponding carboxylic acid with oxidising agent, chromium trioxide ( $\text{CrO}_3$ ) in acidic medium.



$-\text{OH}$  group of carboxylic acid get substituted by  $-\text{Cl}$  in presence of  $\text{SOCl}_2$  (Thionyl chloride).



Further, heating of product leads to intramolecular cyclisation.

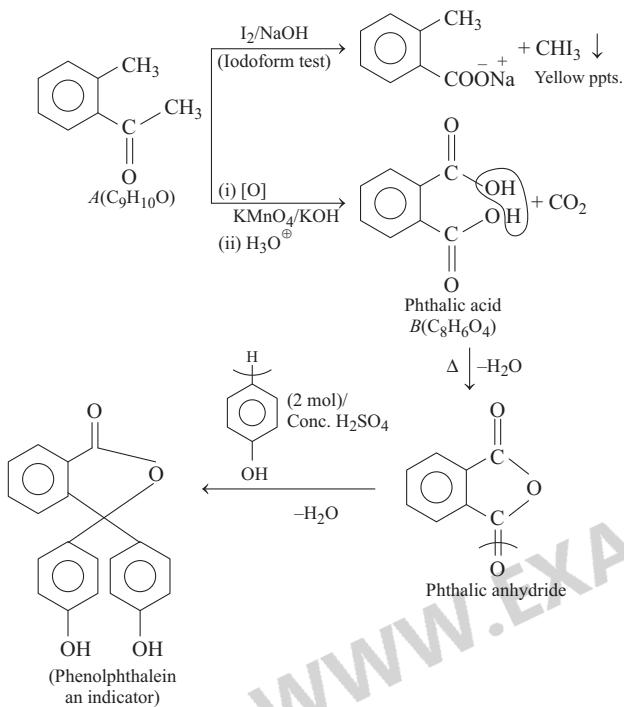
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5. (i)  $C_9H_{10}O$  shows positive iodoform test thus,  $\begin{array}{c} \text{---C---CH}_3 \\ || \\ \text{O} \end{array}$  group is present.

(ii)  $C_9H_{10}O$  on strong oxidation ( $KMnO_4/KOH$ ), gives acid ( $C_8H_6O_4$ ), indicating it can be a dicarboxylic acid. So, 'A' contains  $\text{---COCH}_3$  and one  $\text{---CH}_3$  group which get oxidised into  $\text{---COOH}$  and  $\text{---COOH}$  respectively.

- (iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, 'B' can be phthalic acid (benzene-1,2-dicarboxylic acid) which readily forms anhydride.

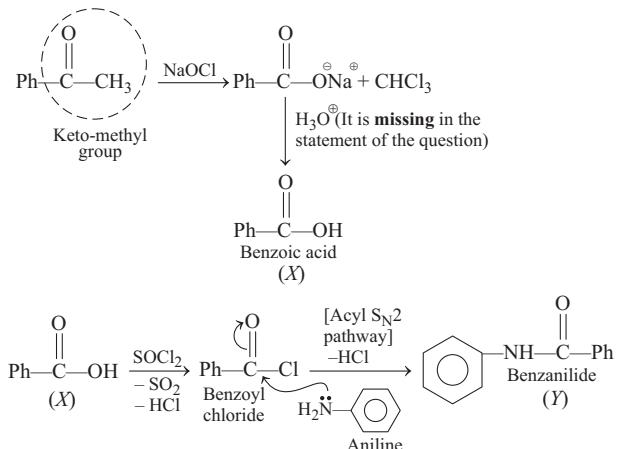
Thus, the reaction sequence is as follows :



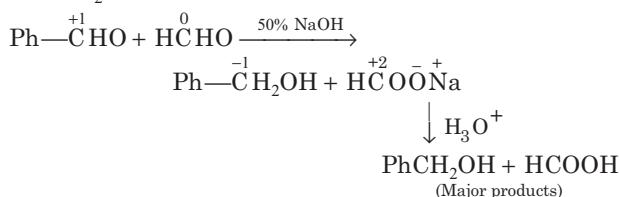
6. NaOCl (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.



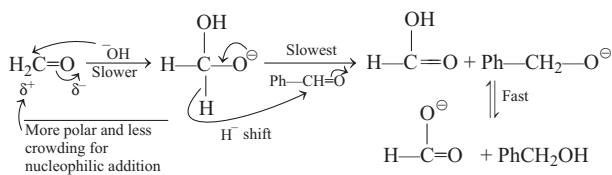
The given reaction takes place as follows :



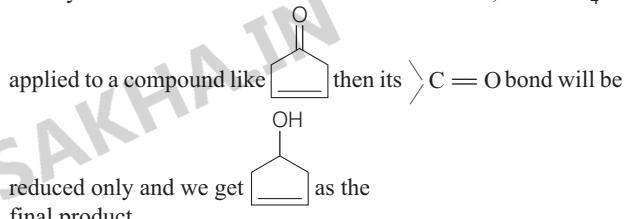
7. The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the  $\text{---CHO}$  groups of  $\text{Ph---CHO}$  and  $\text{H---CHO}$  are +1 and zero respectively. So,  $\text{HCHO}$  is the stronger reducing agent than  $\text{PhCHO}$ . As a result,  $\text{HCHO}$  is oxidised to  $\text{HCOONa}$  (by donation of hydride,  $\text{H}^-$ ) and  $\text{PhCHO}$  ( $\text{H}^+$  acceptor) is reduced to  $\text{PhCH}_2\text{OH}$ .



The reaction proceed via following mechanism.

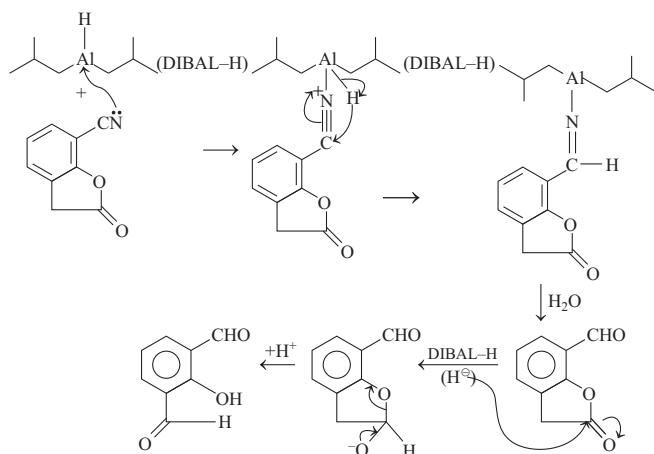


8. Reducing agents like  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , i.e. complex hydrides usually does not affect olifenic or  $\pi$ -bonds. Thus, if  $\text{NaBH}_4$  is



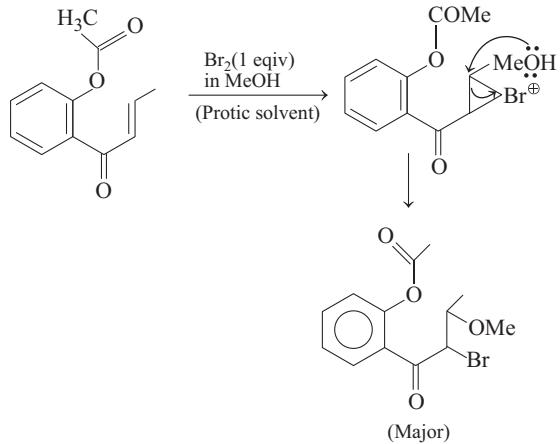
thus, option (a) is correct answer.

9. DIBAL-H (Diisobutylaluminium hydride) is a reducing agent with formula  $[\lambda\text{-Bu}_2\text{AlH}]$ . At ordinary temperatures, nitriles give imines which are readily converted in aldehydes by hydrolysis whereas lactones are reduced directly to aldehydes.

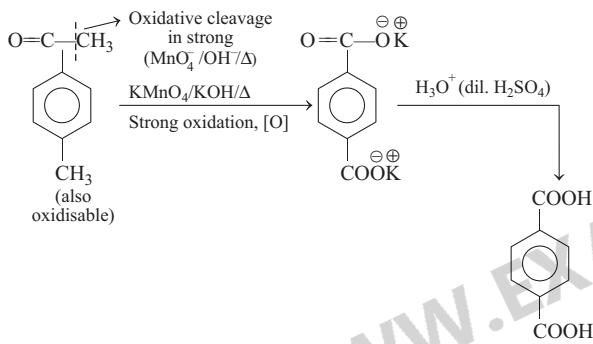


10. In presence of  $\text{Br}_2/\text{EtOH}$ , the reactant containing double bond undergoes electrophilic addition reaction via the formation of

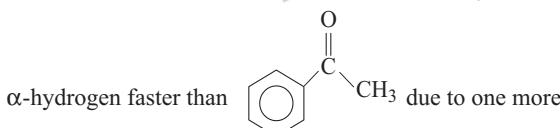
bromonium ion. On further attack of  $\text{MeOH}$  on bromonium ion gives the addition product.



11. In presence of alkaline  $\text{KMnO}_4$ , vigorous oxidation of alkyl or acyl benzene takes place. During oxidation, aromatic nucleus remains intact but the entire chain is oxidised to  $-\text{COOH}$  group irrespective of the length of carbon chain.

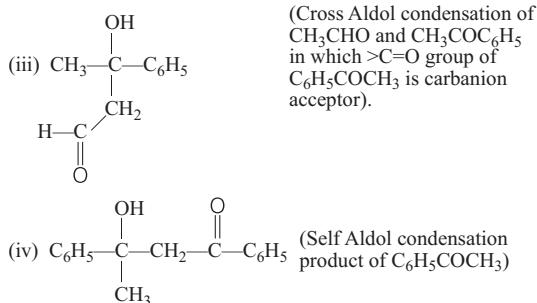
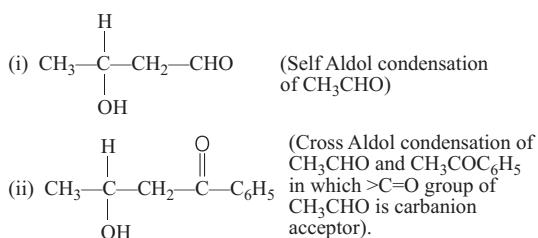


12. In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case  $\text{CH}_3\text{CHO}$  will lose



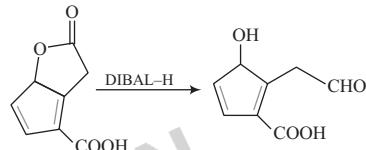
reason, i.e. conjugation between benzene ring and  $>\text{C=O}$  group. Along with sterically less hindered nucleophile of  $\text{CH}_3\text{CHO}$  will also add to the major product formation.

Following four products are possible in the reaction:

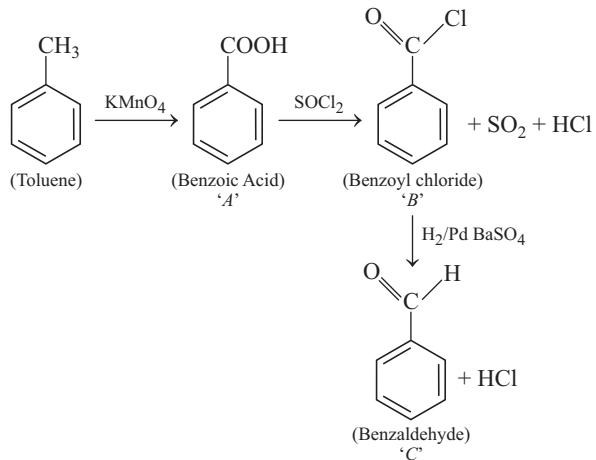


$\text{O}^-$  of base will prefer to attack on  $-\text{CH}_3$  group of  $\text{CH}_3\text{CHO}$  for the formation of carbanion and as among the  $>\text{C=O}$  groups available, the  $>\text{C=O}$  group of  $\text{CH}_3\text{CHO}$  is the best carbanion acceptor. Hence, self condensation product of  $\text{CH}_3\text{CHO}$  will be the major product.

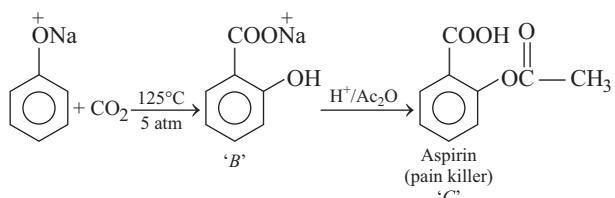
13. DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL-H, Lactones are reduced directly to aldehydes.



14. Toluene undergoes oxidation with  $\text{KMnO}_4$ , forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride ( $\text{SOCl}_2$ ) to give benzoyl chloride which upon reduction with  $\text{H}_2/\text{Pd}$  or  $\text{BaSO}_4$  forms benzaldehyde (Rosenmund reduction). The conversion look like,



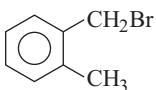
15. It is a Kolbe Schmidt reaction.



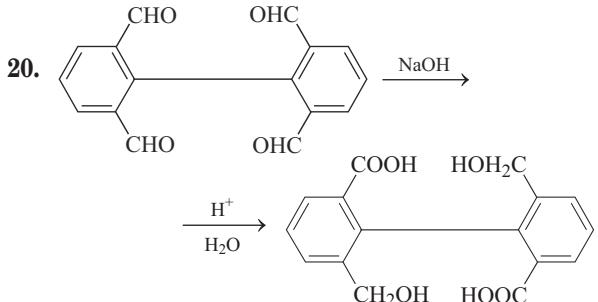
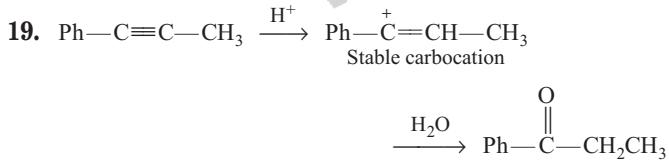
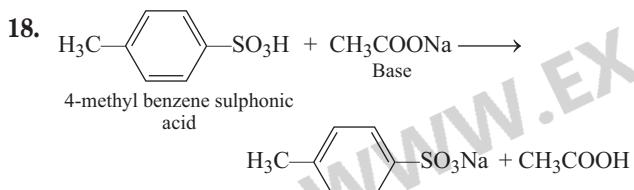
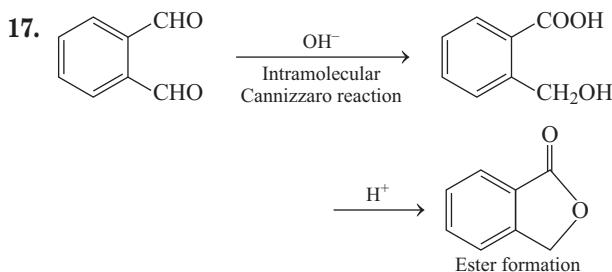
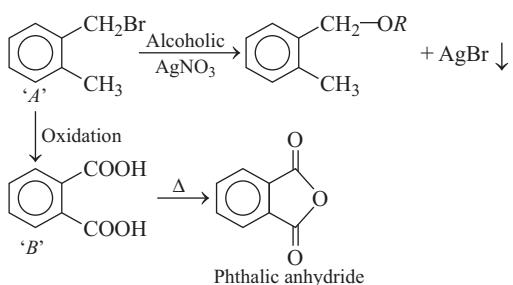
The second step of the reaction is an example of acylation reaction.

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16. Compound *A* gives a precipitate with alcoholic  $\text{AgNO}_3$ , so it must contain Br in side chain. On oxidation, it gives  $\text{C}_8\text{H}_6\text{O}_4$ , which shows the presence of two alkyl chains attached directly with the benzene nucleus. Since, compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position. Thus, *A* must be

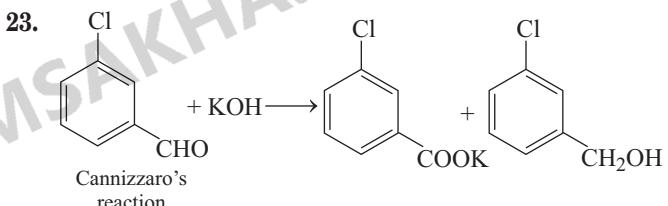
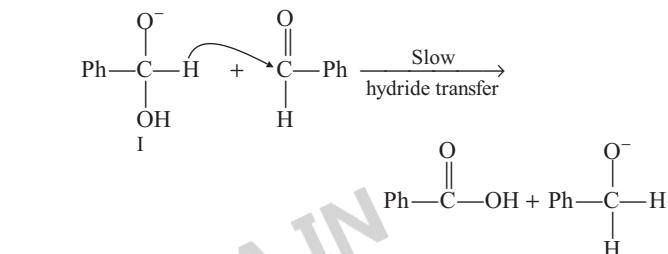
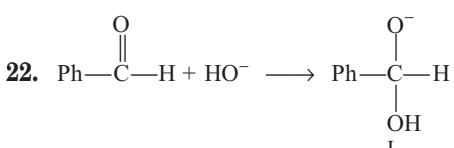
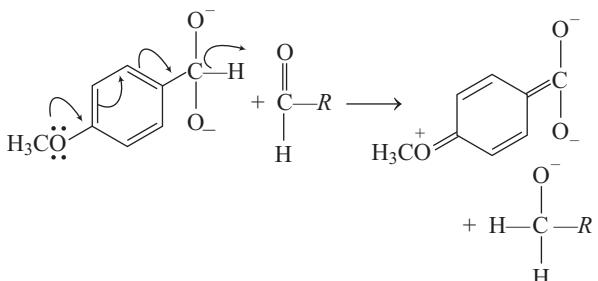


and the reactions are as follows :

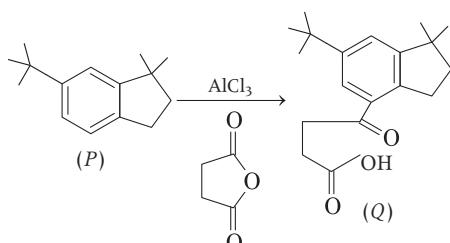


The above reaction is an example of intramolecular Cannizzaro reaction.

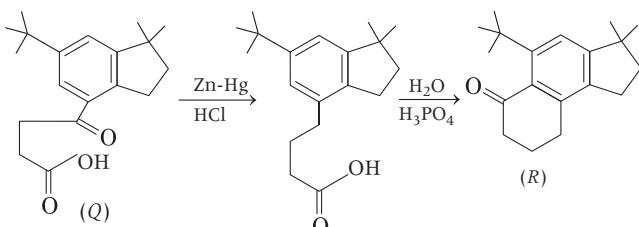
21. Dioxoanion is better hydride donor. Electron donating group at *ortho/para* position further promote  $\text{H}^-$  transfer.



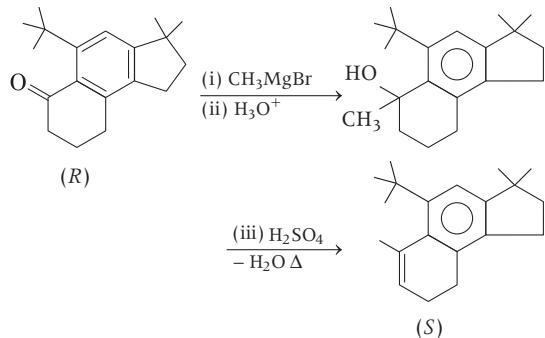
24. Compound (*P*) undergoes Friedel-Crafts acylation reaction in presence of succinic anhydride and  $\text{AlCl}_3$  to gives an acid (*Q*).



Compound (*Q*) on treatment with Zn-Hg/HCl undergoes Clemmensen reduction, where ketone group change into alkane and on further reaction with dehydrating agent  $\text{H}_3\text{PO}_4$  gives compound (*R*).

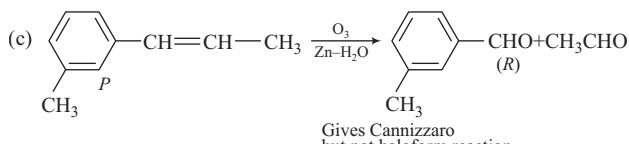
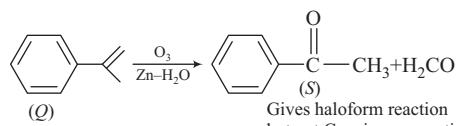
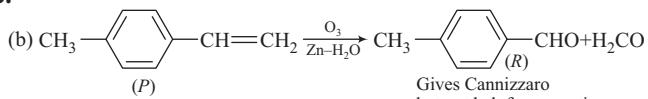


Compound (*R*) on reaction with Grignard reagent and heated in presence of acid gives dehydrating product (*S*).



Thus, the option (b) and (d) are correct.

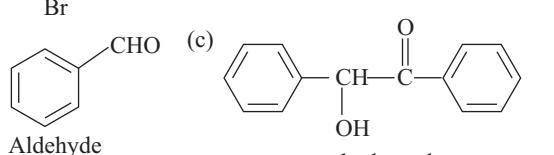
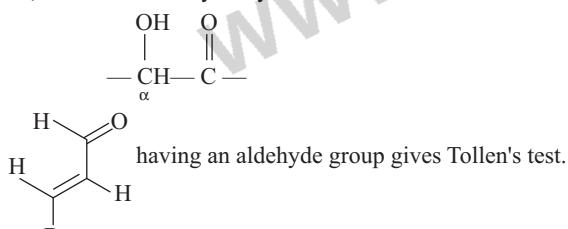
25.



26.

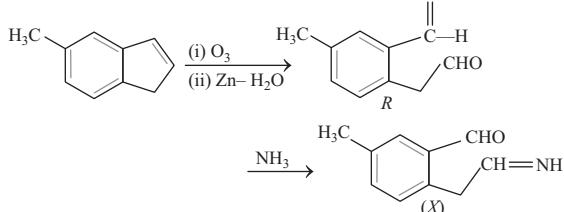


Tollen's test is given by all aldehydes and all reducing sugars as glucose, fructose and  $\alpha$ -hydroxy ketones.

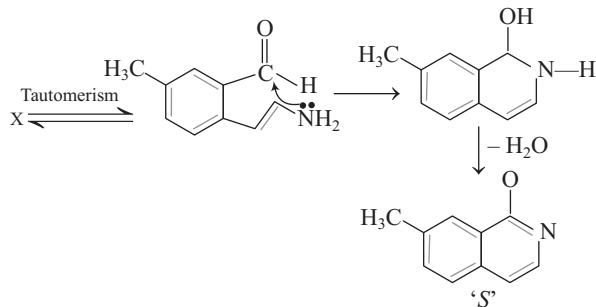


$\alpha$ -hydroxy ketone  
give positive Tollen's test.

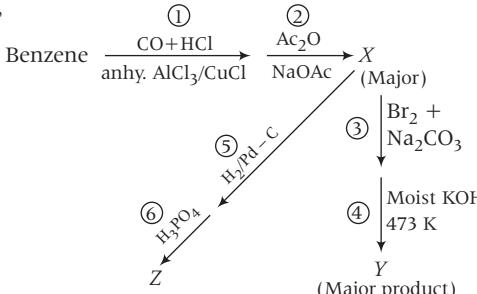
27.



In the above reaction,  $\text{NH}_3$  prefer to attack at aliphatic aldehyde group than an less reactive aromatic aldehyde group.

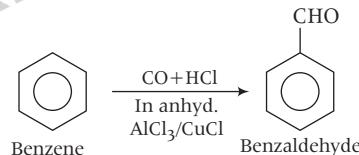


28 Ciwan

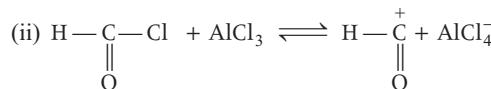
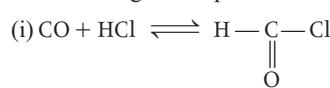


For this question we require only reaction 1 to 4 written above.  
Let us explore them one by one.

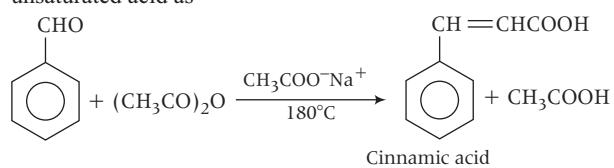
**Reaction 1** It is called formylation or Gatterman Koch reaction. A — CHO group is introduced to benzene ring through this reaction as



The attacking electrophile is  $\text{H}-\overset{+}{\text{C}}=\text{O}$  which is generated as

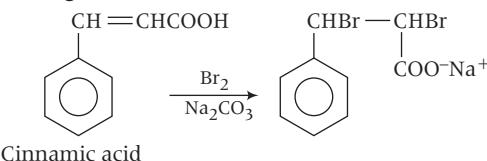


**Reaction 2** It is Perkin condensation which results in  $\alpha, \beta$ -unsaturated acid as



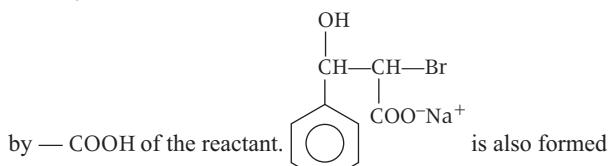
**Note** Besides  $\text{CH}_3\text{COO}^-\text{Na}^+$ , quinoline, pyridine,  $\text{Na}_2\text{CO}_3$ , triethylamine can also be used as bases in this reaction.

**Reaction 3** It is simple addition of bromine to unsaturated acid formed through reaction 2.



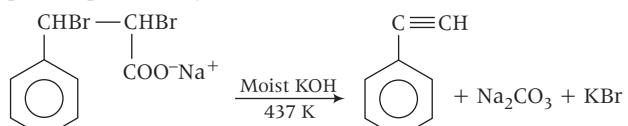
## 482 Aromatic Aldehydes, Ketones and Acids

$\text{Na}_2\text{CO}_3$  works as a base in the reaction to trap  $\text{H}^+$  to be released



in the reaction as the minor product.

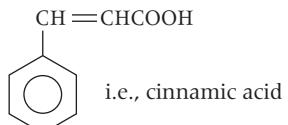
**Reaction 4** It is decarboxylation and dehydrohalogenation of product produced by reaction 3 as



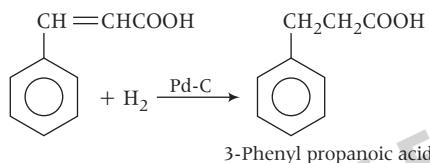
Hence,  $Y$  is

i.e., (c) is the correct answer.

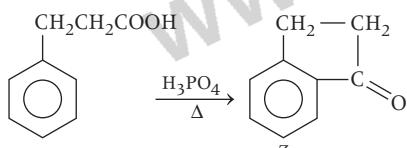
**29. Reaction 5** The Perkin condensation product  $X$  is



This compound on hydrogenation with  $\text{H}_2$  in the presence of Pd activated with charcoal (Pd-C) gives

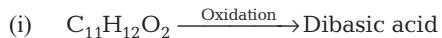


**Reaction 6** The product of reaction 5 on heating with  $\text{H}_3\text{PO}_4$  dehydrates to give



### Passage-2

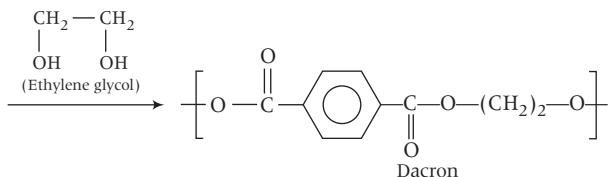
**30. Given,**



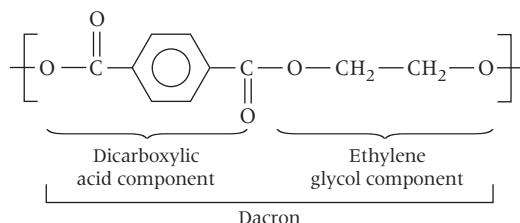
(An organic acid ' $P$ ')

This indicates the presence of alkyl or alkenyl branch in  $P$  along with  $-\text{COOH}$  group.

(ii) Dibasic acid produced by oxidation of  $P$



This indicates presence of benzene ring in  $P$ ; as concluded from the structure of dacron given below.

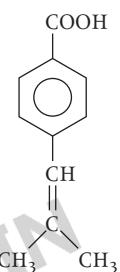


Attachment of  $-\text{COO}$  group in dacron also confirm the *para* position of branch with respect to  $-\text{COOH}$  group in  $P$ .

(iii)  $P \xrightarrow{\text{Ozonolysis}} \text{Aliphatic ketone} + \text{other oxidised products.}$

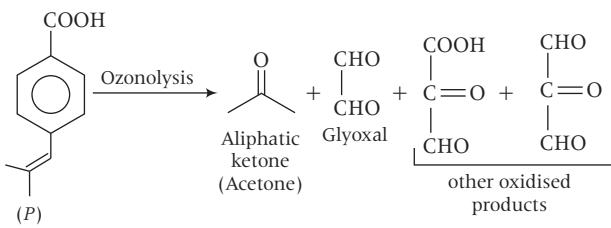
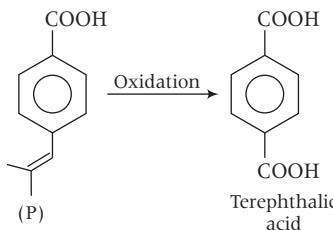
This reaction confirms the presence of multiple bonded branch i.e., alkenyl group in  $P$ .

Thus  $P$  can be



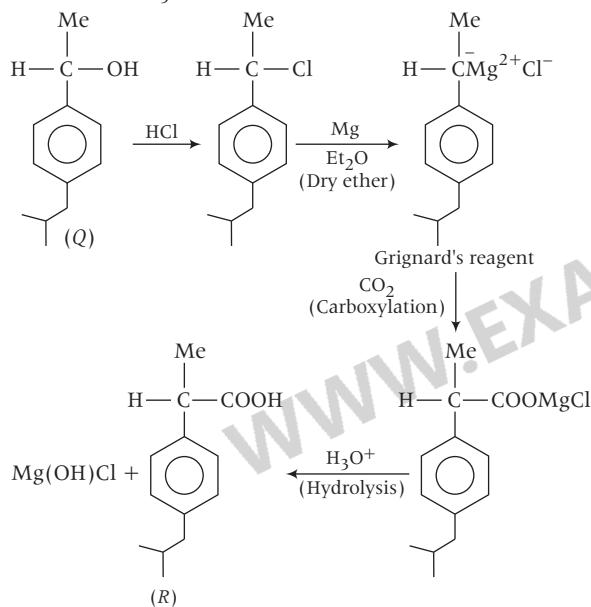
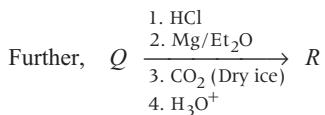
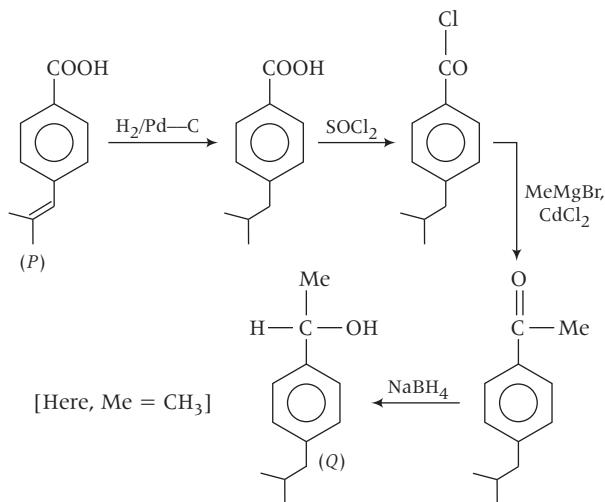
IUPAC name : 4-(2-methyl) prop-1-enyl benzoic acid

Now look for the reactions

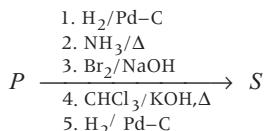


Given,  $P \xrightarrow[4. \text{ NaBH}_4]{1. \text{ H}_2/\text{Pd-C}, 2. \text{ SOCl}_2, 3. \text{ MeMgBr, CdCl}_2} Q$

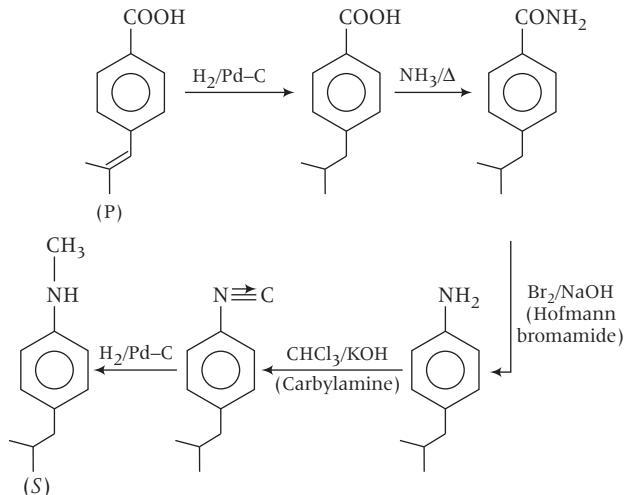
So,



31. Given,

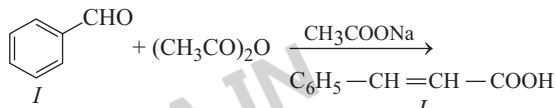


So,

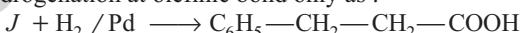


### Passage 3

Sol for (Q. Nos. 34 to 35) The first step of reaction is Perkin's condensation.



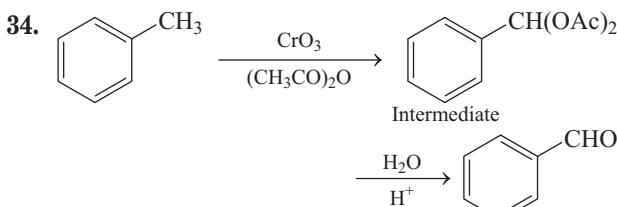
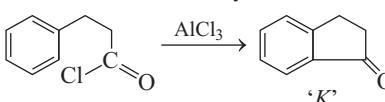
*J* being a carboxylic acid gives effervescence with  $\text{NaHCO}_3$ . Also, *J* has olefinic bond, it will decolourise Baeyer's reagent. In the second step, *J* on treatment with  $\text{H}_2 / \text{Pd} / \text{C}$  undergo hydrogenation at olefinic bond only as :



The hydrogenated acid, on treatment with  $\text{SOCl}_2$  gives acid chloride.



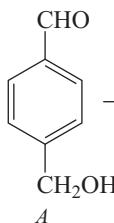
In the final step, acid chloride formed above undergo intramolecular Friedel-Craft acylation as:



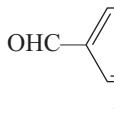
## 484 Aromatic Aldehydes, Ketones and Acids

35. For aldol condensation, presence of at least one  $\alpha$ -H is essential, which is not available to benzaldehyde.

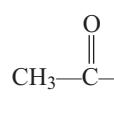
36.



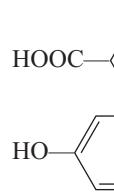
Gives positive Tollen's test but does not give  $\text{FeCl}_3$  test.



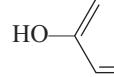
Gives positive Tollen's test and  $\text{FeCl}_3$  test.



Gives positive iodoform test.

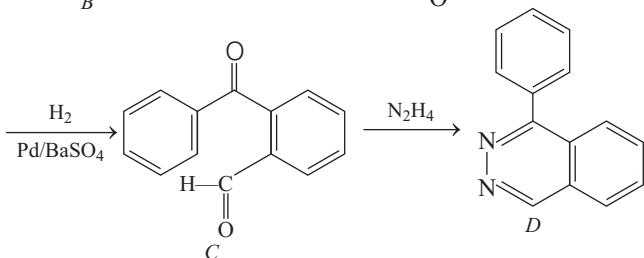
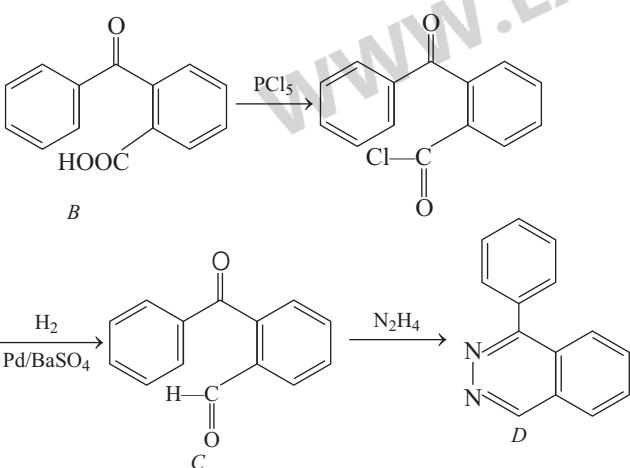
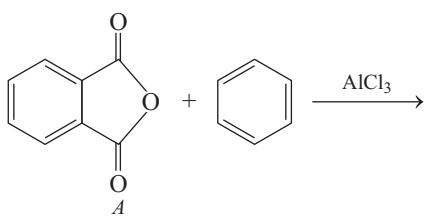


Can be extracted with  $\text{NaHCO}_3$ .

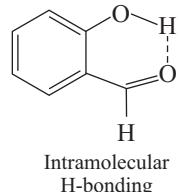


On hydrolysis give 1,4-dihydroxy benzene.

37.

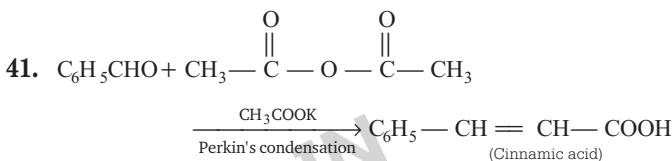
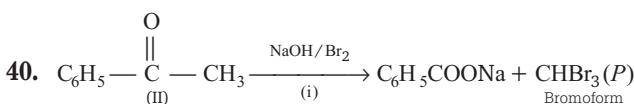
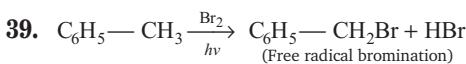


38. Intramolecular H-bonding in *ortho* hydroxy benzaldehyde is responsible for decrease in melting and boiling points.



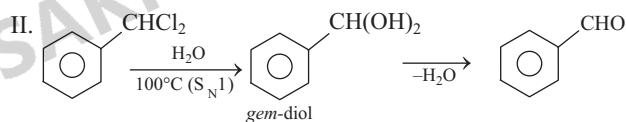
Intramolecular  
H-bonding

*p*-hydroxy benzaldehyde molecules are associated by intermolecular H-bonding, has higher melting and boiling points.



Cinnamic acid shows *cis-trans* isomerism.

42. I. Gattermann-Koch reaction.



III. Rosenmund's reduction.

IV. Acid chloride, anhydride and ester undergo controlled reduction with di-iso-butylaluminium hydride (DIBAL-H) at  $-78^\circ\text{C}$  to give aldehydes.

# 32

## Biomolecules and Chemistry in Everyday Life

### Topic 1 Biomolecules

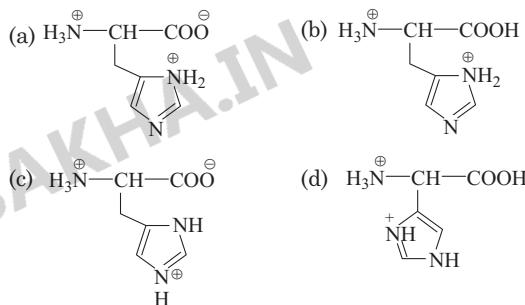
#### Objective Questions I (Only one correct option)

1. Which of the given statements is incorrect about glycogen?  
(2019 Main, 12 April II)  
(a) It is straight chain polymer similar to amylose  
(b) Only  $\alpha$ -linkages are present in the molecule  
(c) It is present in animal cells  
(d) It is present in some yeast and fungi
2. Which of the following statement is not true about RNA?  
(2019 Main, 12 April I)  
(a) It controls the synthesis of protein  
(b) It has always double stranded  $\alpha$ -helix structure  
(c) It usually does not replicate  
(d) It is present in the nucleus of the cell
3. Number of stereo-centers present in linear and cyclic structures of glucose are respectively  
(2019 Main, 10 April II)  
(a) 4 and 5  
(b) 4 and 4  
(c) 5 and 4  
(d) 5 and 5
4. Amylopectin is composed of  
(2019 Main, 10 April I)  
(a)  $\beta$ -D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>2</sub>-C<sub>6</sub> linkages  
(b)  $\alpha$ -D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>2</sub>-C<sub>6</sub> linkages  
(c)  $\beta$ -D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>6</sub> linkages  
(d)  $\alpha$ -D-glucose, C<sub>1</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>6</sub> linkages
5. The peptide that gives positive ceric ammonium nitrate and carbylamine tests is  
(2019 Main, 09 April II)  
(a) Lys-Asp  
(b) Ser-Lys  
(c) Gln-Asp  
(d) Asp-Gln
6. Which of the following statement is not true about sucrose?  
(2019 Main, 09 April I)  
(a) It is also named as invert sugar.  
(b) The glycosidic linkage is present between C<sub>1</sub> of  $\alpha$ -glucose and C<sub>1</sub> of  $\beta$ -fructose  
(c) It is a non-reducing sugar  
(d) On hydrolysis, it produces glucose and fructose
7. Fructose and glucose can be distinguished by  
(2019 Main, 08 April II)  
(a) Fehling's test  
(b) Barfoed's test  
(c) Benedict's test  
(d) Seliwanoff's test

8. Maltose on treatment with dilute HCl gives  
(2019 Main, 08 April I)

- (a) D-glucose and D-fructose  
(b) D-fructose  
(c) D-galactose  
(d) D-glucose

9. The correct structure of histidine in a strongly acidic solution (pH = 2) is  
(2019 Main, 12 Jan II)



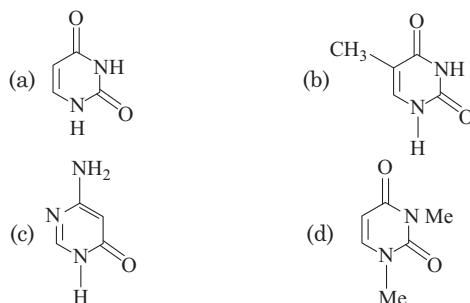
10. The correct match between Item I and Item II is

| Item I                | Item II |
|-----------------------|---------|
| A. Ester test         | P. Tyr  |
| B. Carbylamine test   | Q. Asp  |
| C. Phthalein dye test | R. Ser  |
|                       | S. Lys  |

(2019 Main, 11 Jan II)

- (a) A  $\rightarrow$  Q; B  $\rightarrow$  S; C  $\rightarrow$  R  
(b) A  $\rightarrow$  R, B  $\rightarrow$  Q; C  $\rightarrow$  P  
(c) A  $\rightarrow$  R; B  $\rightarrow$  S; C  $\rightarrow$  Q  
(d) A  $\rightarrow$  Q; B  $\rightarrow$  S; C  $\rightarrow$  P

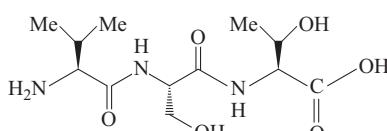
11. Among the following compounds, which one is found in RNA?  
(2019 Main, 11 Jan I)



**486** Biomolecules and Chemistry in Everyday Life



**13.** The correct sequence of amino acids present in the tripeptide given below is (2019 Main, 9 Jan II)



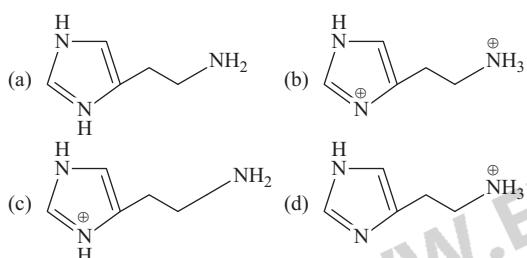


- 14** The increasing order of  $pK_a$  of the following amino acids in aqueous solution is Gly, Asp, Lys, Arg  
**(2019 Main, 9 Jan I)**

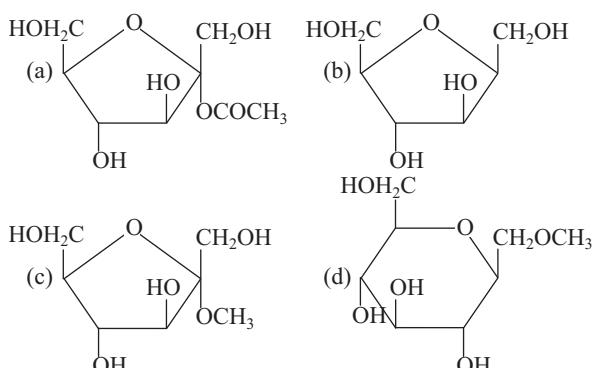
- (a) Asp < Gly < Arg < Lys    (b) Arg < Lys < Gly < Asp  
 (c) Gly < Asp < Arg < Lys    (d) Asp < Gly < Lys < Arg



- 16.** The predominant form of histamine present in human blood is ( $pK_a$ , Histidine = 6.0) (2018 Main)



- 17.** Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? (2017 Main)



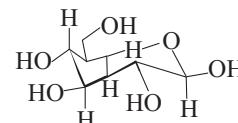




- 21.** Synthesis of each molecule of glucose in photosynthesis involves (2013 Main)

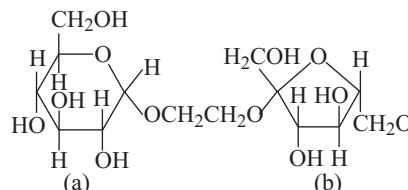
  - (a) 18 molecules of ATP
  - (b) 10 molecules of ATP
  - (c) 8 molecules of ATP
  - (d) 6 molecules of ATP

- 22.** The following carbohydrate is





- 23.** The correct statement about the following disaccharide is



- (a) Ring (a) is pyranose with  $\alpha$ -glycosidic link
  - (b) Ring (a) is furanose with  $\alpha$ -glycosidic link
  - (c) Ring (b) is furanose with  $\alpha$ -glycosidic link
  - (d) Ring (b) is pyranose with  $\beta$ -glycosidic link



- 25.** Which of the following pairs give positive Tollen's test ?  
(2004, 1M)

## Objective Question II

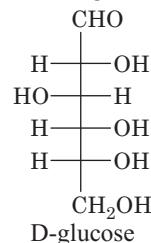
### **Objective Question II**

(One or more than one correct option)

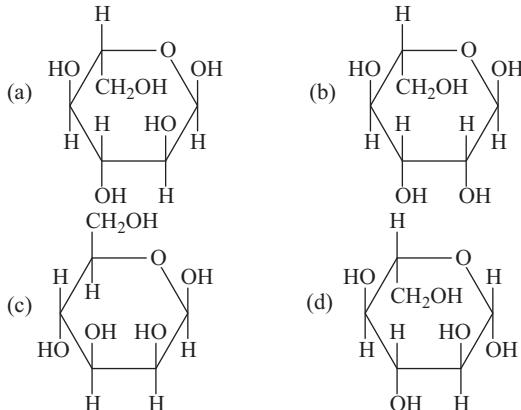
26. Which of the following statement(s) is(are) true? (2019 Adv.)

  - (a) The two six-membered cyclic hemiacetal forms of D-(+)-glucose are called anomers
  - (b) Oxidation of glucose with bromine water gives glutamic acid
  - (c) Monosaccharides cannot be hydrolysed to give polyhydroxy aldehydes and ketones
  - (d) Hydrolysis of sucrose gives dextrorotatory glucose and laevorotatory fructose

- 27.** The Fischer presentation of D-glucose is given below:

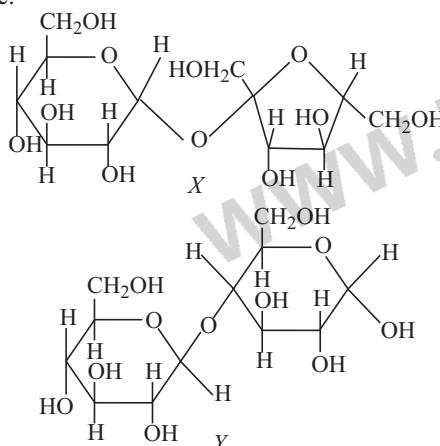


The correct structure(s) of  $\beta$ -D-glucopyranose is (are)  
(2018 Adv.)



- 28.** For 'invert sugar', the correct statement(s) is (are)  
(Given: specific rotations of (+)- sucrose, (+)- maltose, L-(-)-glucose and L-(+)-fructose in aqueous solution are  $+66^\circ$ ,  $+140^\circ$ ,  $-52^\circ$  and  $92^\circ$ , respectively) (2016 Adv.)
- Invert sugar is prepared by acid catalysed hydrolysis of maltose
  - Invert sugar is an equimolar mixture of D-(+)-glucose and D-(+)- fructose
  - Specific rotation of invert sugar is  $-20^\circ$
  - On reaction with  $\text{Br}_2$  water, invert sugar forms saccharic acid as one of the products

- 29.** The correct statement(s) about the following sugars X and Y is/are: (2009)



- X is a reducing sugar and Y is a non-reducing sugar
- X is a non-reducing sugar and Y is a reducing sugar
- The glucosidic linkages in X and Y are  $\alpha$  and  $\beta$ , respectively
- The glucosidic linkages in X and Y are  $\beta$  and  $\alpha$ , respectively

### Assertion and Reason

Read the following questions and answer as per the direction given below :

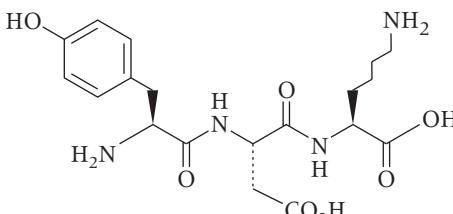
- Statement I is correct; Statement II is correct;  
Statement II is a correct explanation of Statement I.
- Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
- Statement I is correct; Statement II is incorrect.
- Statement I is incorrect; Statement II is correct.

- 30. Statement I** Glucose gives a reddish-brown precipitate with Fehling's solution.

**Statement II** Reaction of glucose with Fehling's solution gives CuO and gluconic acid. (2007, 3M)

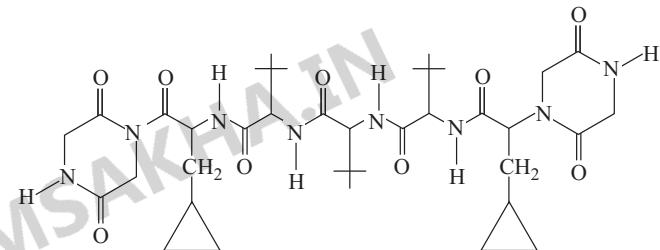
### Integer Answer Type Questions

- 31.** The structure of a peptide is given below.



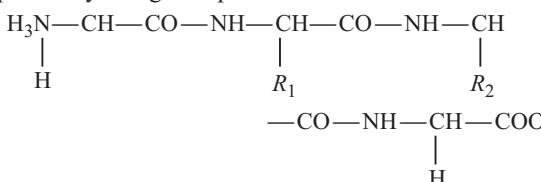
If the absolute values of the net charge of the peptide at pH = 2, pH = 6, and pH = 11 are  $|Z_1|$ ,  $|Z_2|$ , and  $|Z_3|$ , respectively, then what is  $|Z_1| + |Z_2| + |Z_3|$ ? (200 Adv.)

- 32.** The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is (2014 Adv.)



- 33.** A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with —NH<sub>2</sub> group attached to a chiral centre is (2013 Adv.)

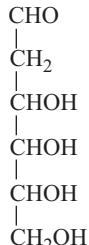
- 34.** The substituents  $R_1$  and  $R_2$  for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0? (2012)



| Peptide | $R_1$                                           | $R_2$                                           |
|---------|-------------------------------------------------|-------------------------------------------------|
| I       | H                                               | H                                               |
| II      | H                                               | CH <sub>3</sub>                                 |
| III     | CH <sub>2</sub> COOH                            | H                                               |
| IV      | CH <sub>2</sub> CONH <sub>2</sub>               | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> |
| V       | CH <sub>2</sub> CONH <sub>2</sub>               | CH <sub>2</sub> CONH <sub>2</sub>               |
| VI      | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> |
| VII     | CH <sub>2</sub> COOH                            | CH <sub>2</sub> CONH <sub>2</sub>               |
| VIII    | CH <sub>2</sub> OH                              | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> |
| IX      | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> | CH <sub>3</sub>                                 |

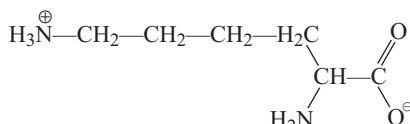
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- 35.** When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form, is (2012)



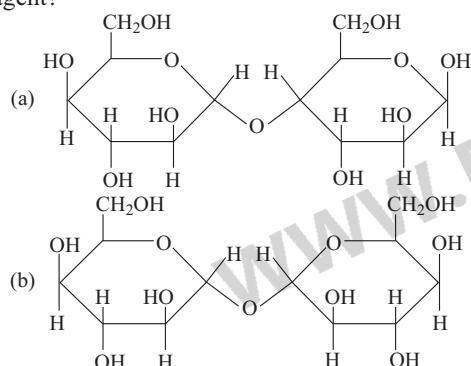
- 36.** A decapeptide (Molecular weight 796) on complete hydrolysis gives glycine (Molecular weight 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is (2011)

- 37.** The total number of basic groups in the following form of lysine is (2010)

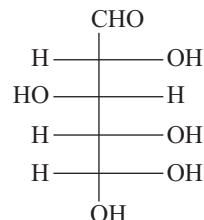


## **Subjective Questions**

- 38.** Which of the following disaccharide will not reduce Tollen's reagent? (2005, 2M)

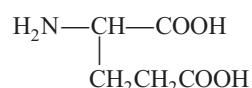
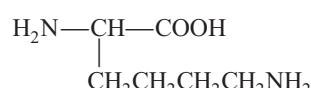


- 39.** The structure of D-glucose is as follows :

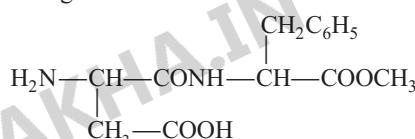


- (i) Draw the structure of L-glucose.  
(ii) Give the reaction of L-glucose with Tollen's reagent.

- 40.** Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides?

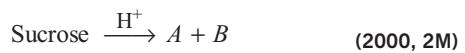


- 41.** Aspartame, an artificial sweetener, is a peptide and has the following structure



- (i) Identify the four functional groups.
  - (ii) Write the Zwitter ionic structure.
  - (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
  - (iv) Which of the two amino acids is more hydrophobic?

- 42.** Give the structures of the products in the following reaction



- 43.** Write the structure of alanine at pH = 2 and pH = 10.  
(2000, 2M)

## **Topic 2 Chemistry in Everyday Life**

### **Objective Questions I** (Only one correct option)

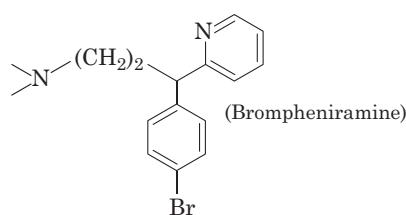
1. The antifertility drug “Novestrol” can react with

(2020 Main, 3 Sep I)

- (a)  $\text{ZnCl}_2$  /  $\text{HCl}$ ;  $\text{FeCl}_3$ ; alcoholic HCN
  - (b)  $\text{Br}_2$ /water;  $\text{ZnCl}_2$  /  $\text{HCl}$ ;  $\text{FeCl}_3$
  - (c) alcoholic HCN;  $\text{NaOCl}$ ;  $\text{ZnCl}_2$  /  $\text{HCl}$
  - (d)  $\text{Br}_2$  /water;  $\text{ZnCl}_2$  /  $\text{HCl}$ ;  $\text{NaOCl}$

- 2** The following molecule acts as an

(2020 Main 5 Sep II)



- (a) antiseptic                          (b) anti-depressant  
(c) anti-bacterial                      (d) anti-histamine

Codes

|     | A   | B  | C  | D   |
|-----|-----|----|----|-----|
| (a) | III | I  | IV | II  |
| (b) | IV  | II | I  | III |
| (c) | II  | IV | I  | III |
| (d) | III | I  | II | IV  |



8. The structure of nylon-6 is

(a)  $\text{+}(\text{CH}_2)_6-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\overset{\text{H}}{\underset{|}{\text{N}}}\text{)}_n$  (b)  $\text{+}\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{(CH}_2)_5-\overset{\text{H}}{\underset{|}{\text{N}}}\text{)}_n$

(c)  $\text{+}(\text{CH}_2)_4-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\overset{\text{H}}{\underset{|}{\text{N}}}\text{)}_n$  (d)  $\text{+}\overset{\text{O}}{\underset{\parallel}{\text{C}}}(\text{CH}_2)_6-\overset{\text{H}}{\underset{|}{\text{N}}}\text{)}_n$

- 9.** The two monomers for the synthesis of nylon 6, 6 are **(2019 Main, 12 Jan II)**

  - (a) HOOC(CH<sub>2</sub>)<sub>4</sub>COOH, H<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>
  - (b) HOOC(CH<sub>2</sub>)<sub>6</sub>COOH, H<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>
  - (c) HOOC(CH<sub>2</sub>)<sub>4</sub>COOH, H<sub>2</sub>N(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>
  - (d) HOOC(CH<sub>2</sub>)<sub>6</sub>COOH, H<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub>

- 10.** Poly- $\beta$ -hydroxybutyrate-Co- $\beta$ -hydroxyvalerate (PHBV) is a copolymer of ..... (2019 Main, 12 Jan I)

  - (a) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid
  - (b) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid
  - (c) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid
  - (d) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

11. The homopolymer formed from 4-hydroxybutanoic acid is

(a)  $\left[ \text{OC}(\text{CH}_2)_3-\text{O} \right]_n$       (b)  $\left[ \text{C}(\text{CH}_2)_2\text{C} \right]_n$

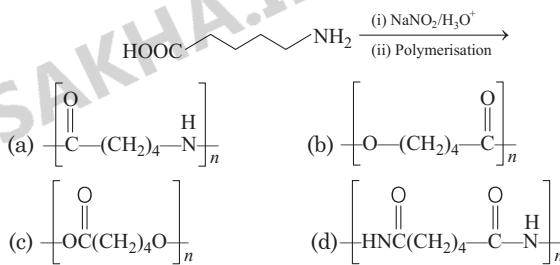
(c)  $\left[ \text{C}(\text{CH}_2)_3-\text{O} \right]_n$       (d)  $\left[ \text{C}(\text{CH}_2)_2\text{C}-\text{O} \right]_n$

- 12.** The correct match between Item I and Item II is

| <b>Item I</b>            | <b>Item II</b>                                                      |
|--------------------------|---------------------------------------------------------------------|
| A. Allosteric effect     | P. Molecule binding to the active site of enzyme.                   |
| B. Competitive inhibitor | Q. Molecule crucial for communication in the body.                  |
| C. Receptor              | R. Molecule binding to a site other than the active site of enzyme. |
| D. Poison                | S. Molecule binding to the enzyme covalently.                       |

- (a)  $A \rightarrow P; B \rightarrow R; C \rightarrow S; D \rightarrow Q$   
 (b)  $A \rightarrow P, B \rightarrow R; C \rightarrow Q; D \rightarrow S$   
 (c)  $A \rightarrow R; B \rightarrow P; C \rightarrow S; D \rightarrow Q$   
 (d)  $A \rightarrow R; B \rightarrow P; C \rightarrow O; D \rightarrow S$

- 13.** The polymer obtained from the following reaction is:  
**(2019 Main, 11 Jan I)**



- 14.** The correct match between item (I) and item (II) is

| Item - I | Item - II     |                   |
|----------|---------------|-------------------|
| (A)      | Norethindrone | (P) Antibiotic    |
| (B)      | Ofloxacin     | (Q) Antifertility |
| (C)      | Equanil       | (R) Hypertension  |
|          |               | (S) Analgesics    |

- (a)  $(A \rightarrow Q); (B \rightarrow R); (C \rightarrow S)$
  - (b)  $(A \rightarrow Q); (B \rightarrow P); (C \rightarrow R)$
  - (c)  $(A \rightarrow R); (B \rightarrow P); (C \rightarrow S)$
  - (d)  $(A \rightarrow R); (B \rightarrow P); (C \rightarrow ($

- 15.** The correct match between Item - I and Item - II is

| <b>Item I (Drug)</b> | <b>Item II (Test)</b>             |
|----------------------|-----------------------------------|
| A. Chloroxylenol     | P. Carbylamine test               |
| B. Norethindrone     | Q. Sodium hydrogen carbonate test |
| C. Sulphapyridine    | R. Ferric chloride test           |
| D. Penicillin        | S. Bayer's test                   |

- (2019 Main, 9 Jan I)

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- 16.** The formation of which of the following polymers involves hydrolysis reaction? (2017 Main)

  - Nylon-6
  - Bakelite
  - Nylon-6, 6
  - Terylene

**17.** Which of the following statements about low density polythene is false? (2016 Main)

  - It is a poor conductor of electricity
  - Its synthesis required dioxygen or a peroxide initiator as a catalyst
  - It is used in the manufacture of buckets, dustbins etc.
  - Its synthesis requires high pressure

**18.** Which of the following is an anionic detergent? (2016 Main)

  - Sodium lauryl sulphate
  - Cetyltrimethyl ammonium bromide
  - Glyceryl oleate
  - Sodium stearate

**19.** On complete hydrogenation, natural rubber produces (2016 Adv.)

  - ethylene-propylene copolymer
  - vulcanised rubber
  - polypropylene
  - polybutylene

**20.** Which polymer is used in the manufacture of paints and lacquers? (2015 Main)

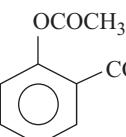
  - Bakelite
  - Glyptal
  - Polypropene
  - Polyvinyl chloride

**21.** Match the polymers in Column I with their main uses in Column II and choose the correct answer:

| Column I               | Column II              |
|------------------------|------------------------|
| (A) Polystyrene        | 1. Paints and lacquers |
| (B) Glyptal            | 2. Raincoats           |
| (C) Polyvinyl chloride | 3. Manufacture of toys |
| (D) Bakelite           | 4. Computer discs      |

**Codes**

| A     | B | C | D | A     | B | C | D |
|-------|---|---|---|-------|---|---|---|
| (a) 2 | 1 | 3 | 4 | (b) 3 | 1 | 2 | 4 |
| (c) 2 | 4 | 3 | 1 | (d) 3 | 4 | 2 | 1 |

**22.**  COOH is used as

  - Insecticide
  - Antihistamine
  - Analgesic
  - Antacid

**23.** Which of the following is not an antacid? (2015 Main)

  - Aluminium hydroxide
  - Cimetidine
  - Phenelzine
  - Ranitidine

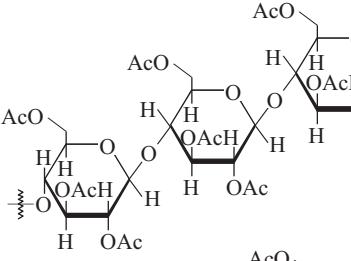
**24.** Which one is classified as a condensation polymer? (2014 Main)

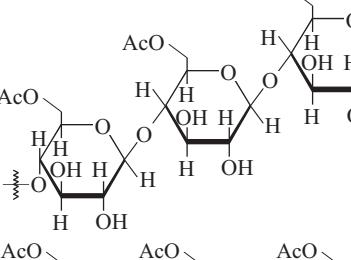
  - Dacron
  - Neoprene
  - Teflon
  - Acrylonitrile

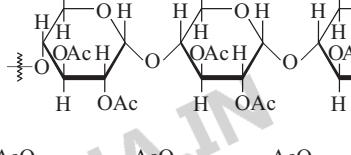
**25.** Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is (2009)

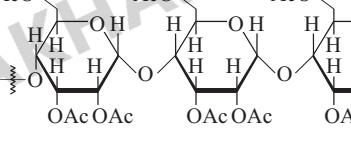
  - nylon
  - poly (vinyl chloride)
  - cellulose
  - natural rubber

**26.** Cellulose upon acetylation with excess acetic anhydride  $\text{H}_2\text{SO}_4$  (catalytic) gives cellulose triacetate whose structure is (2008, 3M)

(a) 

(b) 

(c) 

(d) 

### Objective Question II

(One or more than one correct option)

**27.** Choose the correct option(s) from the following. (2019 Adv.)

  - Teflon is prepared by heating tetrafluoroethene in presence of a persulphate catalyst at high pressure
  - Natural rubber is polyisoprene containing *trans* alkene units
  - Cellulose has only  $\alpha$ -D-glucose units that are joined by glycosidic linkages
  - Nylon-6 has amide linkages

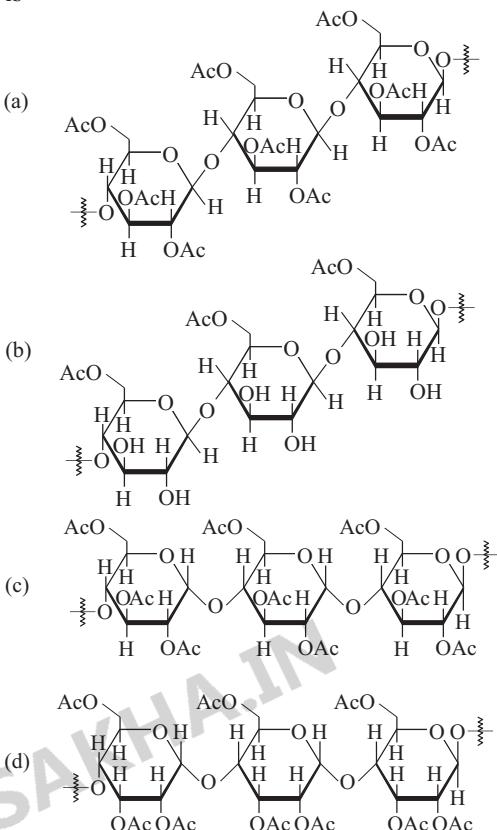
**28.** Under hydrolysis conditions, the compounds used for preparation of linear polymer and for chain termination, respectively are (2012)

  - $\text{CH}_3\text{SiCl}_3$  and  $\text{Si}(\text{CH}_3)_4$
  - $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$
  - $(\text{CH}_3)\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$
  - $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$

**29.** The correct functional group  $X$  and the reagent/reaction conditions  $Y$  in the following schemes are (2011)

$$X-(\text{CH}_2)_4-X \xrightarrow[\text{heat}]{\begin{array}{l} \text{(i)} Y \\ \text{(ii)} \text{HO}-\text{C}(\text{CH}_2)_4-\text{C}(=\text{O})-\text{OH} \end{array}} \text{Condensation polymer}$$

  - $X = \text{COOCH}_3$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$
  - $X = \text{CONH}_2$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$
  - $X = \text{CONH}_2$ ,  $Y = \text{Br}_2/\text{NaOH}$
  - $X = \text{CN}$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$



## Objective Question II

(One or more than one correct option)

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  - $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$
  - $(\text{CH}_3)\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$
  - $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$

**29.** The correct functional group  $X$  and the reagent/reaction conditions  $Y$  in the following schemes are (2011)

$$X-(\text{CH}_2)_4-X \xrightarrow[\substack{\text{O} \\ \text{HO}}]{\substack{\text{(i) } Y \\ \text{heat}}} \text{Condensation polymer}$$

$$\text{HO}-\overset{\text{O}}{\underset{\text{HO}}{\text{C}}}-\text{(CH}_2)_4-\overset{\text{O}}{\underset{\text{OH}}{\text{C}}}-\text{OH}$$

  - $X = \text{COOCH}_3$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$
  - $X = \text{CONH}_2$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$
  - $X = \text{CONH}_2$ ,  $Y = \text{Br}_2/\text{NaOH}$
  - $X = \text{CN}$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$

**Match the Columns**

- 30.** Match the chemical substances in Column I with type of polymers/type of bond in Column II. (2007, 6M)

|    | Column I  | Column II            |
|----|-----------|----------------------|
| A. | Cellulose | p. Natural polymer   |
| B. | Nylon-66  | q. Synthetic polymer |
| C. | Protein   | r. Amide linkage     |
| D. | Sucrose   | s. Glycoside linkage |

**Subjective Questions**

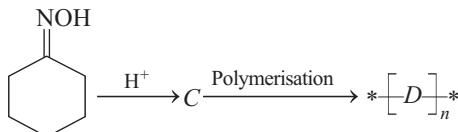
- 31.** Monomer *A* of a polymer on ozonolysis yields two moles of HCHO and one mole of CH<sub>3</sub>COCHO. (2005)

(a) Deduce the structure of *A*.

(b) Write the structure of ‘all *cis*’ – form of polymer of compound *A*.

- 32.** Name the heterogeneous catalyst used in the polymerisation of ethylene. (2003)

- 33.** Give the structures of the products in the following reaction. (2000, 2M)



## Answers

**Topic 1**

- |           |             |         |           |
|-----------|-------------|---------|-----------|
| 1. (a)    | 2. (b)      | 3. (a)  | 4. (d)    |
| 5. (b)    | 6. (b)      | 7. (d)  | 8. (d)    |
| 9. (a)    | 10. (d)     | 11. (a) | 12. (a)   |
| 13. (c)   | 14. (d)     | 15. (a) | 16. (d)   |
| 17. (a)   | 18. (b)     | 19. (a) | 20. (a)   |
| 21. (a)   | 22. (b)     | 23. (a) | 24. (b)   |
| 25. (b)   | 26. (a,c,d) | 27. (d) | 28. (b,c) |
| 29. (b,c) | 30. (c)     | 31. (5) | 32. (1)   |
| 33. (4)   | 34. (4)     | 35. (8) | 36. (6)   |
| 37. (2)   |             |         |           |

**Topic 2**

- |                                         |         |         |         |
|-----------------------------------------|---------|---------|---------|
| 1. (b)                                  | 2. (d)  | 3. (a)  | 4. (a)  |
| 5. (a)                                  | 6. (c)  | 7. (d)  | 8. (b)  |
| 9. (c)                                  | 10. (d) | 11. (c) | 12. (d) |
| 13. (b)                                 | 14. (b) | 15. (b) | 16. (a) |
| 17. (c)                                 | 18. (a) | 19. (a) | 20. (b) |
| 21. (b)                                 | 22. (c) | 23. (c) | 24. (a) |
| 25. (d)                                 | 26. (a) | 27. (d) | 28. (b) |
| 29. (a, b, c, d)                        |         |         |         |
| 30. A → p, s; B → q, r; C → p, r; D → s |         |         |         |

## Hints & Solutions

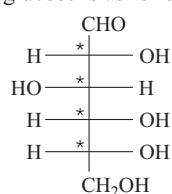
**Topic 1 Biomolecules**

- Statement (a) is incorrect. Glycogen is not a straight chain polymer similar to amylose. It is highly branched structure similar to amylopectin. It is known to be the storage material of animals. It is found in liver, muscles and brain. It breaks down to glucose by the action of enzymes when body needs a glucose. It is also found in yeast and fungi.
- RNA does not have double stranded  $\alpha$ -helix structure. Helices present in RNA are single-stranded but sometimes they fold back on themselves to form a double helix structure. RNA usually does not replicate.

It is present in the nucleus of the cell. It controls the synthesis of protein. RNA molecules are of three types, i.e. messenger's RNA (*m*-RNA), ribosomal RNA (*r*-RNA), transfer RNA (*t*-RNA).

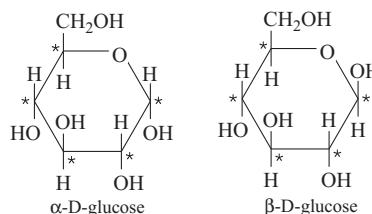
- Key Idea** Chiral centre is also called stereo-centre or stereogenic center.

Linear structure of glucose is as follows :



**Fischer formula** Number of stereo-centre (C\*) = 4.

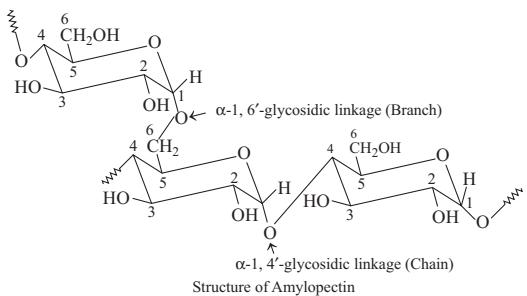
Cyclic structure of glucose are as follows :



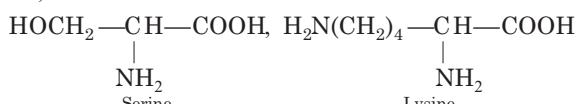
**Haworth formula** Number of stereo-centre (C\*) in each anomer = 5.

- Amylopectin is the water-soluble component of starch. It is a branched-chain polymer of α-D-glucose. The main chain consists of an α - 1, 4'- glycosidic linkages between α - D-glucose units and the branches are connected to the main chain by α - 1,6'- glycosidic linkages. Its structure can be represented as:

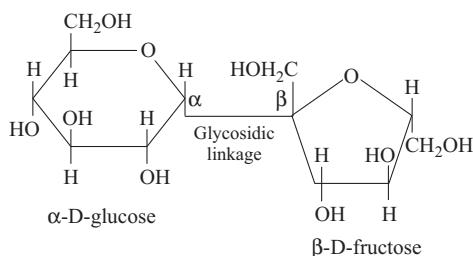
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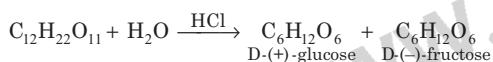
5. The peptide that gives positive cinnic ammonium nitrate and carbyleamine tests is ser - lys. The structures of serine and lysine are



6. Statement-(b) is not true for sucrose. It is linked through a glycosidic linkage between C-1 of  $\alpha$ -glucose and C-2 of  $\beta$ -fructose. Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.



On hydrolysis with acids or enzyme, sucrose gives equimolar mixture of D-(+)-glucose and D-(-)-fructose.



7. Both fructose and glucose give following test positive

(i) Fehling's test (red ppt. of Cu<sub>2</sub>O is obtained).

(ii) Barfoed's test (red ppt. of  $\text{Cu}_2\text{O}$  is obtained)

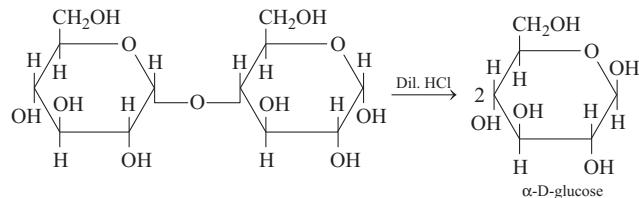
(iii) Benedict's test (red ppt. of  $\text{Cu}_2\text{O}$  is obtained)

Fehling's solution :  $\text{CuSO}_4$  + Na, K-tartrate (Rochelle salt)

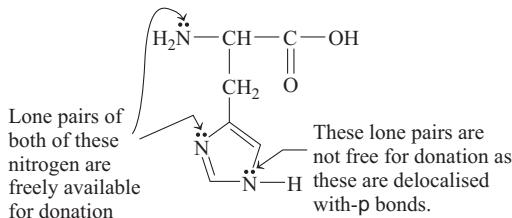
Benedict's solution :  $\text{CuSO}_4$  + Na-citrate +  $\text{Na}_2\text{CO}_3$

Seliwanoff's test is used to differentiate between ketose and aldose. The reagent is a solution of resorcinol in concentrated HCl. The reagent when heated along with a sugar will produce furfural or hydroxy-methylfurfural, which further reacts to give red color. Ketose (fructose) reacts more quickly than aldose (glucose).

8. Maltose on treatment with dil. HCl gives D-glucose. Hydrolysis of maltose yields two moles of  $\alpha$ -D-glucose. Thus, it is composed of two  $\alpha$ -D-glucose units in which C-1 of one glucose unit (I) is linked to C-4 of another glucose unit (II). The free aldehyde group can be produced at C-1 of second glucose in solution and it shows reducing properties. So, it is a reducing sugar.

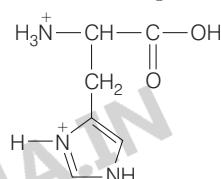


- 9.** Histidine has following structure in



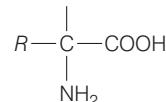
At highly acidic pH, i.e. 2 both the nitrogens with lone pairs will accept one  $\text{H}^+$  each and  $\text{—C}\overset{\text{O}}{\underset{\text{H}}{\text{—}}}\text{OH}$  will not lose its  $\text{H}^+$ . Thus,

the final structure of histidine at pH = 2 will be



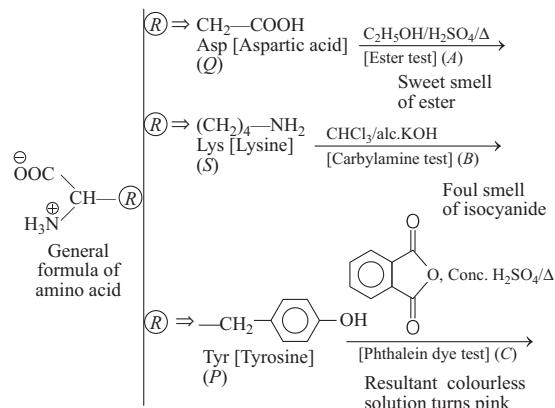
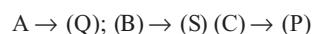
Thus, option (d) is the correct answer.

**Note** Amino acids have following generalise structure:



They have the tendency to lose H<sup>+</sup> of their —COOH group at alkaline (higher) pH while the —NH<sub>2</sub> group present in them have the tendency to gain H<sup>+</sup> at acidic (lower) pH.

- 10.** The correct match is :

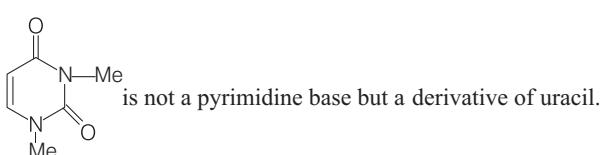
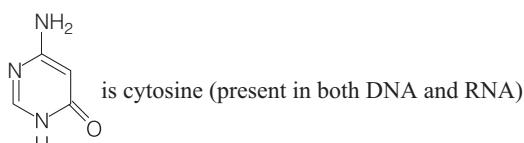
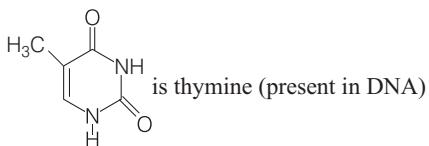
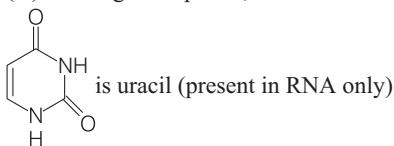


(A) Ester test confirms the presence of  $\text{—COOH}$  group.

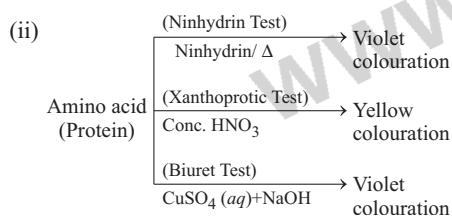
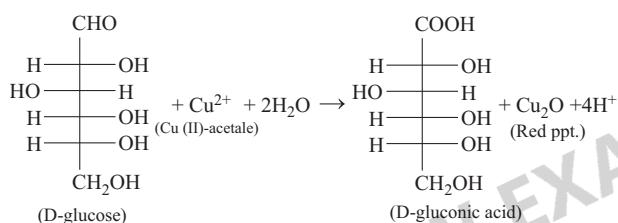
(B) Carbylamine test confirms the presence of  $\text{—NH}_2$  group ( $1^\circ$ ).

(C) Phthalein dye test confirms the presence of phenolic —OH group.

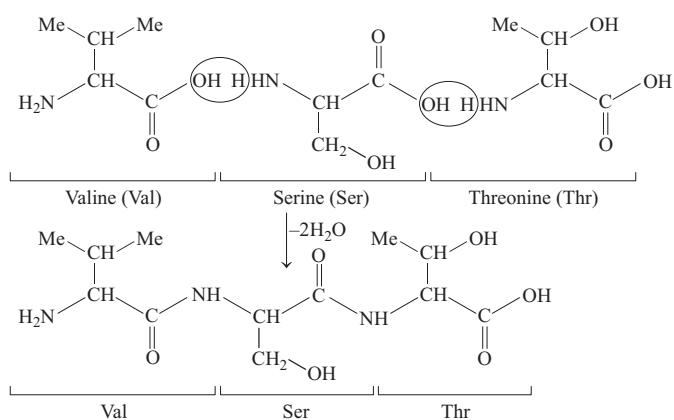
11. RNA contains, adenine (A), guanine (G), cytosine (C) and uracil (U). In the given options,



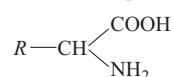
12. (i) Barfoed test is used for detecting the presence of monosaccharides like glucose, fructose etc. Barfoed reagents is Cu (II) acetate solution.



13. Formation of the tripeptide (Val-Ser-Thr) can be shown as:



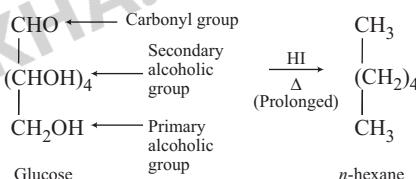
- 14 Amino acid molecules can be represented as,



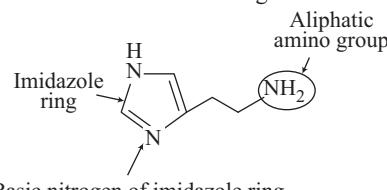
Nature of the 'R' group will determine the basicity (hence,  $pK_a$ ) of an amino acid.

| 'R' in the amino group                                                             | Nature of R | Nature of the amino acids                             |
|------------------------------------------------------------------------------------|-------------|-------------------------------------------------------|
| $-(\text{CH}_2)_3-\text{NH}-\text{C}(=\text{NH}_2)\text{NH}_2$<br>(Arginine : Arg) | Basic       | More basic (due to the presence of acetamidine group) |
| $-\text{CH}_2-\text{C}(=\text{O})\text{O}^-$<br>(Aspartic acid: Asp)               | Acidic      | Acidic                                                |
| $-\text{H}$ (Glycine) : Gly                                                        | Neutral     | Neutral                                               |
| $-(\text{CH}_2)_4-\text{NH}_3^+$<br>(Lysine : Lys)                                 | Basic       | Basic                                                 |

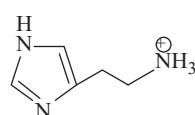
15. HI is a strong reducing agent. It reduces both primary and secondary alcoholic groups of glucose along with the carbonyl group to produce *n*-hexane as



16. Our blood is slightly basic in nature with pH range from 7.35-7.4. The structure of histamine is given below :

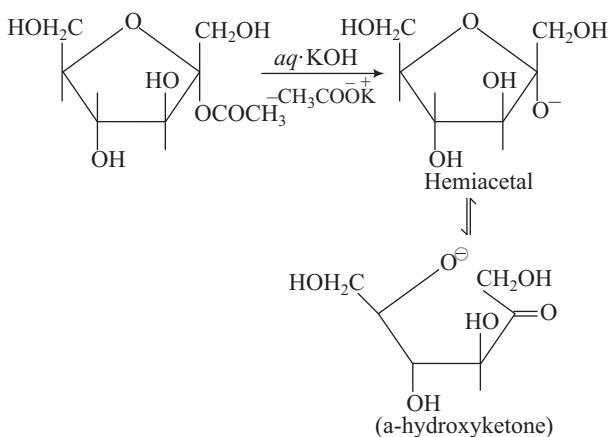


It is produced by decarboxylation of histidine having following structure. It is clearly visible from the above structure that histamine has two basic centres namely aliphatic amino group and basic nitrogen of imidazole ring. The aliphatic amino group has  $pK_a$  around 9.4. In blood with pH around 7.4 the aliphatic amino group of histamine become protonated to give a single charged cation as shown below

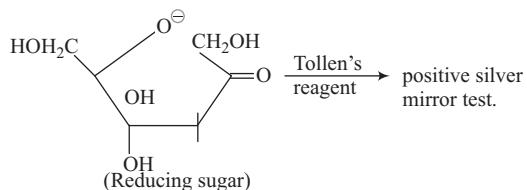


17. Sugars that have an aldehyde, a ketone, a hemiacetal or a hemiketal group is able to reduce an oxidising agent. These sugars are classified as reducing sugars.

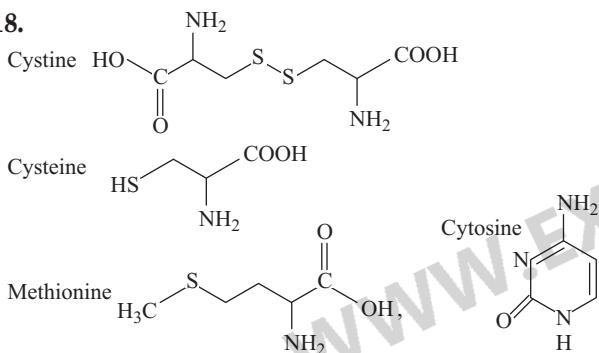
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Hemiacetal can be easily reduced by oxidising agent such as Tollen's reagent.



18.



Thiol group (SH) is present in cysteine.

19. Vitamin B and C are water soluble while vitamin A,D,E and K are fat soluble or water insoluble.

20. Quinoline is an alkaloid, it is not present in DNA. DNA has four nitrogen bases in adenine, guanine, cytosine and thymine.

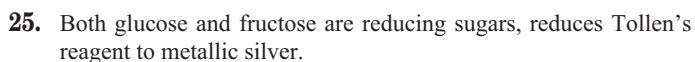
21. 18 ATPs are involved in the formation of 1 glucose molecule as shown in the reaction below :

$$6\text{CO}_2 + 12\text{NADPH} + 18 \text{ATP} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 12\text{NADP} + 18 \text{ADP}$$

22. Here, the — OH of hemiacetal group is equatorial therefore, it is a  $\beta$ -pyranose of an aldohexose.

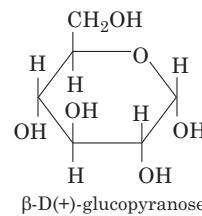
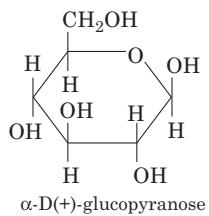
23. The six-membered cyclic ether is known as pyranose while the five membered cyclic ether is known as furanose. Hence, ring (a) is a pyranose and it has ether linkage at  $\alpha$ -position that is known as  $\alpha$ -glycosidic linkage in carbohydrate chemistry.

24. “ $\alpha$ ” and “ $\beta$ ” cyclic hemiacetals of D-glucose having difference in configuration at C-1 only are called anomers.



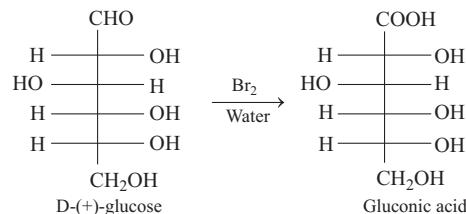
- 26.** The explanation of given statements are as follows:

- (a) Two six membered cyclic hemiacetal form of D-(+)- glucose are called anomers.



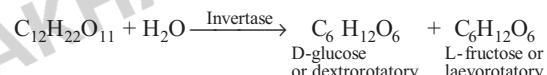
Both are anomers.

- (b) Oxidation of glucose in presence of  $\text{Br}_2$  water gives gluconic acid.



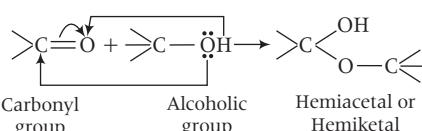
- (c) Monosaccharides can not be hydrolysed into polyhydroxy aldehydes and ketones.

- (d) Hydrolysis of sucrose gives D-glucose and L-fructose.



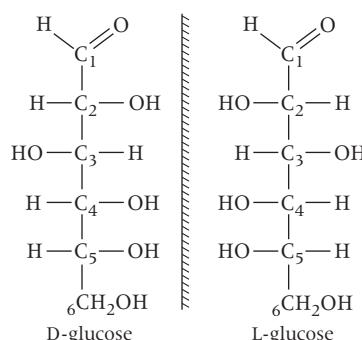
Hence, options (a, c, d) are correct.

27. A pyranose ring is a 6 membered ring having 5 carbon atoms and one oxygen atom. In glucose, it is formed by the reaction between  $>\text{C}=\text{O}$  group at position 1 and  $-\text{OH}$  group at 5th carbon atom. In general reaction between  $>\text{C}=\text{O}$  group and  $\text{---}\overset{\text{---}}{\text{C}}\text{---OH}$  looks like

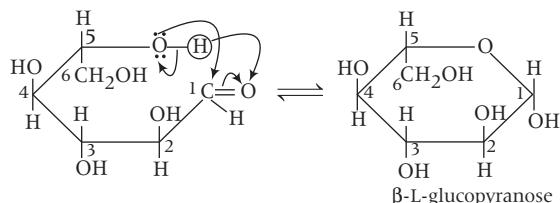


The product formed is called **hemiacetal**.

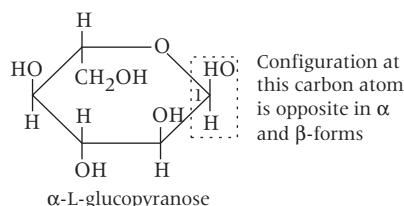
(if  $\text{C}=\text{O}$  group belongs to an aldehyde) or **hemiketal** (if  $>\text{C}=\text{O}$  group belongs to a ketone). L- glucose has the mirror image configuration of D-glucose i.e.,



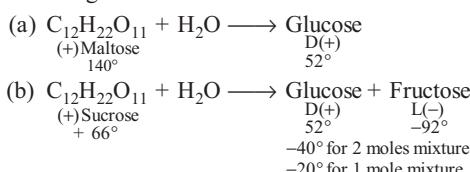
So,  $\beta$ -L glucopyranose is formed as



The  $\alpha$ -L-glucopyranose has configurational change at C<sub>1</sub> only and looks like

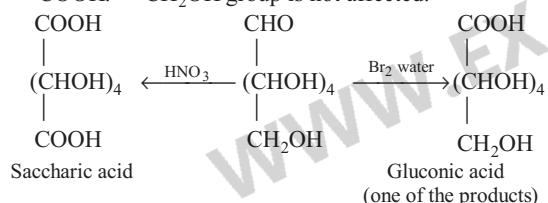


28. If there is inversion of specific rotation from (+) to (-), then invert sugar is formed.



There is formation of invert sugar. Thus, correct.

- (c) Specific rotation of invert sugar is  $-20^\circ$  per mole. Thus, correct.  
 (d)  $Br_2$  water is a weak oxidising agent. It oxidises  $-CHO$  to  $-COOH$ .  $-CH_2OH$  group is not affected.



$HNO_3$  (a strong oxidising agent) oxidises invert sugar to saccharic acid. Thus, incorrect.

29. X is acetal, has no free hemiacetal, hence a non-reducing sugar while Y has a free hemiacetal group, it is reducing sugar. Also, glucosidic linkage of X is ' $\alpha$ ' while that of Y is  $\beta$ -linkage.

30. Statement I is correct Presence of  $-CHO$  group in glucose is tested by Fehling's solution test where a reddish-brown precipitate of  $Cu_2O$  is formed.

Hence, Statement II is incorrect.

31. At pH = 2,

There are two  $-NH_2$  group, and + 1 charge on each group because all amino groups exist in the form of  $-NH_3^+$ .

Therefore,  $|Z_1| = 2$ .

At pH = 6,

$NH_2$  of lysine (+ 1) (pH = 9.47) and  $COOH$  (-1) of glutamic acid (pH = 3.08), so because of dipolar ion exists, therefore  $|Z_2| = 0$ .

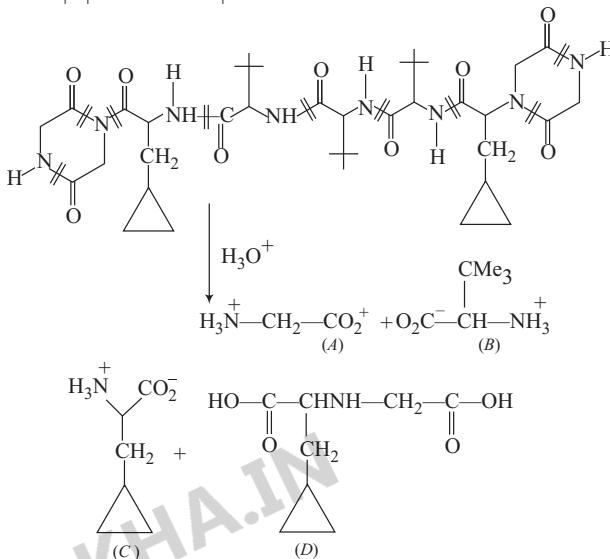
At pH = 11,

$COOH$  of glutamic acid has (- 1),  $COOH$  of lysine (- 1) and  $OH$  of phenol (- 1).

Therefore,  $|Z_3| = |-3| = 3$  (All  $COOH$  and  $OH$  exist in the form of  $-COO^-$  and  $-O^-$ ).

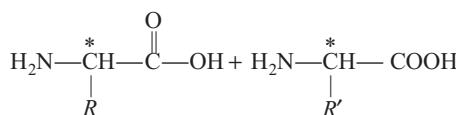
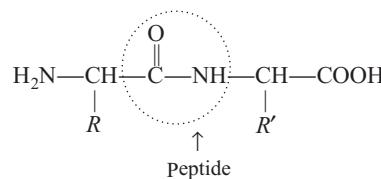
$$\therefore |Z_1| + |Z_2| + |Z_3| = 2 + 0 + 3 = 5$$

32. PLAN This problem can be solved by performing hydrolysis of peptide and deciding the nature of product.  
 Chemical reaction and product formed after hydrolysis of given peptide can be represented as



(A) is glycine which is only naturally occurring amino acid. While (B), (C) and (D) are not the naturally occurring amino acids. Hence, correct integer is (1).

33. PLAN A peptide linkage is hydrolysed to two free amino acids.



$C^*$  is chiral carbon tetrapeptide has four amino acids joined by three peptide linkage.

$-COOH$  group is on alanine part, thus it is at fixed C-terminal position in each combination.

Glycine is optically inactive thus it cannot be on the N-terminal side. Thus, possible combinations are

Phe-Gly-Val-Ala, Phe-Val-Gly-Ala,  
 Val-Gly-Phe-Ala, Val-Phe-Gly-Ala

Thus, in all four combinations are possible.

34. The amino acid remain completely in Zwitter ionic form at its isoelectric point. Amino acids with additional acidic group have their isoelectric pH less than 7.0 and increasing pH above isoelectric point makes them anionic.

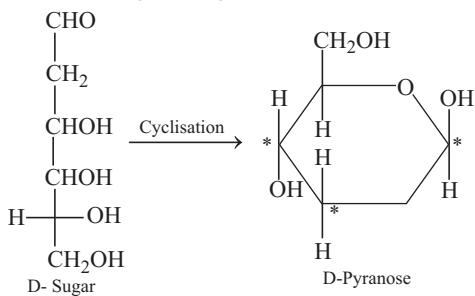
## 496 Biomolecules and Chemistry in Everyday Life

On the other hand, amino acids with additional basic group have their isoelectric pH greater than 7.0 and decreasing pH below isoelectric point (by adding acid solution) makes them cationic. The given peptide with followings  $R_1$  and  $R_2$  are basic, will remain protonated (cationic) at pH = 7.0.

| Peptide | $R_1$                        | $R_2$                        |
|---------|------------------------------|------------------------------|
| IV      | $\text{CH}_2\text{CONH}_2$   | $(\text{CH}_2)_4\text{NH}_4$ |
| VI      | $(\text{CH}_2)_4\text{NH}_2$ | $(\text{CH}_2)_4\text{NH}_4$ |
| VIII    | $\text{CH}_2\text{OH}$       | $(\text{CH}_2)_4\text{NH}_4$ |
| IX      | $(\text{CH}_2)_4\text{NH}_2$ | $\text{CH}_3$                |

Thus, 4 is the correct integer.

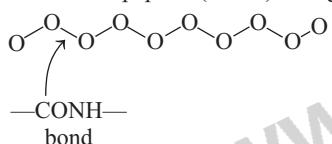
35. The D-form of given sugar is



Configurations at the three chiral carbons (starred) can be changed maintaining D-configuration. Hence, the total number of stereoisomers of D-pyranose =  $2^3 = 8$

Thus, the correct integer is 8.

36. A decapeptide has nine peptide (amide) linkage as



Therefore, on hydrolysis, it will absorb nine water molecules.

Hence, total mass of hydrolysis product =  $796 + 18 \times 9 = 958$

$$\Rightarrow \text{mass of glycine in hydrolysis product} = \frac{958 \times 47}{100} = 450$$

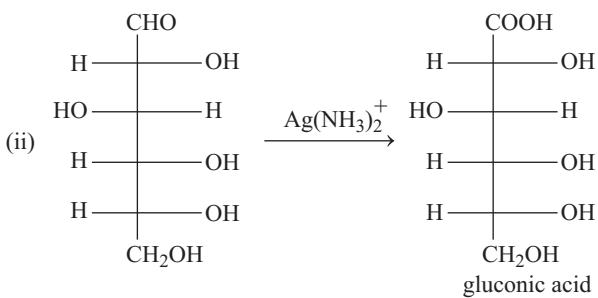
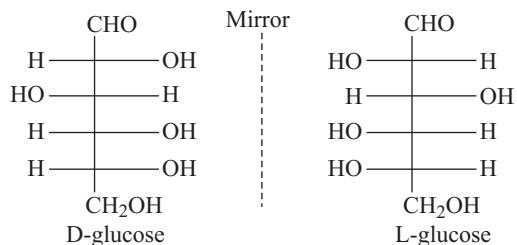
$\Rightarrow$  number of glycine molecule in one

$$\text{molecule of decapeptide} = \frac{450}{75} = 6$$

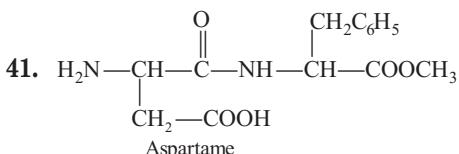
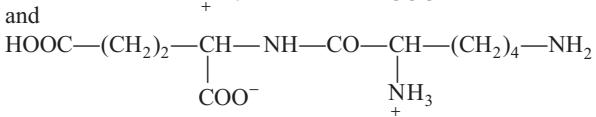
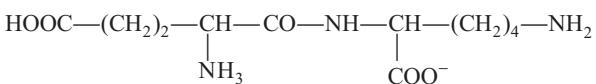
37.  $-\text{OO}^-$  and  $-\text{NH}_2$  are two basic groups in lysine.

38. In structure (a), one ring has a free hemiacetal group, will hydrolyse into open chain in aqueous solution and therefore will reduce Tollen's reagent. Structure (b) has only acetal groups, will not hydrolyse in aqueous solution into open chain, will not reduce Tollen's reagent

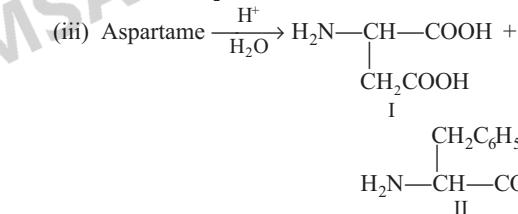
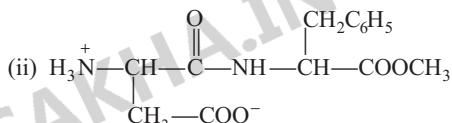
39. (i) D-glucose and L-glucose are enantiomers, hence



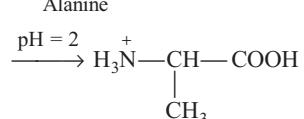
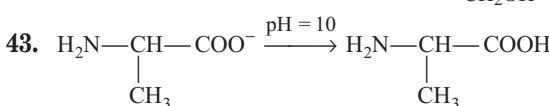
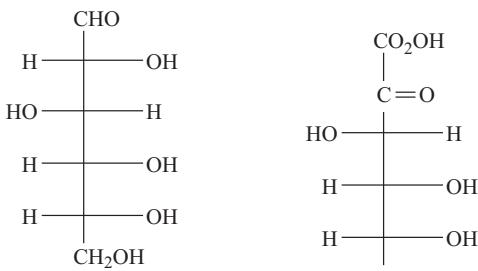
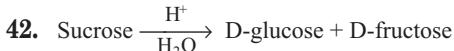
40. The dipeptides are



- (i) Aspartame has amine, acid, amide and ester groups.

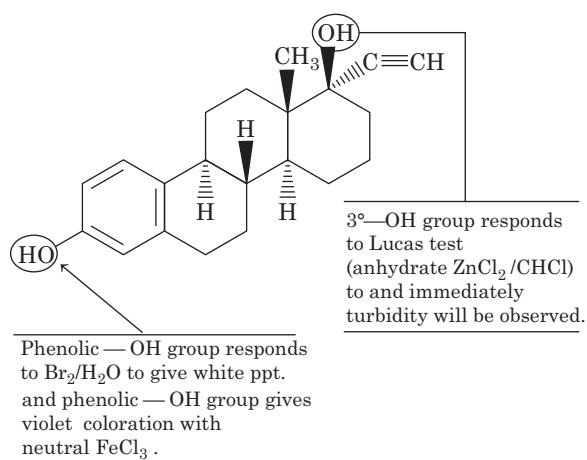


- (iv) II is more hydrophobic due to the presence of phenyl group.



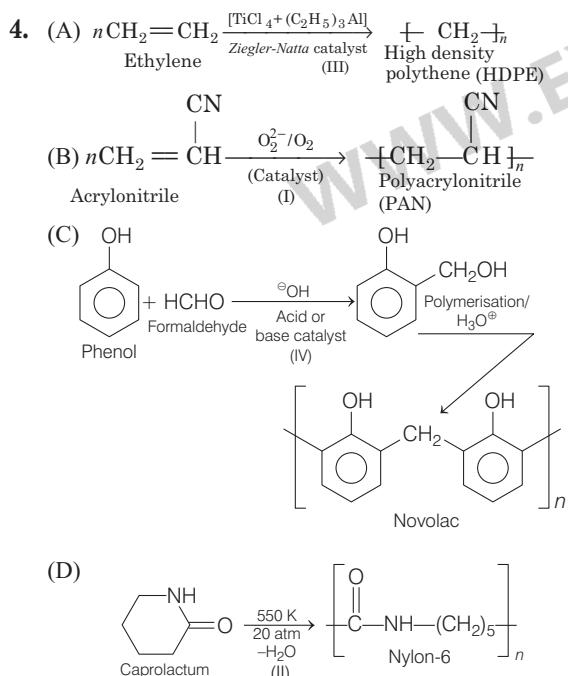
**Topic 2 Chemistry in Everyday Life**

1. The antifertility drug “novestrol” or ethinylestradiol has the following structure :



So, the correct combination of reagents is in option (b).  
i.e.  $Br_2$ /water,  $ZnCl_2/HCl$  and  $FeCl_3$ .

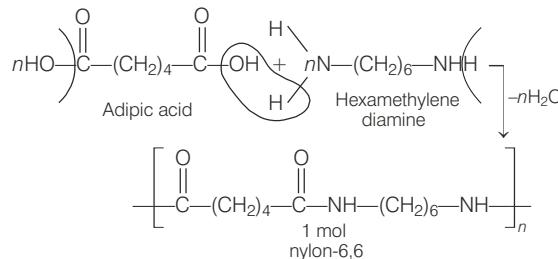
2. Synthetic Brompheniramine is an anti-histamine that is used to treat sneezing, runny nose and itchy or watery eyes caused by allergies, hay fever and the common cold.
3. Bakelite is a thermosetting polymer. These polymers are cross-linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. Once they get set, they cannot be reshaped and reused.



Thus, the correct match is as follows :

- (A)  $\rightarrow$  (III), (B)  $\rightarrow$  (I), (C)  $\rightarrow$  (IV), (D)  $\rightarrow$  (II)

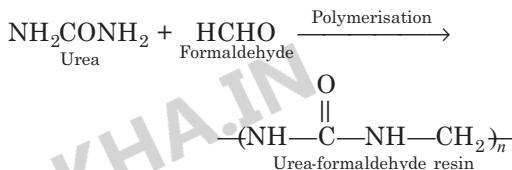
5. Nylon-6, 6 (an amide) is a condensation copolymer because it is obtained by condensation between adipic acid and hexamethylenediamine.



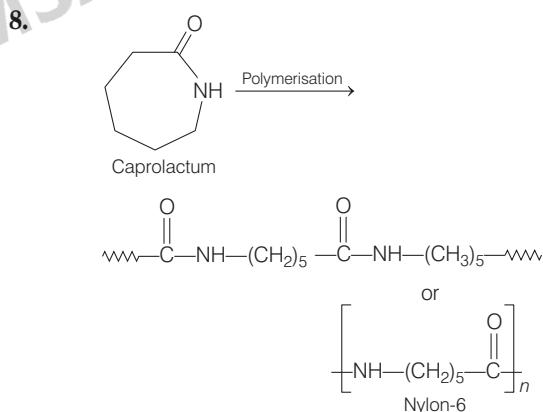
Neoprene, teflon and buna-S are addition polymers.

6. Noradrenaline is one of the example of neurotransmitters. It plays a major role in mood changes. If the level of noradrenaline is low for some reason, then signal-sending activity becomes low and the person suffers from depression.

7. Monomer of  $-\text{NH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}-\text{CH}_2-$  is formaldehyde. The polymer is also known as urea-formaldehyde resin. It is made from urea ( $NH_2CONH_2$ ) and formaldehyde ( $HCHO$ ).

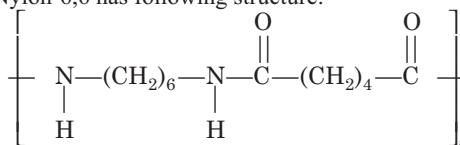


It is used for making unbreakable cups and laminated sheets.



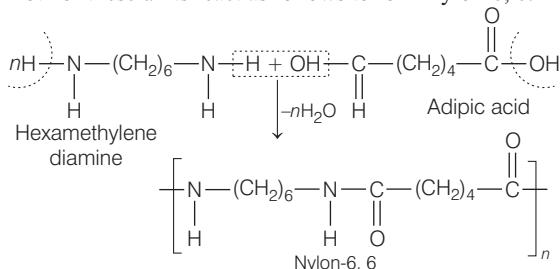
Nylon-6 is prepared by ring opening polymerisation of caprolactum. It is heated about 533 K in an inert atmospheric nitrogen about 4-5 hrs. Nylon-6 fibres are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkle proof and highly resistant to abrasion and chemicals such as acids and alkalis.

9. Nylon-6,6 has following structure:

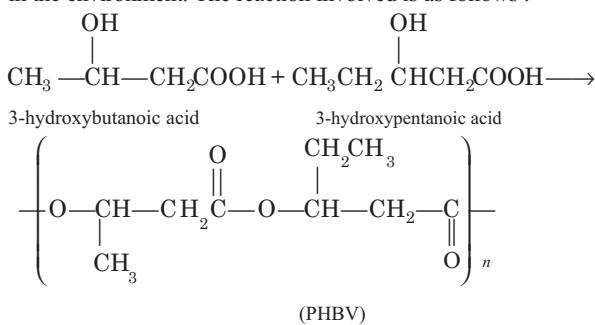


## 498 Biomolecules and Chemistry in Everyday Life

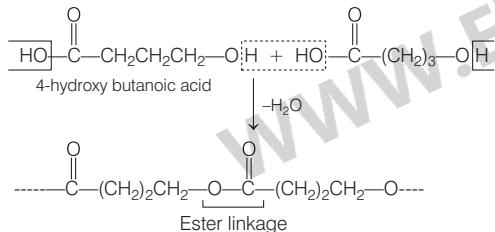
As it is a condensation polymer hence, each of its monomeric unit must contain 6 carbon atoms in them. Hence, a combination of adipic acid and hexamethylene diamine is the correct answer. Both of these units react as follows to form nylon-6, 6.



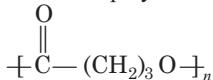
10. Poly- $\beta$ -hydroxy butyrate Co- $\beta$ -hydroxyvalerate (PHBV) is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. It is used in specialty packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment. The reaction involved is as follows :



11. On polymerisation, 4-hydroxy butanoic acid will produce a condensation homopolymer by loss of  $H_2O$  molecules.

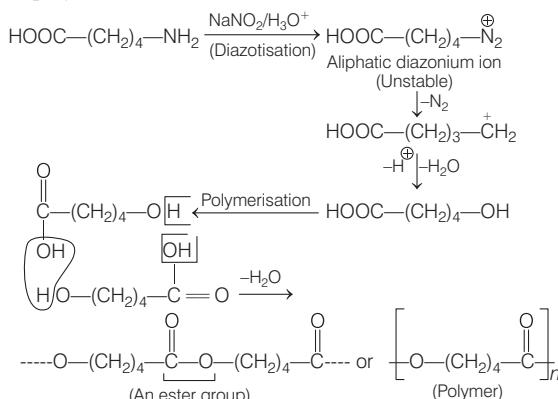


The homopolymer obtained can also be represented as



12. (A) Molecule binding to a site other than the active site of enzyme is called allosteric effect.  
 (B) Molecule binding to the active site of enzyme is called competitive inhibitor.  
 (C) Molecule crucial for communication in the body is called receptor.  
 (D) Molecule binding to the enzyme covalently is called poison.  
 Thus, the correct match is : A  $\rightarrow$  R, B  $\rightarrow$  P, C  $\rightarrow$  Q, D  $\rightarrow$  S
13. Given amino acid on reaction with  $NaNO_2/H_3O^+$  gives diazotisation reaction which further evolves  $N_2$  gas along with formation of carbocation. On further reaction with water, it

form  $HOOC-(CH_2)-OH$  that undergoes polymerisation to give polymer.



14. The correct match is:

A  $\rightarrow$  (Q) B  $\rightarrow$  (P) C  $\rightarrow$  (R)

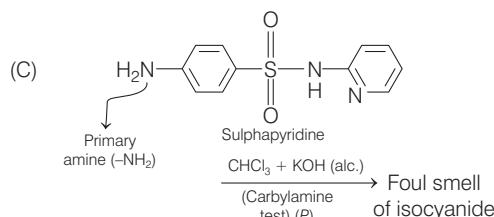
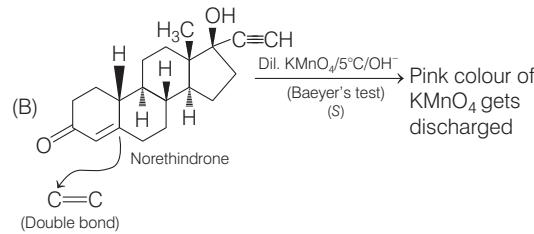
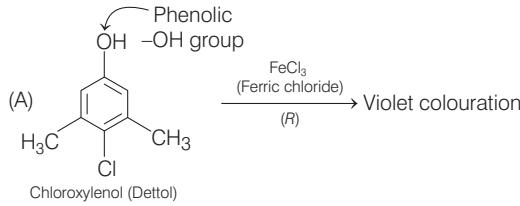
(A) **Norethindrone** It is an antifertility drug (Q) containing synthetic progesterone derivative. [Other similar drug, is ethinylestradiol (novestrol)].

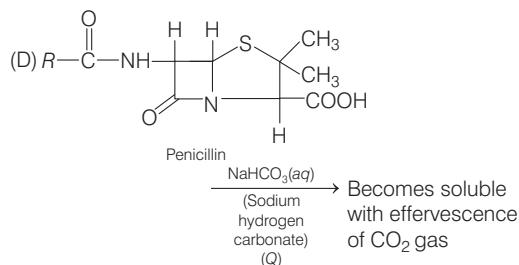
(B) **Oflaxacin** It is an antibiotic (P), i.e produced wholly or partly by chemical synthesis with low concentration of microorganism. [Some other similar drugs : Penicillin, chloramphenicol, salvarsan etc.]

(C) **Equanal (meprobamate)** It is a mild tranquilizer for relieving hypertension. It relieve anxiety, stress, excitement by inducing a sense of well being.

(Other similar drug is chlordiazepoxide.)

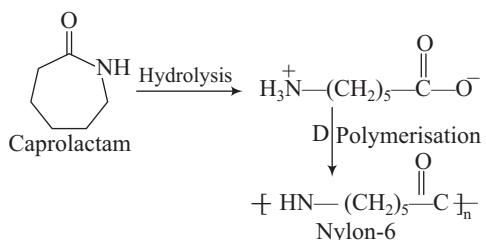
- 15.





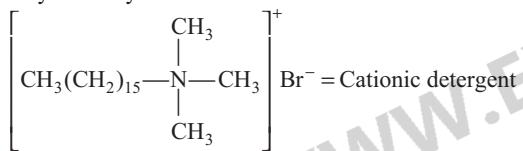
Thus, the correct match is: A  $\rightarrow$  R; B  $\rightarrow$  S; C  $\rightarrow$  P; D  $\rightarrow$  Q

- 16.** Nylon-6 or perlon is prepared by polymerisation of amino caproic acid at high temperature. Caprolactam is first hydrolysed with water to form amino acid which on heating undergoes polymerisation to give nylon-6.



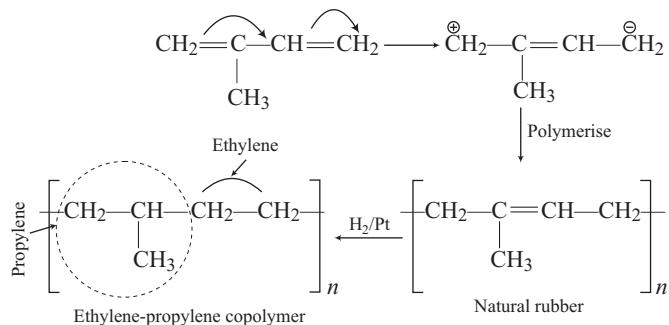
- 17.** High density polythene is used in the manufacture of buckets, dustbins etc.  
**18.** Sodium lauryl sulphate  $[(\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3^-\text{Na}^+)]$  = Anionic detergent

Cetyltrimethyl ammonium bromide

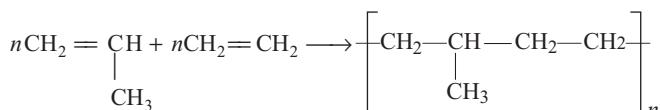


Glyceryl oleate  $[(\text{C}_{17}\text{H}_{32}\text{COO})_3\text{C}_3\text{H}_5]$  = Non-ionic detergent  
 Sodium stearate  $[\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+]$  = Anionic soap

- 19.** Natural rubber is formed by polymerisation of isoprene.



This co-polymer is formed from propylene and ethylene.

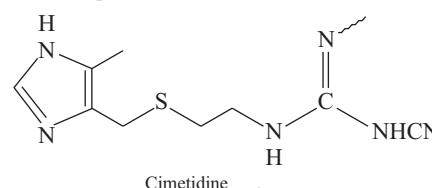


- 20.** (a) Bakelite is used for making gears, protective coating and electrical fittings.  
 (b) Glyptal is used in the manufacture of paints and lacquers.  
 (c) PP is used in the manufacture of textile, packaging materials etc.  
 (d) Polyvinyl chloride (PVC) is used in the manufacture of rain coats, hand bags, leather clothes etc.

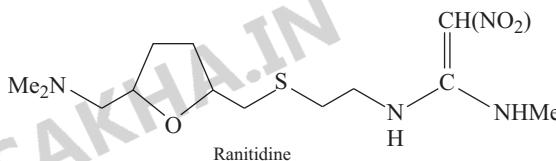
- 21.** (a) Polystyrene- manufacturing toys      (b) Glyptal- Paints and lacquers  
 (c) Polyvinyl chloride (PVC)- Raincoats      (d) Bakelite- computer discs  
 Thus, the correct match is A  $\rightarrow$  (1), B  $\rightarrow$  (1), C  $\rightarrow$  (2), D  $\rightarrow$  (4)

- 22.** The given structure is of aspirin which is used as analgesic.

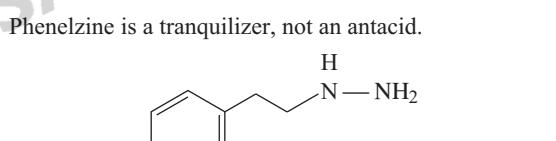
- 23.** Aluminium hydroxide  $\text{Al(OH)}_3$ , cimetidine and ranitidine are antacids while phenelzine is not.



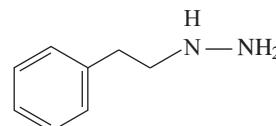
Cimetidine



Ranitidine

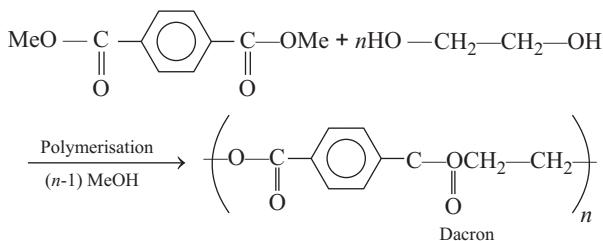


Phenelzine is a tranquilizer, not an antacid.



Phenelzine is used as antidepressant drug.

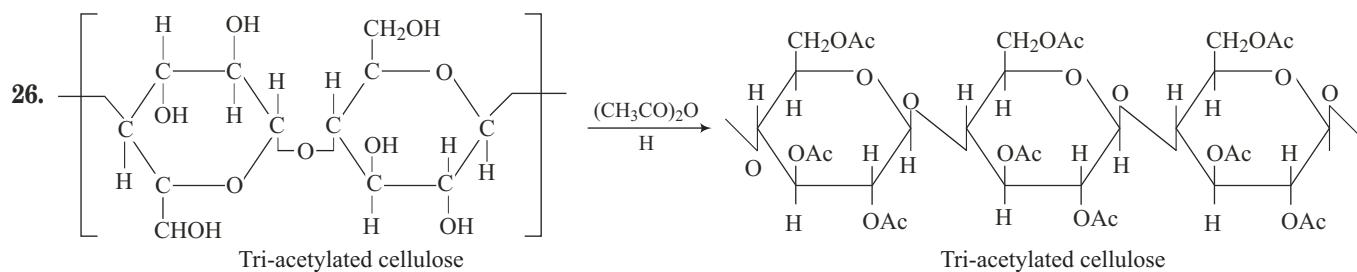
- 24.** Dacron is a condensation polymer of ethylene glycol and methyl terephthalate. Formation of dacron can be shown as



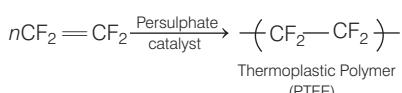
Here, elimination of  $\text{MeOH}$  occurs as a by product. So, this reaction is known as condensation polymerisation.

- 25.** Cellulose and nylons have H-bonding type of intermolecular attraction while poly (vinyl chloride) is polar. Natural rubber is hydrocarbon and has the weakest intermolecular force of attraction, i.e. van der Waals' force of attraction.

## 500 Biomolecules and Chemistry in Everyday Life

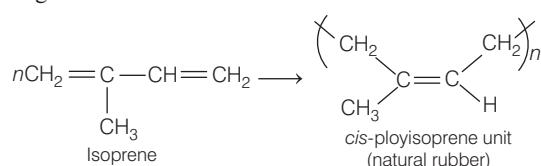


27. The explanation of given statements are as follows: (a) Teflon is prepared by heating tetrafluoroethene in presence of persulphate catalyst at higher pressure.



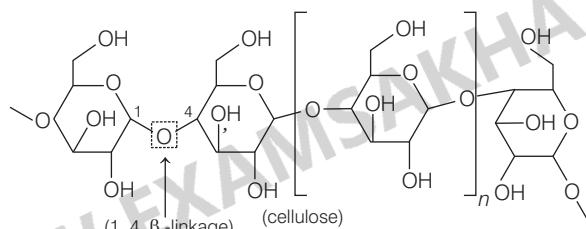
Thus, option (a) is correct.

(b) Natural rubber is polyisoprene containing *cis* alkene units.



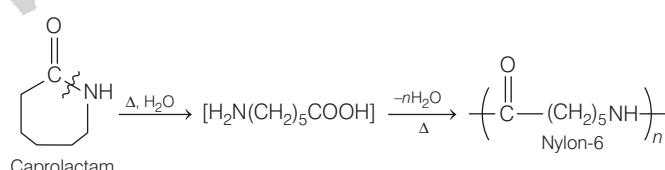
Thus, option (b) is incorrect.

(c) Cellulose has only  $\beta$ -D-glucose units that are joined together by glycosidic linkages as shown in the following structure:



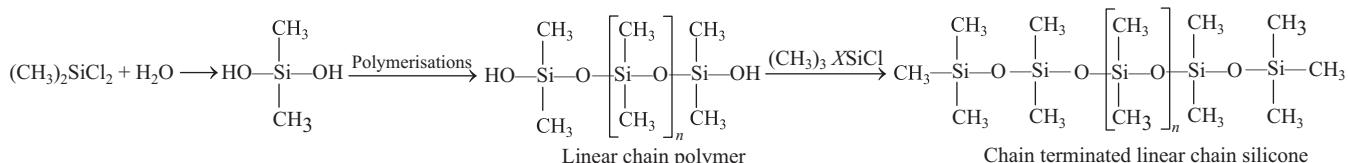
Thus, option (c) is incorrect.

(d) Nylon-6 has amide linkages.

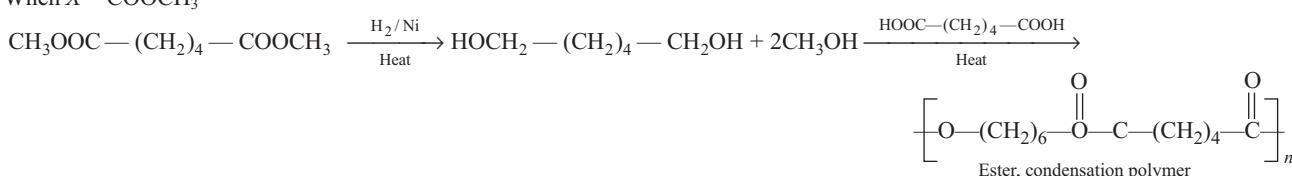


Thus, option (d) is correct.

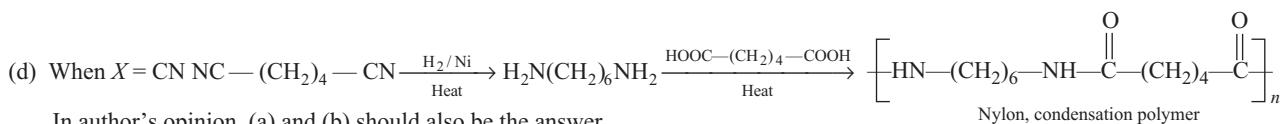
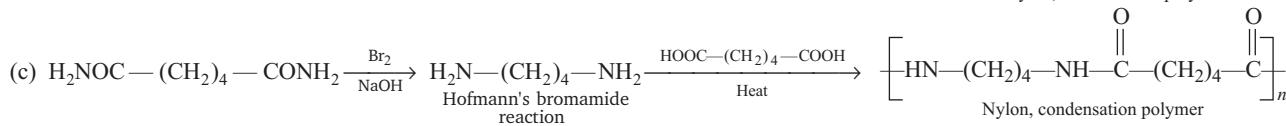
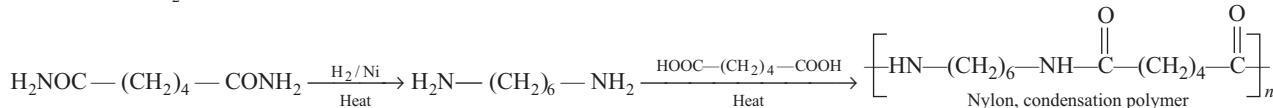
- 28.



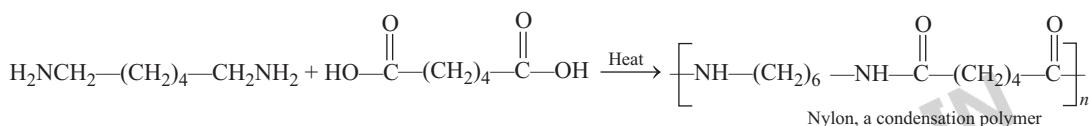
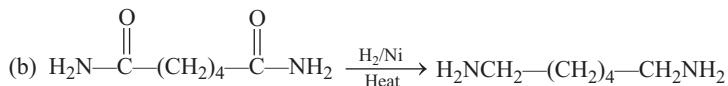
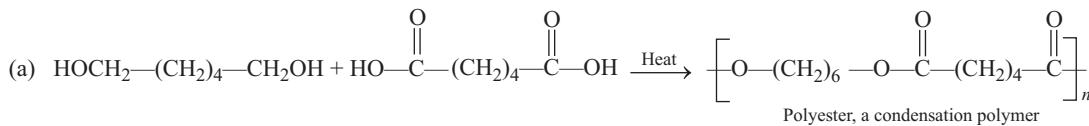
29. (a) When  $X = \text{COOCH}_3$



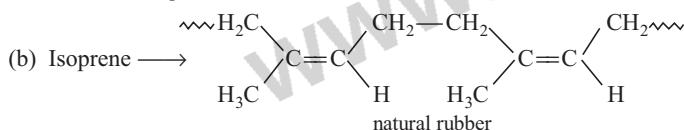
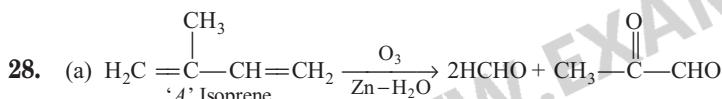
(b) When  $X = \text{CONH}_2$



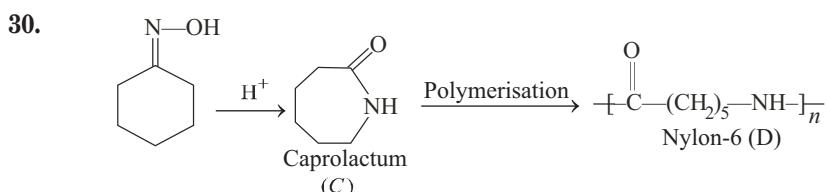
In author's opinion (a) and (b) should also be the answer.



- 27.** (A) Cellulose—a natural polymer of  $\alpha$ -D-glucose, linked by glycoside linkage.  
 (B) Nylon-6, 6—a synthetic polymer of adipic acid and 1,6-diaminohexane. The diacid is linked with diamine through amide linkage.  
 (C) Protein—a natural polymer of  $\alpha$ -amino acids where individual amino acid units are linked by amide linkage.  
 (D) Sucrose—has glycoside linkage, a disaccharide.



- 29.** Zeigler-Natta catalyst, which is a mixture of triethylaluminium ' $(\text{C}_2\text{H}_5)_3\text{Al}$ ' and  $\text{TiCl}_4$ , is used as heterogeneous catalyst in polymerisation of ethylene.



33

# **Environmental Chemistry**

## **Objective Questions I** (Only one correct option)

- 21.** The condition for methemoglobinemia by drinking water is  
 (2019 Main, 9 Jan II)  
 (a) > 50 ppm nitrate      (b) > 50 ppm chloride  
 (c) > 50 ppm lead      (d) > 100 ppm sulphate

- 22.** A water sample has ppm level concentration of the following metals: Fe = 0.2; Mn = 5.0; Cu = 3.0; Zn = 5.0. The metal that makes the water sample unsuitable for drinking is  
 (2019 Main, 9 Jan I)  
 (a) Cu      (b) Fe      (c) Mn      (d) Zn

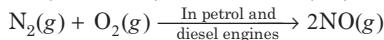
## Answers

1. (b)      2. (c)      3. (b)      4. (b)  
 5. (a)      6. (d)      7. (d)      8. (c)  
 9. (d)      10. (d)      11. (a)      12. (d)

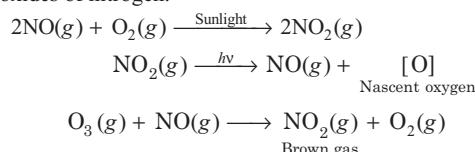
13. (a)      14. (d)      15. (a)      16. (d)  
 17. (b)      18. (a)      19. (d)      20. (c)  
 21. (a)      22. (c)

## Hints & Solutions

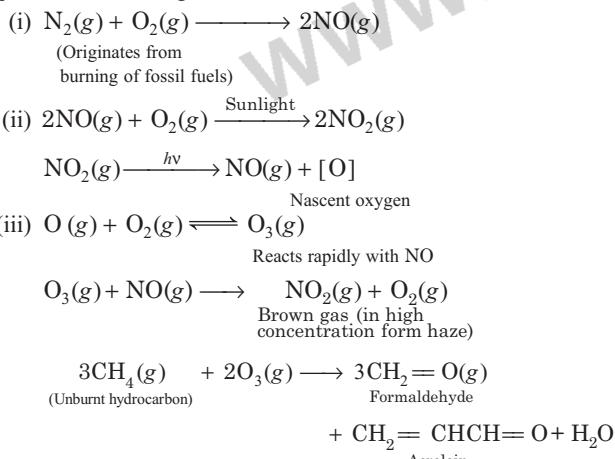
- 1.** The primary pollutant that leads to photochemical smog is nitrogen oxides. Burning of fossil fuels such as petrol and diesel in automobiles, reaction between nitrogen and oxygen and other such reactions result in a variety of pollutants, two main of which are hydrocarbons (unburnt fuel) and nitric oxide (NO).



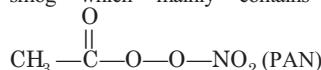
When the concentration of these pollutants is sufficiently high, a chain reaction initiate because of the interaction of sunlight with oxides of nitrogen.



- 2.** The correct set of species responsible for the photochemical smog is NO, NO<sub>2</sub>, O<sub>3</sub> and hydrocarbons. Photochemical smog appears in warm, dry and sunny climate which are obtained by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides. Following reactions are involved during the formation of photochemical smog.



- 3.** In sunlight oxidising smog or photochemical smog or Los-Angeles smog is formed. This smog is brown in colour. It occurs in warm, dry and sunny climate. In presence of sunlight, NO<sub>x</sub> (N-oxides), O<sub>2</sub> and unburnt hydrocarbons of air combine to produce photochemical smog which mainly contains peroxyacetyl nitrate (PAN).



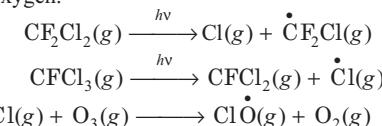
- 4.** The lowest region of atmosphere is troposphere which extends upto the height of 10 km (approx) from sea level. We live in the tropospheric region. It contains air, water vapour and dust which can form clouds with the help of strong air movement.

Above the troposphere, stratospheric region extends upto 50 km from sea level. It contains mainly N<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub> and little water vapour. O<sub>3</sub> in the stratosphere absorbs 99.5% of the sun's harmful UV radiations and thus protects the lives on the earth.

- 5.** The atmosphere between the heights 10 to 50 km above the sea level is stratosphere. Atmosphere is not of the same thickness at heights.  
**6.** The effect of release of CO<sub>2</sub> gas into atmosphere is global warming.  
**7.** According to W.H.O. and US environmental protection agency guidelines, maximum allowable concentration of metals in drinking water are as follows :

| Metal | Maximum concentration<br>(ppm or mg dm <sup>-3</sup> ) |
|-------|--------------------------------------------------------|
| Cd    | 0.005                                                  |
| Mn    | 0.05 (option-c)                                        |
| Al    | 0.2                                                    |
| Fe    | 0.2                                                    |
| Cu    | 3.0 (option-d)                                         |
| Zn    | 5.0 (option-a)                                         |

- 8.** Ozone is destroyed by CFCs in the upper stratosphere. These compounds ultimately reach the stratosphere where they get broken down by powerful UV radiations and release chlorine free radical. The chlorine free radicals react with ozone and cause its depletion by converting it into chlorine monoxide radical and molecular oxygen.



Ozone holes increase the amount of UV radiation reaching the earth. These radiations can cause skin cancer, sunburns, ageing of skin.

- 9.** Using plastic bags is wrong with respect to responsibility as a human being to protect our environment. Plastic bags are non-biodegradable in nature. It remains in the environment as such and does not degraded by bacteria. If it is not disposed properly then it may lead serious threat to the environment. The activities that can be used to protect our environment are as follows:

- Restricting the use of vehicles.
- Avoiding the use of flood lighted facilities.
- Setting up compost tin in gardens.



# JEE ADVANCED

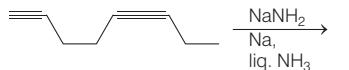
## Solved Paper 2021

### Paper 1

#### SECTION 1

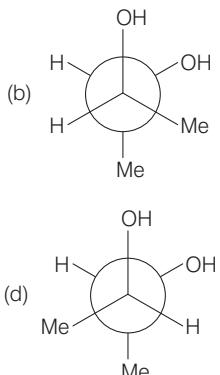
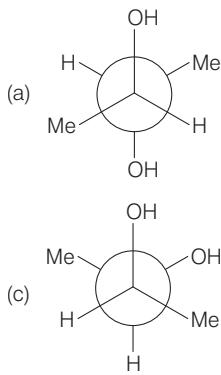
- This section contains **FOUR (04)** questions.
- Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:  
Full Marks : +3 If ONLY the correct option is chosen;  
Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered);  
Negative Marks : -1 In all other cases.

1. The major product formed in the following reaction is



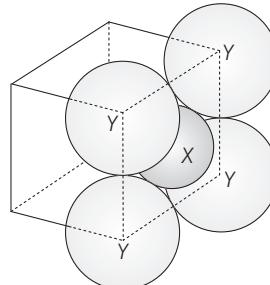
- (a)
- (b)
- (c)
- (d)

2. Among the following, the conformation that corresponds to the most stable conformation of meso-butane-2,3-diol is



3. For the given close packed structure of a salt made of cation X and anion Y shown below (ions of only one face are shown for clarity), the packing fraction is approximately

$$\text{packing fraction} = \frac{\text{packing efficiency}}{100}$$



- (a) 0.74  
(b) 0.63  
(c) 0.52  
(d) 0.48

4. The calculated spin only magnetic moments of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $[\text{CuF}_6]^{3-}$  in BM, respectively, are (Atomic numbers of Cr and Cu are 24 and 29, respectively)

- (a) 3.87 and 2.84  
(b) 4.90 and 1.73  
(c) 3.87 and 1.73  
(d) 4.90 and 2.84

**2 JEE Advanced Solved Paper 2021**

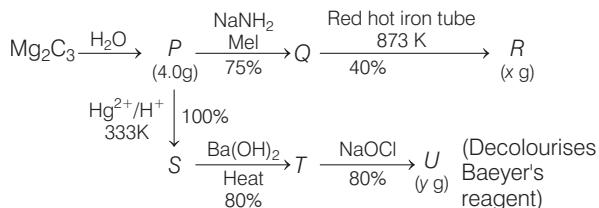
SECTION 2

- This section contains **THREE (03)** question stems.
  - There are **TWO (02)** questions corresponding to each question stem.
  - The answer to each question is a **NUMERICAL VALUE**.
  - For each question, enter the correct numerical value corresponding to the answer in the designated place using the mouse and the on-screen virtual numeric keypad.
  - If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
  - Answer to each question will be evaluated according to the following marking scheme:  
**Full Marks** : +2 If ONLY the correct numerical value is entered at the designated place;  
**Zero marks** : 0 In all other cases.

***Question Stem for Question Nos. 5 and 6***

## Question Stem

For the following reaction scheme, percentage yields are given along the arrow:



$x$  g and  $y$  g are mass of  $R$  and  $U$ , respectively.

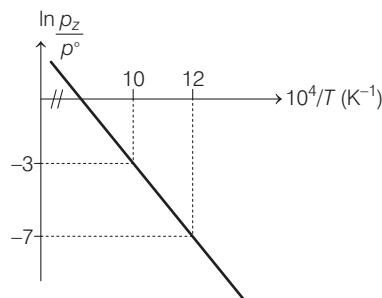
(Use Molar mass (in g mol<sup>-1</sup>) of H, C and O as 1, 12 and 16, respectively)

- 5.** The value of  $x$  is ..... .  
**6.** The value of  $y$  is ..... .

**Question Stem for Question Nos. 7 and 8**

## Question Stem

For the reaction,  $X(s) \rightleftharpoons Y(s) + Z(g)$ , the plot of  $\ln \frac{p_Z}{p^\circ}$  versus  $\frac{10^4}{T}$  is, given below (in solid line), where  $p_Z$  is the pressure (in bar) of the gas  $Z$  at temperature  $T$  and  $p^\circ = 1$  bar.



(Given,  $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}$ , where the equilibrium

constant,  $K = \frac{p_Z}{p^\circ}$  and the gas constant,  
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

7. The value of standard enthalpy,  $\Delta H^\circ$  (in  $\text{kJ mol}^{-1}$ ) for the given reaction is ..... .

8. The value of,  $\Delta S^\circ$  (in  $\text{JK}^{-1} \text{mol}^{-1}$ ) for the given reaction, at 1000 K is ..... .

***Question Stem for Question Nos. 9 and 10***

## Question Stem

The boiling point of water in a 0.1 molal silver nitrate solution (solution *A*) is  $x^{\circ}\text{C}$ . To this solution *A*, an equal volume of 0.1 molal aqueous barium chloride solution is added to make a new solution *B*. The difference in the boiling points of water in the two solutions *A* and *B* is  $y \times 10^{-2}^{\circ}\text{C}$ .

(Assume: Densities of the solutions *A* and *B* are the same as that of water and the soluble salts dissociate completely).

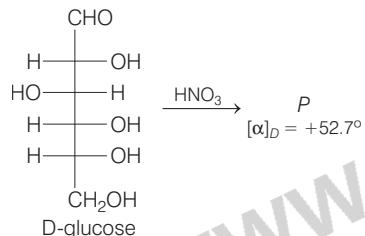
Use Molal elevation constant (Ebullioscopic constant),  $K_b = 0.5 \text{ K kg mol}^{-1}$ ; (Boiling point of pure water as 100°C.)

- 9.** The value of  $x$  is .....  
**10.** The value of  $|y|$  is .....

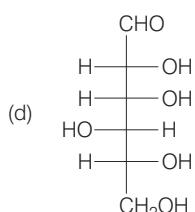
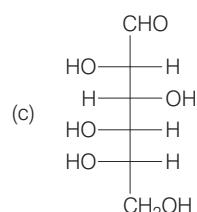
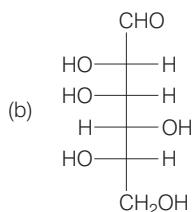
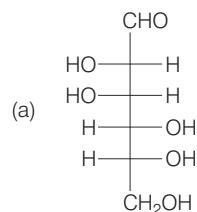
### SECTION 3

- This section contains **SIX (06)** questions.
  - Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct answer(s).
  - For each question, choose the option(s) corresponding to (all) the correct answer(s).
  - Answer to each question will be evaluated according to the following marking scheme:
- Full Marks** : +4 If only (all) the correct option(s) is(are) chosen;  
**Partial Marks** : +3 If all the four options are correct but ONLY three options are chosen;  
**Partial Marks** : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct;  
**Partial Marks** : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option;  
**Zero Marks** : 0 If unanswered;  
**Negative Marks** : -2 In all other cases.
- For example, in a question, if (a), (b) and (d) are the ONLY three options corresponding to correct answers, then choosing ONLY (a), (b) and (d) will get +4 marks;  
 choosing ONLY (a) and (b) will get +2 marks;  
 choosing ONLY (a) and (d) will get +2 marks;  
 choosing ONLY (b) and (d) will get +2 marks;  
 choosing ONLY (a) will get +1 mark;  
 choosing ONLY (b) will get +1 mark;  
 choosing ONLY (d) will get +1 mark;  
 choosing no option(s) (i.e. the question is unanswered) will get 0 marks and choosing any other option(s) will get -2 marks.

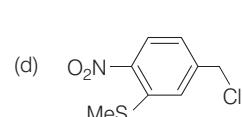
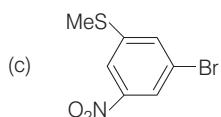
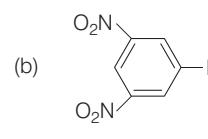
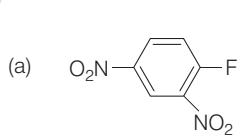
11. Given,



The compound(s), which on reaction with  $\text{HNO}_3$  will give the product having degree of rotation,  $[\alpha]_D = -52.7^\circ$  is (are)



12. The reaction of *Q* with  $\text{PhSNa}$  yields an organic compound (major product) that gives positive Carius test on treatment with  $\text{Na}_2\text{O}_2$  followed by addition of  $\text{BaCl}_2$ . The correct option(s) for *Q* is(are)

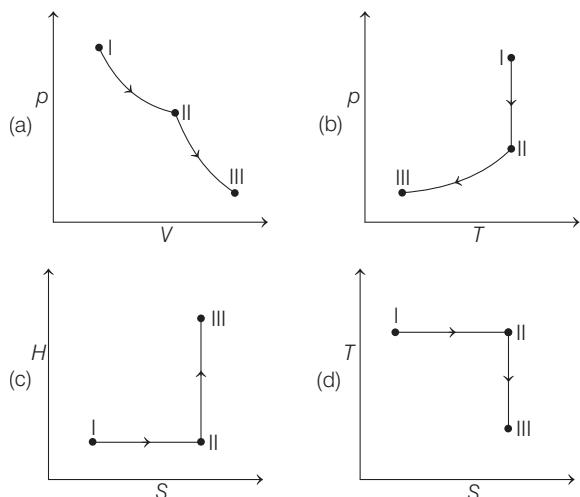


13. The correct statement(s) related to colloids is(are)

- the process of precipitating colloidal sol by an electrolyte is called peptisation.
- colloidal solution freezes at higher temperature, than the true solution at the same concentration.
- surfactants form micelle above critical micelle concentration (CMC). CMC depends on temperature.
- micelles are macromolecular colloids

14. An ideal gas undergoes a reversible isothermal expansion from state I to state II followed by a reversible adiabatic expansion from state II to state III. The correct plot(s) representing the changes from state I to state III is(are) ( $p$  = pressure,  $V$  = volume,  $T$  = temperature,  $H$  = enthalpy,  $S$  = entropy)

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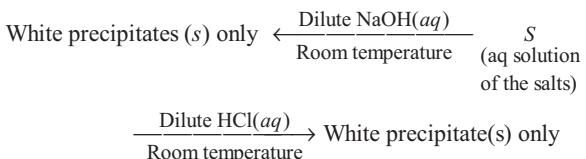


- 15.** The correct statement(s) related to the metal extraction processes is(are)

(a) a mixture of PbS and PbO undergoes self-reduction to produce Pb and SO<sub>2</sub>.

- (b) in the extraction process of copper from copper pyrites, silica is added to produce copper silicate.  
 (c) partial oxidation of sulphide ore of copper by roasting, followed by self-reduction produces blister copper.  
 (d) in cyanide process, zinc powder is utilised to precipitate gold from Na[Au(CN)<sub>2</sub>]

- 16.** A mixture of two salts is used to prepare a solution *S*, which gives the following results



The correct option(s) for the salt mixture is (are)

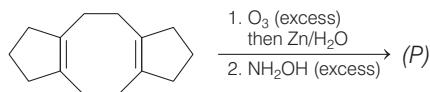
- (a) Pb(NO<sub>3</sub>)<sub>2</sub> and Zn(NO<sub>3</sub>)<sub>2</sub>  
 (b) Pb(NO<sub>3</sub>)<sub>2</sub> and Bi(NO<sub>3</sub>)<sub>3</sub>  
 (c) AgNO<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub>  
 (d) Pb(NO<sub>3</sub>)<sub>2</sub> and Hg(NO<sub>3</sub>)<sub>2</sub>

## SECTION 4

- This section contains **THREE (03)** questions.
  - The answer to each question is a **NON-NEGATIVE INTEGER**.
  - For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
  - Answer to each question will be evaluated according to the following marking scheme:
- Full Marks : +4 If ONLY the correct integer is entered;  
 Zero Marks : 0 In all other cases.

- 17.** The maximum number of possible isomers (including stereoisomers) which may be formed on mono-bromination of 1-methylcyclohex-1-ene using Br<sub>2</sub> and UV light is .....

- 18.** In the reaction given below, the total number of atoms having sp<sup>2</sup> hybridisation in the major product *P* is .....



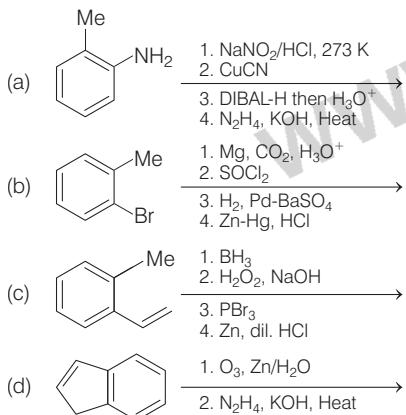
- 19.** The total number of possible isomers for [Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] Br<sub>2</sub> is .....

# Paper 2

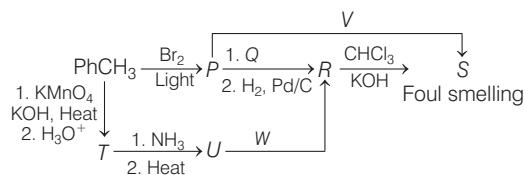
## Section 1

- This section contains **SIX (06)** questions.
  - Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct answer(s).
  - For each question, choose the option(s) corresponding to (all) the correct answer(s).
  - Answer to each question will be evaluated according to the following marking scheme:  
*Full Marks* : +4 If only (all) the correct option(s) is(are) chosen;  
*Partial Marks* : +3 If all the four options are correct but ONLY three options are chosen;  
*Partial Marks* : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct;  
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*Negative Marks* : -2 In all other cases.
  - For example, in a question, if (a), (b) and (d) are the ONLY three options corresponding to correct answers, then choosing ONLY (a), (b) and (d) will get +4 marks;  
choosing ONLY (a) and (b) will get +2 marks;  
choosing ONLY (a) and (d) will get +2 marks;  
choosing ONLY (b) and (d) will get +2 marks;  
choosing ONLY (a) will get +1 mark;  
choosing ONLY (b) will get +1 mark;  
choosing ONLY (d) will get +1 mark;  
choosing no option(s) (i.e. the question is unanswered) will get 0 marks and  
choosing any other option(s) will get -2 marks.

**1.** The reaction sequence(s) that would lead to *o*-xylene as the major product is(are)



**2.** Correct option(s) for the following sequence of reactions is(are)



- (a) Q =  $\text{KNO}_2$ , W =  $\text{LiAlH}_4$   
 (b) R = benzenamine, V =  $\text{KCN}$   
 (c) Q =  $\text{AgNO}_2$ , R = phenylmethanamine  
 (d) W =  $\text{LiAlH}_4$ , V =  $\text{AgCN}$

3. For the following reaction,  $2X + Y \xrightarrow{k} P$

the rate of reaction is  $\frac{d[P]}{dt} = k[X]$ . Two moles of  $X$  are mixed with one mole of  $Y$  to make 1.0 L of solution. At 50 s, 0.5 mole of  $Y$  is left in the reaction mixture. The correct statement(s) about the reaction is(are)  
**(Use  $\ln 2 = 0.693$ )**

- (a) the rate constant  $k$ , of the reaction is  $13.86 \times 10^{-4} \text{ s}^{-1}$ .  
 (b) half-life of  $X$  is 50 s.  
 (c) at 50 s,  $-\frac{d[X]}{dt} = 13.86 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ .  
 (d) at 100 s,  $-\frac{d[Y]}{dt} = 3.46 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ .

**4.** Some standard electrode potentials at 298 K are given below :

$$\text{Pb}^{2+} / \text{Pb} = -0.13 \text{ V} \quad \text{Ni}^{2+} / \text{Ni} = -0.24 \text{ V}$$

To a solution containing 0.001 M of  $X^{2+}$  and 0.1 M of  $Y^{2+}$ , the metal rods  $X$  and  $Y$  are inserted (at 298 K) and connected by a conducting wire. This resulted in dissolution of  $X$ . The correct combination(s) of  $X$  and  $Y$ , respectively, is(are)

(Given, Gas constant,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ , Faraday constant,  $F = 96500 \text{ C mol}^{-1}$ )

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5. The pair(s) of complexes where in both exhibit tetrahedral geometry is(are)

(Note py = pyridine)

(Given atomic numbers of Fe, Co, Ni and Cu are 26, 27, 28 and 29, respectively)

- (a)  $[\text{FeCl}_4]^-$  and  $[\text{Fe}(\text{CO})_4]^2-$     (b)  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{CoCl}_4]^{2-}$   
(c)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$     (d)  $[\text{Cu}(\text{py})_4]^{+}$  and  $[\text{Cu}(\text{CN})_4]^{3-}$

6. The correct statement(s) related to oxoacids of phosphorous is(are)

- (a) upon heating,  $\text{H}_3\text{PO}_3$  undergoes disproportionation reaction to produce  $\text{H}_3\text{PO}_4$  and  $\text{PH}_3$ .  
(b) while  $\text{H}_3\text{PO}_3$  can act as reducing agent,  $\text{H}_3\text{PO}_4$  cannot.  
(c)  $\text{H}_3\text{PO}_3$  is a monobasic acid.  
(d) the H atom of P—H bond in  $\text{H}_3\text{PO}_3$  is not ionisable in water.

## SECTION 2

- This section contains **THREE (03)** question stems.
- There are **TWO (02)** questions corresponding to each question stem.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value corresponding to the answer in the designated place using the mouse and the on-screen virtual numeric keypad.
- If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +2 If ONLY the correct numerical value is entered at the designated place;  
Zero Marks : 0 In all other cases.

### Question Stem for Question Nos. 7 and 8

#### Question Stem

At 298 K, the limiting molar conductivity of a weak monobasic acid is  $4 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$ . At 298 K, for an aqueous solution of the acid the degree of dissociation is  $\alpha$  and the molar conductivity is  $y \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$ . At 298 K, upon 20 times dilution with water, the molar conductivity of the solution becomes  $3y \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$ .

7. The value of  $\alpha$  is .....

8. The value of  $y$  is .....

### Question Stem for Question Nos. 9 and 10

#### Question Stem

Reaction of  $x$  g of Sn with HCl quantitatively produced a salt. Entire amount of the salt reacted with  $y$  g of nitrobenzene in the presence of required amount of HCl to produce 1.29 g of an organic salt (quantitatively).

(Use molar masses (in  $\text{g mol}^{-1}$ ) of H, C, N, O, Cl and Sn as 1, 12, 14, 16, 35 and 119, respectively).

9. The value of  $x$  is .....

10. The value of  $y$  is .....

### Question Stem for Question Nos. 11 and 12

#### Question Stem

A sample (5.6 g) containing iron is completely dissolved in cold dilute HCl to prepare a 250 mL of solution. Titration of 25.0 mL of this solution requires 12.5 mL of 0.03 M  $\text{KMnO}_4$  solution to reach the end point. Number of moles of  $\text{Fe}^{2+}$  present in 250 mL solution is  $x \times 10^{-2}$  (consider complete dissolution of  $\text{FeCl}_2$ ). The amount of iron present in the sample is  $y\%$  by weight.

(Assume:  $\text{KMnO}_4$  reacts only with  $\text{Fe}^{2+}$  in the solution  
Use Molar mass of iron as  $56 \text{ g mol}^{-1}$ )

11. The value of  $x$  is .....

12. The value of  $y$  is .....

## SECTION 3

- This section contains **TWO (02) paragraphs**. Based on each paragraph, there are **TWO (02)** questions.
- Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
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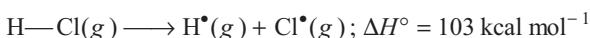
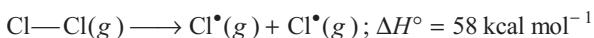
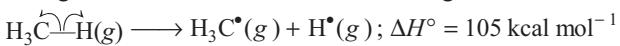
Full Marks : +3 If ONLY the correct option is chosen;

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered);

Negative Marks : -1 In all other cases.

**Paragraph**

The amount of energy required to break a bond is same as the amount of energy released, when the same bond is formed. In gaseous state, the energy required for homolytic cleavage of a bond is called Bond Dissociation Energy (BDE) or Bond Strength. BDE is affected by *s*-character of the bond and the stability of the radicals formed. Shorter bonds are typically stronger bonds. BDEs for some bonds are given below



13. Correct match of the C—H bonds (shown in bold) in Column J with their BDE in Column K is

|     | Column J<br>(Molecule)              | Column K<br>(BDE (kcal mol <sup>-1</sup> )) |
|-----|-------------------------------------|---------------------------------------------|
| (P) | H—CH(CH <sub>3</sub> ) <sub>2</sub> | (i) 132                                     |
| (Q) | H—CH <sub>2</sub> Ph                | (ii) 110                                    |
| (R) | H—CH=CH <sub>2</sub>                | (iii) 95                                    |
| (S) | H—C≡CH                              | (iv) 88                                     |

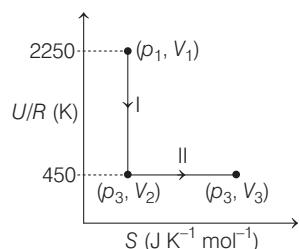
**Codes**

| P         | Q    | R     | S     |
|-----------|------|-------|-------|
| (a) (iii) | (iv) | (ii)  | (i)   |
| (b) (i)   | (ii) | (iii) | (iv)  |
| (c) (iii) | (ii) | (i)   | (iv)  |
| (d) (ii)  | (i)  | (iv)  | (iii) |

## SECTION 4

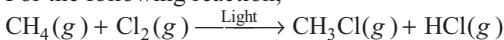
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  - The answer to each question is a **NON-NEGATIVE INTEGER**.
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Zero Marks : 0 In all other cases.

17. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two processes are same, the value of  $\ln V_3/V_2$  is .....



( $U$  = internal energy,  $S$  = entropy,  
 $p$  = pressure,  $V$  = volume,  $R$  = gas constant)

14. For the following reaction,



the correct statement is

- initiation step is exothermic with  $\Delta H^\circ = -58 \text{ kcal mol}^{-1}$ .
- propagation step involving  $\cdot\text{CH}_3$  formation is exothermic with  $\Delta H^\circ = -2 \text{ kcal mol}^{-1}$ .
- propagation step involving  $\text{CH}_3\text{Cl}$  formation is endothermic with  $\Delta H^\circ = +27 \text{ kcal mol}^{-1}$ .
- The reaction is exothermic with  $\Delta H^\circ = -25 \text{ kcal mol}^{-1}$ .

**Paragraph**

The reaction of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with freshly prepared  $\text{FeSO}_4$  solution produces a dark blue precipitate called Turnbull's blue. Reaction of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  with the  $\text{FeSO}_4$  solution in complete absence of air produces a white precipitate  $X$ , which turns blue in air. Mixing the  $\text{FeSO}_4$  solution with  $\text{NaNO}_3$ , followed by a slow addition of concentrated  $\text{H}_2\text{SO}_4$  through the side of the test tube produces a brown ring.

15. Precipitate  $X$  is

- |                                                   |                                          |
|---------------------------------------------------|------------------------------------------|
| (a) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$       | (b) $\text{Fe}[\text{Fe}(\text{CN})_6]$  |
| (c) $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ | (d) $\text{KFe}[\text{Fe}(\text{CN})_6]$ |

16. Among the following, the brown ring is due to the formation of

- |                                                    |                                                           |
|----------------------------------------------------|-----------------------------------------------------------|
| (a) $[\text{Fe}(\text{NO})_2(\text{SO}_4)_2]^{2-}$ | (b) $[\text{Fe}(\text{NO})_2(\text{H}_2\text{O})_4]^{3+}$ |
| (c) $[\text{Fe}(\text{NO})_4(\text{SO}_4)_2]$      | (d) $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$   |

(Given, molar heat capacity at constant volume,  $C_{V,m}$  of the gas is  $\frac{5}{2} R$ )

18. Consider a helium ( $\text{He}$ ) atom that absorbs a photon of wavelength 330 nm. The change in the velocity (in  $\text{cm/s}^{-1}$ ) of He atom after the photon absorption is .....  
(Assume, momentum is conserved, when photon is absorbed.)

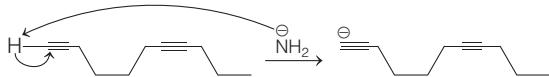
Use Planck's constant =  $6.6 \times 10^{-34} \text{ J s}$ , Avogadro's number =  $6 \times 10^{23} \text{ mol}^{-1}$ , Molar mass of He =  $4 \text{ g mol}^{-1}$

19. Ozonolysis of  $\text{ClO}_2$  produces an oxide of chlorine. The average oxidation state of chlorine in this oxide is .....

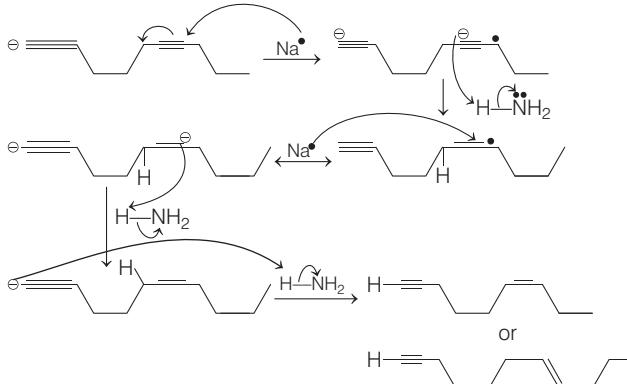
# Answer with Explanations

## Paper 1

- 1. (b)**  $\text{NaNH}_2$  acts as a base and takes the acidic proton from terminal alkyne to form acetylide ion.

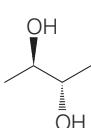


Na/ liq.  $\text{NH}_3$  is a reducing agent that reduces alkynes to *trans*-alkene. Na-atom gives one electron to the alkyne. In above step, an acetylide ion is formed, so reduction of terminal alkyne does not take place because negative charge repulses the incoming electron. Thus, the alkyne group is reduced to alkene.

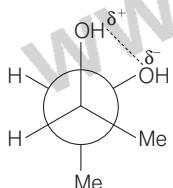


- 2. (b)**

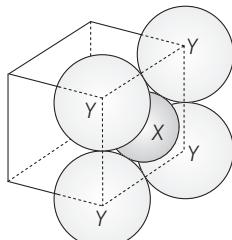
The structure of *meso*-butane-2,3-diol is



The most stable conformation of *meso*-butane-2,3-diol is the one in which there is hydrogen-bonding between two alcohol groups. The conformation is



- 3. (b)**



$$\text{Radius of cation } X = r_+$$

$$\text{Number of cation } X \text{ present} = 6 \times \frac{1}{2} = 3$$

$$\text{Radius of anion } Y = r_-$$

$$\text{Number of anion } Y \text{ present} = \frac{1}{8} \times 8 = 1$$

$$\text{Side of unit cell} = a$$

As two anions are touching each other, so side of unit cell,

$$a = 2r_-$$

$$\text{Volume of unit cell} = a^3 = (2r_-)^3 = 8r_-^3$$

$$\text{Volume of cations } X = \text{Number of cation} \times \text{Volume of one cation} = 3 \times \frac{4}{3} \pi r_+^3$$

$$\text{Volume of anions } Y = \text{Number of anion} \times \text{Volume of one anion} = 1 \times \frac{4}{3} \pi r_-^3$$

$$\text{Radius ratio for close packed structure, } \frac{r_+}{r_-} = 0.414$$

Packing efficiency

$$\text{Packing efficiency} = \frac{\text{Volume of cation} \times \text{Number of cations} + \text{Volume of anion} \times \text{Number of anions}}{\text{Volume of unit cell}} \times 100$$

$$\text{Packing fraction} = \frac{\text{Packing efficiency}}{100}$$

$$= \frac{1 \times \frac{4}{3} \pi r_-^3 + 3 \times \frac{4}{3} \pi r_+^3}{8r_-^3}$$

$$= \frac{4\pi}{3 \times 8} \left[ \frac{r_-^3}{r_-^3} + \frac{3r_+^3}{r_-^3} \right] = \frac{\pi}{6} [1 + 3(0.414)^3]$$

$$= \frac{3.14}{6} (1 + 3 \times 0.0710) = \frac{3.14}{6} \times 1.213 = 0.63$$

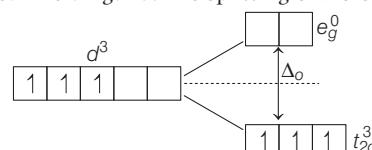
- 4. (a)**  $[\text{Cr}(\text{NH}_3)_6]^{3+}$

Atomic number of Cr = 24

Electronic configuration of Cr =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

Electronic configuration of  $\text{Cr}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^0$

$\text{NH}_3$  is a weak field ligand. The splitting of *d*-orbital occur.



Number of unpaired electrons,  $n = 3$

$$\text{Magnetic moment (spin only), } \mu_s = \sqrt{n(n+2)} \text{ BM}$$

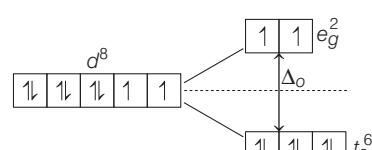
$$= \sqrt{3(3+2)} = \sqrt{3 \times 5} = \sqrt{15} = 3.87 \text{ BM}$$

- [CuF<sub>6</sub>]<sup>3-</sup>** Atomic number of Cu = 29.

Electronic configuration of Cu =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^10 4s^1$

Electronic configuration of  $\text{Cu}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^0$

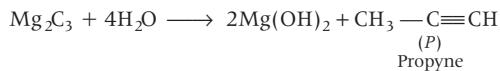
$\text{F}^-$  is a weak field ligand, so splitting of *d*-orbitals occur as follows.



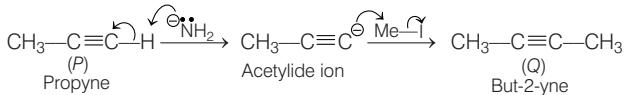
Number of unpaired electrons,  $n = 2$

$$\text{Spin only magnetic moment, } \mu_s = \sqrt{n(n+2)} \text{ BM} \\ = \sqrt{2(2+2)} = \sqrt{2 \times 4} = 2\sqrt{2} = 2.84 \text{ BM}$$

5. (1.62)  $\text{Mg}_2\text{C}_3$  reacts with water to give propyne.



Sodium amide ( $\text{NaNH}_2$ ) takes proton from alkyne to form acetylide ion which, attacks on Me—I to give an alkyne with one more carbon.



Mass of  $P$  formed = 4.0 g

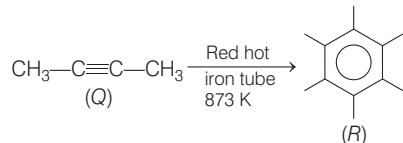
Molar mass of  $P$  formed = 40 g mol<sup>-1</sup>

$$\text{Number of moles of } P = \frac{\text{Mass of } P(W)}{\text{Molar mass of } P(M)} = \frac{4}{40} = 0.1 \text{ mol}$$

1 mole of  $P$  forms 75% i.e., 0.75 mole of  $Q$ .

So, 0.1 mole of  $P$  forms  $0.75 \times 0.1 = 0.075$  mole of  $Q$

Polymerisation of alkyne (Butyne) occurs in presence of red hot iron tube to form benzene derivative.



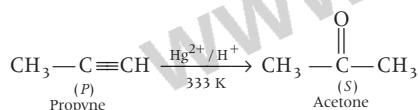
3 moles of alkyne forms 40% i.e., 0.40 mole of benzene derivative,  $R$ .

$$0.075 \text{ mole of } Q \text{ forms } \frac{0.40}{3} \times 0.075 = 0.01 \text{ mole of } R.$$

Molar mass of  $R$  = 162 g/mol

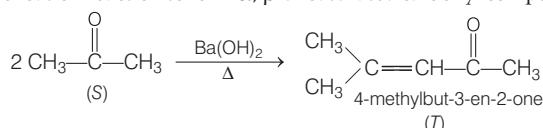
$$\text{Mass of } R \text{ formed or value of } x = \text{Molar mass} \times \text{Number of moles} \\ = 162 \times 0.01 = 1.62 \text{ g}$$

6. (3.2) Alkyne,  $P$  oxidises to ketone on reacting with  $\text{Hg}^{2+}/\text{H}^+$ .



As reaction efficiency is 100%, so 0.1 mole of  $P$  forms 0.1 mole of  $S$ .

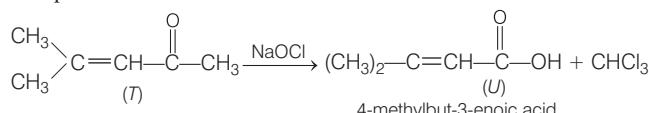
' $S$ ' in presence of base,  $\text{Ba}(\text{OH})_2$  followed by heating leads to aldol condensation reaction to form  $\alpha, \beta$ -unsaturated carbonyl compound.



2 moles of  $S$  forms 80% i.e. 0.8 mole of  $T$ .

$$\text{So, } 0.1 \text{ mole of } S \text{ forms } \frac{0.8}{2} \times 0.1 = 0.04 \text{ mole of } T.$$

Ketone oxidises to carboxylic acid in presence of  $\text{NaOCl}$ . Complete reaction is as follows :



1 mole of  $T$  forms 80% i.e., 0.8 mole of  $U$ .

So, 0.04 mole of  $T$  forms  $0.8 \times 0.04 = 0.032$  mole of  $U$

Molar mass of  $U$  = 100 g mol<sup>-1</sup>

Mass of  $U$  formed or value of  $y$  = Molar mass × Number of moles of  $U$

$$= 100 \times 0.032 = 3.2 \text{ g}$$

7. (166.28)

$$\Delta G^\circ = -RT \ln K \quad \dots(i)$$

$$\text{Also, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots(ii)$$

Comparing Eqs. (i) and (ii),

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\text{Given, } K = \frac{p_Z}{p^\circ} \text{ and } p^\circ = 1 \text{ bar}$$

$$\text{So, } -RT \ln \left( \frac{p_Z}{1} \right) = \Delta H^\circ - T\Delta S^\circ$$

$$\ln \left( \frac{p_Z}{1} \right) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \dots(iii)$$

$$\text{In graph, slope} = \frac{-\Delta H^\circ}{R}$$

$$\text{Slope} = 10^4 \left( \frac{Y_2 - Y_1}{X_2 - X_1} \right) = 10^4 \left( \frac{-7 + 3}{12 - 10} \right)$$

$$= 10^4 \left( -\frac{4}{2} \right) = -2 \times 10^4$$

$$\text{Therefore, } -2 \times 10^4 = -\frac{\Delta H^\circ}{R} \Rightarrow 2 \times 10^4 \times 8.314 = \Delta H^\circ$$

$$\Rightarrow \Delta H^\circ = 166280 \text{ J mol}^{-1} = 166.28 \text{ kJ mol}^{-1}$$

8. (141.34) From graph,  $\frac{10^4}{T} = 10$

Therefore,  $T = 10^3 \text{ K}$

$$\text{Also, } \ln \left( \frac{p_2}{1} \right) = -3$$

Substituting the value in Eq. (iii),

$$\ln \left( \frac{p}{1} \right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$-3 = -\frac{2 \times 10^4 \times R}{R \times 10^3} + \frac{\Delta S^\circ}{R}$$

$$\Rightarrow \frac{\Delta S^\circ}{R} = 20 - 3 = 17$$

$$\Rightarrow \Delta S^\circ = +17 \times R = +17 \times 8.314 = 141.34 \text{ JK}^{-1} \text{ mol}^{-1}$$

9. (100.10) Complete reaction as follows :



Concentration,  $m = 0.1 \text{ m}$

van't Hoff factor,  $i = 2$

$$\Delta T_b = iK_b m;$$

where,  $\Delta T_b$  is change in boiling point of  $\text{H}_2\text{O}$ .  
 $K_b$  is ebullioscopic constant = 0.5 K kg mol<sup>-1</sup>

$m$  is concentration of solution

$$\Delta T_b = 2 \times 0.5 \times 0.1 = 0.1^\circ\text{C}$$

$T_b^\circ$  = boiling point of pure water

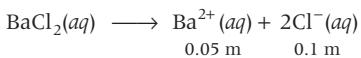
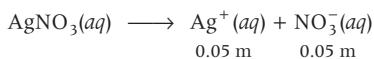
$T_b$  = boiling point of solution

$$T_b - T_b^\circ = 0.1 \Rightarrow T_b = 100 + 0.1 = 100.1^\circ\text{C}$$

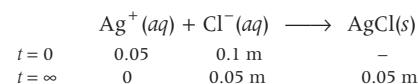
Boiling of solution,  $x^\circ\text{C} = 100.1^\circ\text{C}$

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- 10.** (2.5) By adding equal volume of 0.1 M  $\text{BaCl}_2$ , the volume of solution doubles and concentration becomes half.



$\text{Ag}^+$  reacts with  $\text{Cl}^-$  to form ppt. of  $\text{AgCl}$ .



Total species in solution are  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Ba}^{2+}$ . So, van't Hoff factor,  $i = 3$ .

Concentration of each species,  $m = 0.05 \text{ m}$

Elevation of boiling point

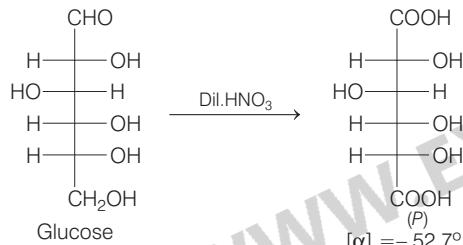
$$\begin{aligned} \Delta T_b &= iK_b m \\ \Delta T_b &= 3 \times 0.5 \times 0.05 = 0.075^\circ\text{C} \\ T_b' - 100 &= 0.075 \\ T_b' &= 100.075^\circ\text{C} \end{aligned}$$

Difference in boiling point,  $T_b - T_b' = 100.1 - 100.075 = 0.025 = 2.5 \times 10^{-2} \text{ }^\circ\text{C}$

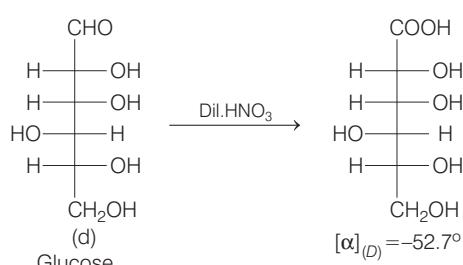
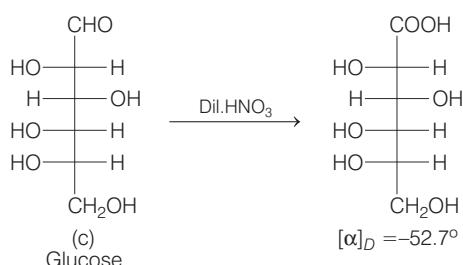
So,  $y = 2.5$

- 11.** (c, d) Monosaccharide oxidises on reacting with  $\text{HNO}_3$  to form carboxylic acids. Primary alcohols also oxidise to carboxylic acid alongwith aldehyde.

Complete reaction is as follows :



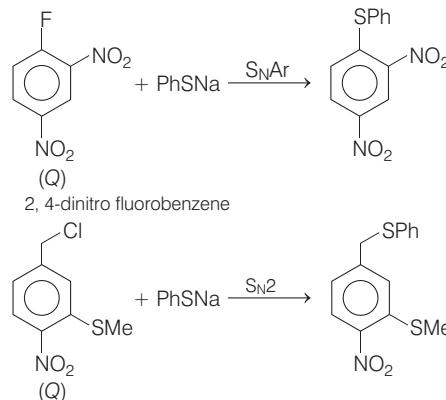
The enantiomer of product (P) has rotation  $-52.7^\circ$ . The two enantiomers (c and d) with their reactions are as follows :



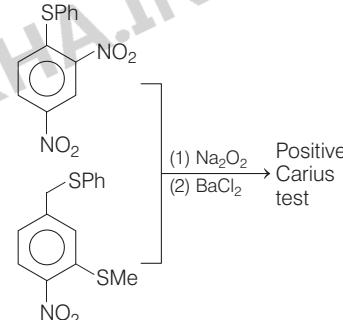
- 12.** (a, d)  $\text{PhSNa}$  replaces F from *o*- and *p*-dinitro- fluorobenzene via nucleophilic aromatic substitution.

$\text{PhSNa}$  replaces Cl from compound D via nucleophilic bimolecular substitution reaction.

In case of compound B and C, nucleophilic substitution is not possible neither by  $\text{S}_{\text{N}}\text{Ar}$  or  $\text{S}_{\text{N}}2$  because, the electron withdrawing group is present at *meta*-position and halogen is attached to  $sp^2$ -carbon.



Positive Carius test is given by compound containing halogen, sulphur and phosphorus. So, only compound A and D reacts with  $\text{PhSNa}$  to give a positive Carius test on treatment with  $\text{Na}_2\text{O}_2$  followed by addition of  $\text{BaCl}_2$ .



- 13.** (b, c) Statements (b) and (c) are correct whereas statements (a) and (d) are incorrect.

- Process of precipitating colloidal sol is known as **coagulation**.
- Concentration of colloidal solutions is small due to large molar mass and thus, their colligative properties are very small compared to true solutions. Hence, these solutions freeze at higher temperature.
- Micelles are formed at the critical micelle concentration (CMC) which depends on temperature.
- Micelles and macromolecular colloids are two different types of colloid.

- 14.** (a, b and d)

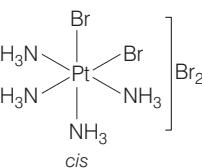
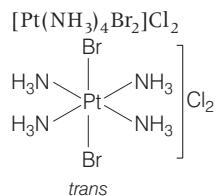
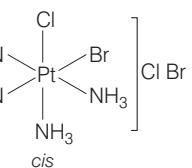
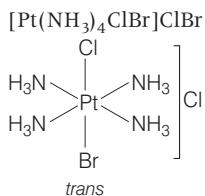
**From state I to II** Reversible isothermal expansion takes place. So, following changes take place,

- pressure decreases.
- Volume increases.
- Temperature remains constant.
- Enthalpy,  $H$  remains constant.
- Entropy,  $S$  for expansion increases.

So, all options follow the above mentioned conditions, so all graphs are correct for state I and II.



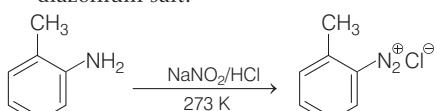
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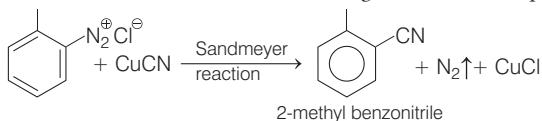
### Paper 2

1. (a, b) Complete reaction sequences are as follows :

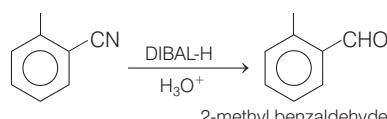
(a) *o*-toluidine reacts with  $\text{NaNO}_2/\text{HCl}$  at 273 K to give diazonium salt.



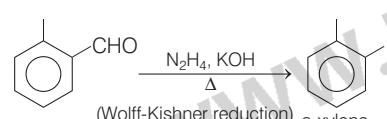
Diazonium salt reacts with  $\text{CuCN}$  to give benzonitrile product.



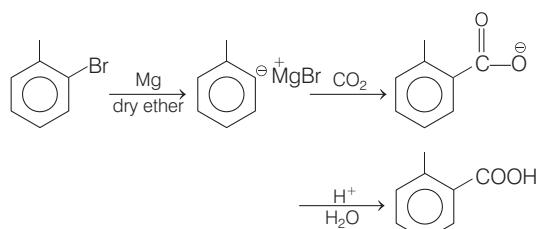
DIBAL-H is a reducing agent that reduces cyanide group to aldehyde group.



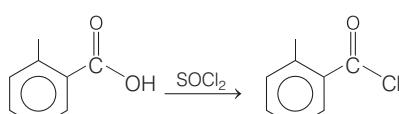
Carbonyl compounds are reduced to alkane by treating them with  $\text{N}_2\text{H}_4$  with KOH.



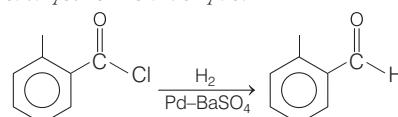
(b) Treatment of 1-bromo-2-methyl benzene with Mg in dry ether gives Grignard reagent which attacks on carbon dioxide to give carboxylate ion which give carboxylic acid upon hydrolysis.



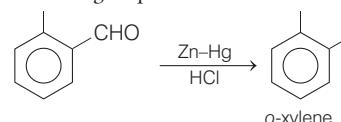
Carboxylic acids react with thionyl chloride ( $\text{SOCl}_2$ ) to form acid chlorides.



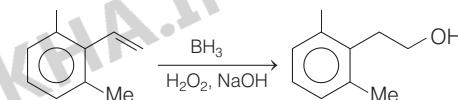
Acid chlorides on treating with hydrogen gas in presence of  $\text{Pd-BaSO}_4$  catalyst forms aldehyde.



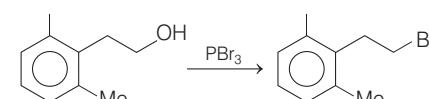
**Clemmensen reduction** Carbonyl compounds gives alkanes on treating with Zn-Hg in presence of HCl.



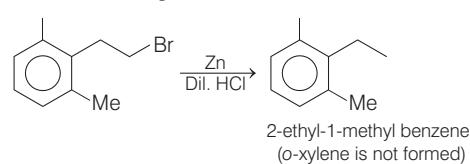
(c) Alkenes gives alcohol on treating with  $\text{BH}_3$  followed by  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$ . The OH group attaches to the least substituted carbon.



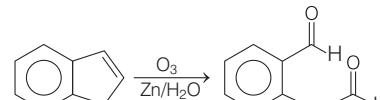
Alcohols reacts with  $\text{PBr}_3$  to give alkyl bromide. Bromine replaces hydroxide group.



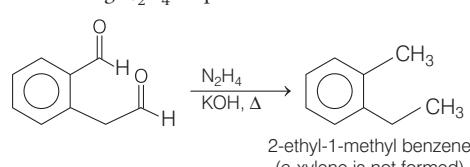
Alkyl halides on treating with Zn and dil. HCl reduce to alkanes.



(d) Ozonolysis of alkenes give carbonyl compound. Double bond breaks to give two carbonyl groups.



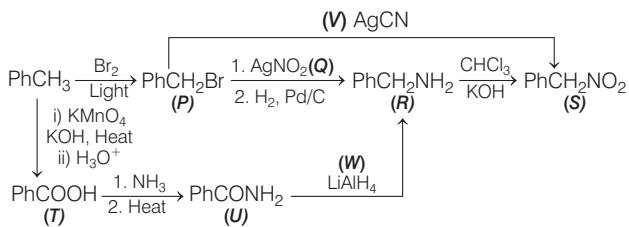
**Wolff-Kishner reduction** Carbonyl compounds reduce to alkane on treating  $\text{N}_2\text{H}_4$  in presence of KOH.



Therefore, options (a) and (b) give only o-xylene products.

**2. (c, d)**

Sequence of reactions involved are



- (a) If  $\text{KNO}_2(\text{Q})$  reacts with  $\text{PhCH}_2\text{Br}(P)$  gives  $\text{PhCH}_2\text{ONO}$  which on reduction with  $\text{LiAlH}_4$  does not give  $\text{PhCH}_2\text{NH}_2$ .
- (b) If product  $R$  formed is benzylamine not benzene amine.  $\text{KCN}$  reacts with  $\text{PhCH}_2\text{Br}$  to give  $\text{PhCH}_2\text{CN}$  which does not have foul smelling.
- (c) If  $\text{AgNO}_2(\text{Q})$  reacts with  $\text{PhCH}_2\text{Br}$  to give  $\text{PhCH}_2\text{NO}_2$  which on reduction give  $\text{PhCH}_2\text{NH}_2$  (Phenyl methanamine or benzyl amine).
- (d) If amide reacts with  $\text{LiAlH}_4(\text{W})$  to give amine.  $\text{PhCH}_2\text{Br}$  reacts with  $\text{AgCN}$  to give  $\text{PhCH}_2\text{NO}_2$ .

**3. (b, c and d)**

$$\begin{array}{ccccc}
 2X & + & Y & \xrightarrow{k} & P \\
 t=0 & 2 \text{ mol} & 1 \text{ mol} & - & \\
 t=50 \text{ s} & (2-1) \text{ mol} & (1-0.5) \text{ mol} & 0.5 \text{ mol} & \\
 & = 1 \text{ mol} & = 0.5 \text{ mol} & &
 \end{array}$$

As the concentration of reactant becomes half at  $t = 50 \text{ s}$ .

So, half-time of reaction is 50 s.

$$\text{Given, } \frac{dP}{dt} = k[X]^l$$

$$\begin{aligned}
 \Rightarrow -\frac{1}{2} \frac{dX}{dt} &= \frac{dP}{dt} = k[X]^l \\
 -\frac{dX}{dt} &= 2k[X]^l \\
 \frac{-dX}{[X]} &= 2k dt \\
 -\int_{X_0}^X \frac{dX}{X} &= 2k \int_0^t dt \\
 -[\ln X]_{X_0}^X &= 2k [t]_0^t \\
 -\ln X + \ln X_0 &= 2kt \\
 \ln \frac{X_0}{X} &= 2kt
 \end{aligned}$$

$$\text{At } t_{1/2}, X = \frac{X_0}{2}$$

$$\ln \frac{2X_0}{X_0} = 2kt_{1/2}$$

$$k = \frac{\ln 2}{2t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ s}^{-1}$$

$$\text{At, } t = 50 \text{ s}, -\frac{dx}{dt} = 2k[X]^l; [X] = 1 \text{ mol}$$

$$\text{So, } \frac{-dX}{dt} = 2 \times 6.93 \times 10^{-3} \times 1 = 13.86 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{At } t = 100 \text{ s}, -\frac{1}{2} \frac{dX}{dt} = \frac{-dY}{dt} \Rightarrow \frac{-dY}{dt} = k[Y]^l; [Y] = \frac{1}{2}$$

$$-\frac{dY}{dt} = 6.93 \times 10^{-3} \times \frac{1}{2} = 3.46 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

So, options (b), (c) and (d) are correct.

**4. (a, b and c)**

Given,

$$\text{At anode } X(s) \longrightarrow X^{2+}(aq) + 2e^- \quad (0.001 \text{ M})$$

$$\text{At cathode } Y^{2+}(aq) + 2e^- \longrightarrow Y(s) \quad (0.1 \text{ M})$$

$$\text{Overall reaction } X(s) + Y^{2+}(aq) \longrightarrow X^{2+}(aq) + Y(s)$$

Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.06}{2} \log \frac{[X^{2+}]}{[Y^{2+}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - 0.03 \log \frac{0.001}{0.1}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ + 0.06$$

$E_{\text{cell}}$  should be positive for a reaction to be spontaneous.

$$(a) E_{\text{Cd}^{2+}/\text{Cd}}^\circ = -0.40 \text{ V}, E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.24 \text{ V}$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.24 - (-0.40)$$

$$E_{\text{cell}}^\circ = 0.16$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ + 0.06 = 0.16 + 0.06 = 0.22 \text{ V}$$

Reaction is spontaneous.

$$(b) E_{\text{Cd}^{2+}/\text{Cd}}^\circ = -0.40 \text{ V}, E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$$

$$E_{\text{cell}}^\circ = -0.44 + 0.40 = -0.04 \text{ V}$$

$$E_{\text{cell}} = -0.04 + 0.06 = 0.02 \text{ V}$$

Reaction is spontaneous.

$$(c) E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.24 \text{ V}$$

$$E_{\text{Pb}^{2+}/\text{Pb}}^\circ = -0.13 \text{ V}$$

$$E_{\text{cell}}^\circ = -0.13 + 0.24 = 0.11 \text{ V}$$

$$E_{\text{cell}} = 0.11 + 0.06 = 0.17 \text{ V}$$

Reaction is spontaneous.

$$(d) E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.24 \text{ V}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$$

$$E_{\text{cell}}^\circ = -0.44 + 0.24 = -0.20 \text{ V}$$

$$E_{\text{cell}}^\circ = -0.20 + 0.06 = -0.14 \text{ V}$$

Reaction is non-spontaneous.

Therefore, the correct combinations of  $X$  and  $Y$  are (a), (b) and (c).

**5. (a, b, and d)**

$$(a) [\text{FeCl}_4]^-$$

Atomic number of Fe = 26.

Oxidation number of Fe =  $x + 4(-1) = -1$

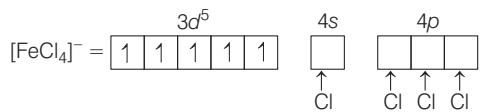
$$\Rightarrow x = 3$$

Electronic configuration of Fe =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Electronic configuration of  $\text{Fe}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$

$\text{Cl}^-$  is a weak field ligand, so, no pairing of electrons occurs.

## 14 JEE Advanced Solved Paper 2021



Hybridisation is  $sp^3$ .

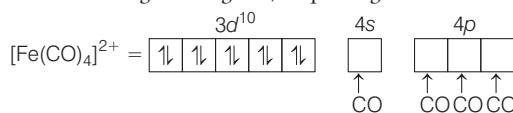
Geometry is tetrahedral.

$[\text{Fe}(\text{CO})_4]^{2+}$  Oxidation number of Fe =  $x + 4(0) = +2$

$$\Rightarrow x = +2$$

Electronic configuration of  $\text{Fe}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

CO is a strong field ligand, so pairing of electrons occurs.



Hybridisation is  $sp^3$ .

Geometry is tetrahedral.

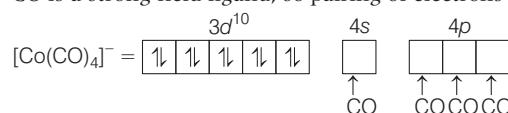
(b)  $[\text{Co}(\text{CO})_4]^-$  Atomic number of Co = 27.

Oxidation number of Co =  $x + 4(0) = -1 \Rightarrow x = -1$

Electronic configuration of Co =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

Electronic configuration of  $\text{Co}^- = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

CO is a strong field ligand, so pairing of electrons occurs.



Hybridisation is  $sp^3$ .

Geometry is tetrahedral.

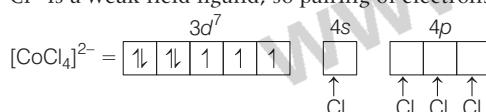
$[\text{CoCl}_4]^{2-}$

Oxidation number of Co =  $x + 4(-1) = -2$

$$\Rightarrow x = +2$$

Electronic configuration of  $\text{Co}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^0$

$\text{Cl}^-$  is a weak field ligand, so pairing of electrons do not occur.



Hybridisation is  $sp^3$ .

Geometry is tetrahedral.

(c)  $[\text{Ni}(\text{CO})_4]$

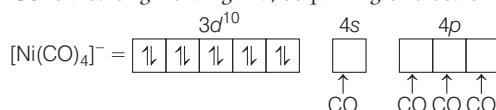
Oxidation number of Ni =  $x + 4(0) = 0$

$$\Rightarrow x = 0$$

Atomic number of Ni = 28

Electronic configuration of Ni =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

CO is a strong field ligand, so pairing of electrons occur.



Hybridisation is  $sp^3$ .

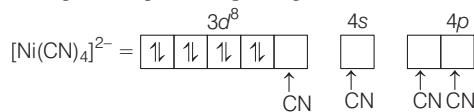
Geometry is tetrahedral.

$[\text{Ni}(\text{CN})_4]^{2-}$

Oxidation number of Ni =  $x + 4(-1) = -2 \Rightarrow x = +2$

Electronic configuration of  $\text{Ni}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^0$

CN is a strong field ligand, so pairing of electrons occur.



Hybridisation is  $dsp^2$ .

Geometry is square planar.

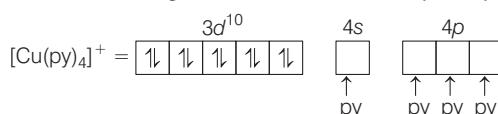
(d)  $[\text{Cu}(\text{py})_4]^+$

Oxidation number of Cu =  $x + 4(0) = +1 \Rightarrow x = +1$

Atomic number of Cu = 29

Electronic configuration of Cu =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Electronic configuration of  $\text{Cu}^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$

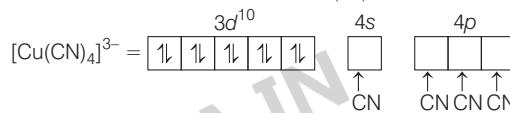


Hybridisation is  $sp^3$ .

Geometry is tetrahedral.

$[\text{Cu}(\text{CN})_4]^{3-}$

Oxidation number of Cu =  $x + 4(-1) = -3 \Rightarrow x = +1$

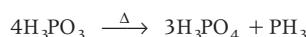


Hybridisation is  $sp^3$ .

Geometry is tetrahedral.

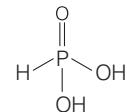
6. (a, b, and d)

(a)  $\text{H}_3\text{PO}_3$  gives  $\text{H}_3\text{PO}_4$  and  $\text{PH}_3$  on heating. This reaction is known as disproportionation reaction.



(b) P in  $\text{H}_3\text{PO}_4$  is in its highest oxidation state i.e., +5 hence, it cannot act as reducing agent. But P in  $\text{H}_3\text{PO}_3$  is in oxidation state, +3 hence, it can act as reducing agent.

(c)  $\text{H}_3\text{PO}_3$  contains two —OH groups, hence it is a dibasic acid.



(d) Hydrogen attached to P, does not ionise in water.  
Therefore, options (a), (b) and (d) are correct.

7. (0.22)

Degree of dissociation =  $\alpha$

Limiting molar conductivity,  $\Lambda_m^\circ = 4 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$

Molar conductivity,  $\Lambda_m = y \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$

Molar conductivity of dilution,  $\Lambda_m^\circ = 3y \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$

Concentration before dilution =  $C$

Concentration after dilution =  $\frac{C}{20}$

Using relation,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} \quad \dots(i)$$

$$\text{Dissociation constant, } K_a = \frac{C\alpha^2}{(1 - \alpha)}$$

Putting Eq. (i),

$$K_a = \frac{C\Lambda_m^2}{\Lambda_m^{\circ 2} \left(1 - \frac{\Lambda_m}{\Lambda_m^{\circ}}\right)} = \frac{C\Lambda_m^2}{\Lambda_m^{\circ} (\Lambda_m^{\circ} - \Lambda_m)}$$

Dissociation constant before dilution,

$$K_a = \frac{C(y \times 10^2)^2}{(4 \times 10^2)(4 \times 10^2 - y \times 10^2)} \quad \dots(\text{ii})$$

Dissociation constant after dilution,

$$K_a = \frac{\frac{C}{20} (3y \times 10^2)^2}{(4 \times 10^2)(4 \times 10^2 - 3y \times 10^2)} \quad \dots(\text{iii})$$

Comparing Eqs. (ii) and (iii),

$$\begin{aligned} \frac{C(y \times 10^2)^2}{(4 \times 10^2)(4 \times 10^2 - y \times 10^2)} &= \frac{C(3y \times 10^2)^2}{20(4 \times 10^2)(4 \times 10^2 - 3y \times 10^2)} \\ \frac{y^2 \times 10^4}{10^2(4 - y)} &= \frac{9y^2 \times 10^4}{10^2 \times 20(4 - 3y)} \\ \frac{1}{(4 - y)} &= \frac{9}{20(4 - 3y)} \\ 80 - 60y &= 36 - 9y \\ 80 - 36 &= 60y - 9y \\ 44 &= 51y \\ \Rightarrow y &= \frac{44}{51} \end{aligned} \quad \dots(\text{iv})$$

Putting in Eq. (i),

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{y \times 10^2}{4 \times 10^2}$$

$$\alpha = \frac{44}{51 \times 4} = \frac{11}{51}$$

$$\alpha = 0.22$$

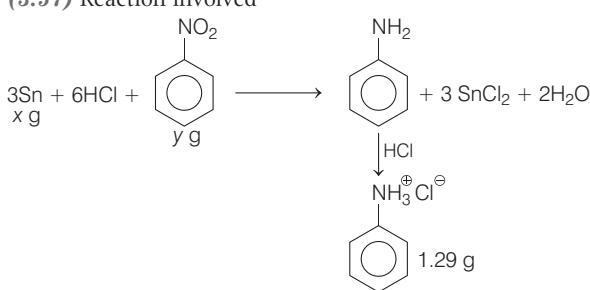
The value of  $\alpha$  is 0.22.

**8. (0.86)** From equation (iv),

$$y = \frac{44}{51} \Rightarrow y = 0.86$$

The value of  $y$  is 0.86.

**9. (3.57)** Reaction involved



Mass of organic salt produced (aniline) = 1.29 g

Molar mass of organic salt (aniline)

$$\begin{aligned} &= 12 \times 6 + 1 \times 8 + 14 \times 1 + 35 \times 1 \\ &= 72 + 8 + 14 + 35 \\ &= 129 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Moles of organic salt} = \frac{\text{Mass of organic salt}}{\text{Molar mass}}$$

$$= \frac{1.29}{129} = 0.01 \text{ mol}$$

From reaction 1 moles of salt is produced from 3 mole of Sn. So, 0.01 mole of organic salt is produced by 0.03 mole Sn. Atomic mass of Sn = 119 g mol<sup>-1</sup>

Mass of Sn =  $x$  = mole of Sn × Molar mass

$$x = 0.03 \times 119 \Rightarrow x = 3.57 \text{ g}$$

The value of  $x$  is 3.57

**10. (1.23)**

1 mole of organic salt is produced by 1 mole of nitrobenzene 0.01 mole of organic salt is produced by 0.01 mole nitrobenzene.

Molar mass of nitrobenzene

$$\begin{aligned} &= 12 \times 6 + 1 \times 5 + 14 \times 1 + 16 \times 2 \\ &= 72 + 5 + 14 + 32 = 123 \text{ g mol}^{-1} \end{aligned}$$

Mass of nitrobenzene required,  $y$  = moles of nitrobenzene × molar mass

$$= 0.01 \times 123 = 1.23 \text{ g}$$

The value of  $y$  is 1.23.

**11. (1.88)**



$$(x \times 10^{-2} \text{ mol}) \quad (x \times 10^{-2} \text{ mol})$$

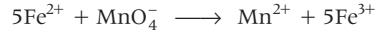
$$\text{Concentration of Fe}^{2+}, M_1 = \frac{x \times 10^{-2}}{250} \times 1000$$

$$= \frac{10x}{250} \text{ M} = \frac{x}{25} \text{ M}$$

Volume of  $\text{Fe}^{2+}$  solution titrated,  $V_1 = 25.0 \text{ mL}$

Concentration of  $\text{MnO}_4^-$ ,  $M_2 = 0.03 \text{ M}$

Volume of  $\text{MnO}_4^-$  used,  $V_2 = 12.5 \text{ mL}$



Using relation,

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$n_2 M_1 V_1 = n_1 M_2 V_2$  [  $n_1$  and  $n_2$  are number of moles of  $\text{Fe}^{2+}$  and  $\text{MnO}_4^-$  reacting]

$$1 \times \frac{x}{25} \times 25 = 5 \times 0.03 \times 12.5 \Rightarrow x = 1.88$$

The value of  $x$  is 1.88.

**12. (18.75)** Mass of sample = 5.6 g

Number of moles of Fe =  $1.88 \times 10^{-2} \text{ mol}$

Molar mass of Fe = 56 g/mol

Mass of Fe = Moles of Fe × Molar mass

$$= 1.88 \times 10^{-2} \times 56 = 1.05 \text{ g}$$

$$\% \text{ Fe} = \frac{\text{Mass of Fe}}{\text{Mass of sample}} \times 100 = \frac{1.05}{5.6} \times 100$$

$$\Rightarrow y = 18.75\%$$

The value of  $y$  is 18.75.

