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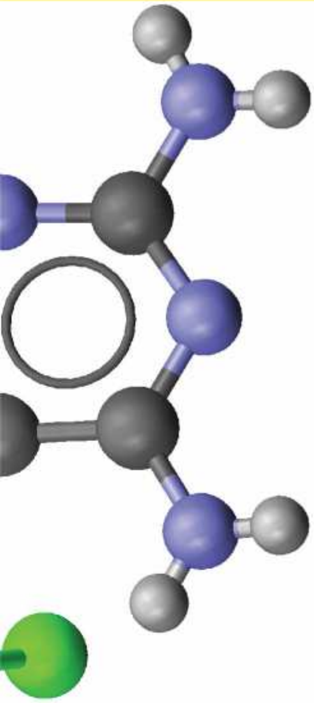

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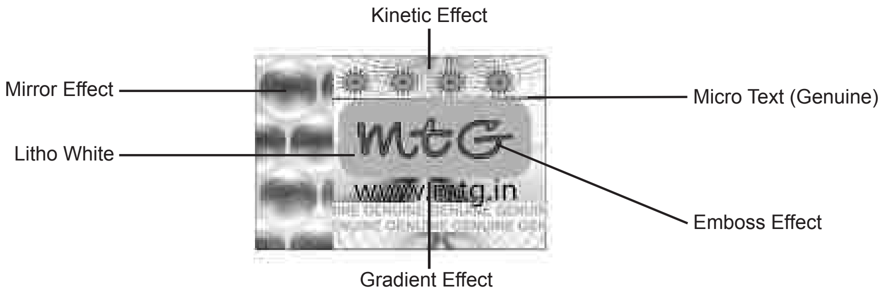


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Contents

Class XI

Class XII

Syllabus*

Class XI

UNIT I Some Basic Concepts of Chemistry

- General Introduction: Important and scope of chemistry.
- Laws of chemical combination, Dalton's atomic theory: concept of elements, atoms and molecules.
- Atomic and molecular masses. Mole concept and molar mass; percentage composition and empirical and molecular formula; chemical reactions, stoichiometry and calculations based on stoichiometry.

UNIT II Structure of Atom

- Atomic number, isotopes and isobars. Concept of shells and subshells, dual nature of matter and light, de Broglie's relationship, Heisenberg uncertainty principle, concept of orbital, quantum numbers, shapes of *s*, *p* and *d* orbitals, rules for filling electrons in orbitals- Aufbau principle, Pauli exclusion principles and Hund's rule, electronic configuration of atoms, stability of half filled and completely filled orbitals.

UNIT III Classification of Elements and Periodicity in Properties

- Modern periodic law and long form of periodic table, periodic trends in properties of elements atomic radii, ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity, valence.

UNIT IV Chemical Bonding and Molecular Structure

- Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, valence bond theory, resonance, geometry of molecules, VSEPR theory, concept of hybridization involving *s*, *p* and *d* orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only). Hydrogen bond.

UNIT V States of Matter: Gases and Liquids

- Three states of matter, intermolecular interactions, types of bonding, melting and boiling points, role of gas laws of elucidating the concept of the molecule, Boyle's law, Charle's law, Gay Lussac's law, Avogadro's law, ideal behaviour of gases, empirical derivation of gas equation. Avogadro number, ideal gas equation. Kinetic energy and molecular speeds (elementary idea), deviation from ideal behaviour, liquefaction of gases, critical temperature.
- Liquid State- Vapour pressure, viscosity and surface tension (qualitative idea only, no mathematical derivations).

UNIT VI Thermodynamics

- First law of thermodynamics-internal energy and enthalpy, heat capacity and specific heat, measurement of *U* and *H*, Hess's law of constant heat summation, enthalpy of : bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution.
- Introduction of entropy as state function, Second law of thermodynamics, Gibbs energy change for spontaneous and non-spontaneous process, criteria for equilibrium and spontaneity.
- Third law of thermodynamics- Brief introduction.

UNIT VII Equilibrium

- Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of chemical equilibrium, equilibrium constant, factors affecting equilibrium- Le Chatelier's principle; ionic equilibrium- ionization of acids and bases, strong and weak electrolytes, degree of ionization, ionization of polybasic acids, acid strength, concept of pH., Hydrolysis of salts (elementary idea)., buffer solutions, Henderson equation, solubility product, common ion effect (with illustrative examples).

UNIT VIII Redox Reactions

- Concept of oxidation and oxidation and reduction, redox reactions oxidation number, balancing redox reactions in terms of loss and gain of electron and change in oxidation numbers.

UNIT IX Hydrogen

- Occurrence, isotopes, preparation, properties and uses of hydrogen; hydrides, ionic, covalent and interstitial; physical and chemical properties of water, heavy water; hydrogen peroxide-preparation, reactions, uses and structure.

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

- Group I and group 2 elements:
- General introduction, electronic configuration, occurrence, anomalous properties of the first element of each group, diagonal relationship, trends in the variation of properties (such as ionization enthalpy, atomic and ionic radii), trends in chemical reactivity with oxygen, water, hydrogen and halogens; uses.

**For details, refer to latest prospectus*

- Preparation and Properties of Some important Compounds: Sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate, biological importance of sodium and potassium.
- Industrial use of lime and limestone, biological importance of Mg and Ca.

UNIT XI Some *p*-Block Elements

- General Introduction to *p*-Block Elements.
- Group 13 elements: General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the group; Boron, some important compounds: borax, boric acids, boron hydrides. Aluminium: uses, reactions with acids and alkalies.
- General 14 elements: General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first element. Carbon, allotropic forms, physical and chemical properties: uses of some important compounds: oxides.
- Important compounds of silicon and a few uses: silicon tetrachloride, silicones, silicates and zeolites, their uses.

UNIT XII Organic Chemistry- Some Basic Principles and Techniques

- General introduction, methods of purification qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds.
- Electronic displacements in a covalent bond: inductive effect, electromeric effect, resonance and hyperconjugation.
- Homolytic and heterolytic fission of a covalent bond: free radials, carbocations, carbanions; electrophiles and nucleophiles, types of organic reactions.

UNIT XIII Hydrocarbons

- Alkanes- Nomenclature, isomerism, conformations (ethane only), physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis.
- Alkenes-Nomenclature, structure of double bond (ethene), geometrical isomerism, physical properties, methods of preparation: chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition.
- Alkynes-Nomenclature, structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions: acidic character of alkynes, addition reaction of hydrogen, halogens, hydrogen halides and water.
- Aromatic hydrocarbons- Introduction, IUPAC nomenclature; Benzene; resonance, aromaticity; chemical properties: mechanism of electrophilic substitution-Nitration sulphonation, halogenation, Friedel—Crafts alkylation and acylation; directive influence of functional group in mono-substituted benzene; carcinogenicity and toxicity.

UNIT XIV Environmental Chemistry

- Environmental pollution: Air, water and soil pollution, chemical reactions in atmosphere, smogs, major atmospheric pollutants; acid rain ozone and its reactions, effects of depletion of ozone layer, greenhouse effect and global warming-pollution due to industrial wastes; green chemistry as an alternative tool for reducing pollution, strategy for control of environmental pollution.

Class XII

UNIT I Solid State

- Classification of solids based on different binding forces; molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea), unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties, Band theory of metals, conductors, semiconductors and insulators.

UNIT II Solutions

- Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties-relative lowering of vapour pressure, Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties abnormal molecular mass, van Hoff factor.

UNIT III Electrochemistry

- Redox reactions, conductance in electrolytic solutions, specific and molar conductivity variation of conductivity with concentration, Kohlrausch's Law, electrolysis and Laws of electrolysis (elementary idea), dry cell- electrolytic cells and Galvanic cells; lead accumulator, EMF of a cell, standard electrode potential, Relation between Gibbs energy change and EMF of a cell, fuel cells; corrosion.

UNIT IV Chemical Kinetics

- Rate of a reaction (average and instantaneous), factors affecting rates of reaction; concentration, temperature, catalyst; order and molecularity of a reaction; rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions); concept of collision theory (elementary idea, no mathematical treatment), Activation energy, Arrhenious equation.

UNIT V Surface Chemistry

- Adsorption-physisorption and chemisorption; factors affecting adsorption of gases on solids, catalysis homogeneous and heterogeneous, activity and selectivity: enzyme catalysis; colloidal state: distinction between true solutions, colloids and suspensions; lyophillic, lyophobic multimolecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation; emulsions- types of emulsions.

UNIT VI General Principles and Processes of Isolation of Elements

- Principles and methods of extraction- concentration, oxidation, reduction, electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

UNIT VII *p*-Block Elements

- Group 15 elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; preparation and properties of ammonia and nitric acid, oxides of nitrogen (structure only); Phosphorous- allotropic forms; compounds of phosphorous: preparation and properties of phosphine, halides (PCl_3, PCl_5) and oxoacids (elementary idea only).
- Group 16 elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; dioxygen: preparation, properties and uses; classification of oxides; ozone. Sulphur – allotropic forms; compounds of sulphur: preparation, properties and uses of sulphur dioxide; sulphuric acid: industrial process of manufacture, properties and uses, oxoacids of sulphur (structures only).
- Group 17 elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens: preparation, properties and uses of chlorine and hydrochloric acid, interhalogen compounds oxoacids of halogens (structures only).
- Group 18 elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.

UNIT VIII *d*- and *f*-Block Elements

- General introduction, electronic configuration, characteristics of transition metals, general trends in properties of the first row transition metals-metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation. Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.
- Lanthanoids- electronic configuration, oxidation states, chemical reactivity, and lanthanoid contraction and its consequences.
- Actinoids: Electronic configuration, oxidation states and comparison with lanthanoids.

UNIT IX Coordination Compounds

- Coordination compounds: Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds, isomerism (structural and stereo) bonding, Werner's theory VBT,CFT; importance of coordination compounds (in qualitative analysis, biological systems).

UNIT X Haloalkanes and Haloarenes

- Haloalkanes: Nomenclature, nature of C—*X* bond, physical and chemical properties, mechanism of substitution reactions. Optical rotation.
- Haloarenes: Nature of C—*X* bond, substitution reactions (directive influence of halogen for monosubstituted compounds only).
- Uses and environment effects of – dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

UNIT XI Alcohols, Phenols and Ethers

- Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only); identification of primary, secondary and tertiary alcohols; mechanism of dehydration, uses with special reference to methanol and ethanol.
- Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols.
- Ethers: Nomenclature, methods of preparation, physical and chemical properties uses.

UNIT XII Aldehydes, Ketones and Carboxylic Acids

- Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties; and mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes; uses.
- Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

UNIT XIII Organic Compounds Containing Nitrogen

- Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary secondary and tertiary amines.
- Cyanides and Isocyanides- will be mentioned at relevant places.
- Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

UNIT XIV Biomolecules

- Carbohydrates- Classification (aldoses and ketoses), monosaccharide (glucose and fructose), *D.L.* configuration, oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen): importance.
- Proteins- Elementary idea of – amino acids, peptide bond, polypeptides, proteins, primary structure, secondary structure, tertiary structure and quaternary structure (qualitative idea only), denaturation of proteins; enzymes.
- Hormones- Elementary idea (excluding structure).
- Vitamins- Classification and function.
- Nucleic Acids: DNA and RNA

UNIT XV Polymers

- Classification- Natural and synthetic, methods of polymerization (addition and condensation), copolymerization. Some important polymers: natural and synthetic like polyesters, bakelite; rubber, Biodegradable and non-biodegradable polymers.

UNIT XVI Chemistry in Everyday Life

- Chemicals in medicines- analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines.
- Chemicals in food- preservatives, artificial sweetening agents, elementary idea of antioxidants.
- Cleansing agents- soaps and detergents, cleansing action.

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CLASS

XI

CHAPTER
1

Some Basic Concepts of Chemistry

1.3 Properties of Matter and their Measurement

1. The dimensions of pressure are the same as that of
(a) force per unit volume
(b) energy per unit volume
(c) force (d) energy *(1995)*

1.4 Uncertainty in Measurement

2. Given the numbers : 161 cm, 0.161 cm, 0.0161 cm. The number of significant figures for the three numbers is
(a) 3, 3 and 4 respectively
(b) 3, 4 and 4 respectively
(c) 3, 4 and 5 respectively
(d) 3, 3 and 3 respectively. *(1998)*

1.5 Laws of Chemical Combinations

3. Equal masses of H_2, O_2 and methane have been taken in a container of volume V at temperature 27 °C in identical conditions. The ratio of the volumes of gases $H_2 : O_2$: methane would be
(a) 8 : 16 : 1 (b) 16 : 8 : 1
(c) 16 : 1 : 2 (d) 8 : 1 : 2 *(2014)*

4. What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely 1 L of propane gas (C_3H_8) measured under the same conditions?
(a) 5 L (b) 10 L
(c) 7 L (d) 6 L *(2008)*

5. 0.24 g of a volatile gas, upon vaporisation, gives 45 mL vapour at NTP. What will be the vapour density of the substance? (Density of H_2 = 0.089 g/L)
(a) 95.93 (b) 59.93
(c) 95.39 (d) 5.993 *(1996)*

6. The molecular weight of O_2 and SO_2 are 32 and 64 respectively. At 15°C and 150 mmHg pressure, one litre of O_2 contains 'N' molecules. The number of molecules in two litres of SO_2 under the same conditions of temperature and pressure will be
(a) $N/2$ (b) N
(c) $2\,N$ (d) $4\,N$ *(1990)*

7. What is the weight of oxygen required for the complete combustion of 2.8 kg of ethylene?
(a) 2.8 kg (b) 6.4 kg
(c) 9.6 kg (d) 96 kg *(1989)*

1.7 Atomic and Molecular Masses

8. An element, X has the following isotopic composition :
^{200}X : 90% ^{199}X : 8.0% ^{202}X : 2.0%
The weighted average atomic mass of the naturally occurring element X is closest to
(a) 201 amu (b) 202 amu
(c) 199 amu (d) 200 amu *(2007)*

9. Boron has two stable isotopes, ^{10}B(19%) and ^{11}B(81%). Calculate average at. wt. of boron in the periodic table.
(a) 10.8 (b) 10.2
(c) 11.2 (d) 10.0 *(1990)*

1.8 Mole Concept and Molar Masses

10. Which one of the followings has maximum number of atoms?
(a) 1 g of $Ag_{(s)}$ [Atomic mass of Ag = 108]
(b) 1 g of $Mg_{(s)}$ [Atomic mass of Mg = 24]
(c) 1 g of $O_{2(g)}$ [Atomic mass of O = 16]
(d) 1 g of $Li_{(s)}$ [Atomic mass of Li = 7]
(NEET 2020)

11. In which case is number of molecules of water maximum?
(a) 18 mL of water
(b) 0.18 g of water
(c) 0.00224 L of water vapours at 1 atm and 273 K
(d) 10^{-3} mol of water *(NEET 2018)*

12. Suppose the elements X and Y combine to form two compounds XY_2 and X_3Y_2. When 0.1 mole of XY_2 weighs 10 g and 0.05 mole of X_3Y_2 weighs 9 g, the atomic weights of X and Y are

(a) 40, 30 (b) 60, 40
(c) 20, 30 (d) 30, 20 *(NEET-II 2016)*

13. If Avogadro number N_A, is changed from 6.022×10^{23} mol^{-1} to 6.022×10^{20} mol^{-1}, this would change
(a) the mass of one mole of carbon
(b) the ratio of chemical species to each other in a balanced equation
(c) the ratio of elements to each other in a compound
(d) the definition of mass in units of grams. *(2015)*

14. The number of water molecules is maximum in
(a) 1.8 gram of water
(b) 18 gram of water
(c) 18 moles of water
(d) 18 molecules of water. *(2015)*

15. A mixture of gases contains H_2 and O_2 gases in the ratio of 1 : 4 (*w*/*w*). What is the molar ratio of the two gases in the mixture?
(a) 16 : 1 (b) 2 : 1
(c) 1 : 4 (d) 4 : 1 *(2015, Cancelled)*

16. Which has the maximum number of molecules among the following?
(a) 44 g CO_2 (b) 48 g O_3
(c) 8 g H_2 (d) 64 g SO_2
(Mains 2011)

17. The number of atoms in 0.1 mol of a triatomic gas is ($N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 6.026×10^{22} (b) 1.806×10^{23}
(c) 3.600×10^{23} (d) 1.800×10^{22} *(2010)*

18. The maximum number of molecules is present in
(a) 15 L of H_2 gas at STP
(b) 5 L of N_2 gas at STP
(c) 0.5 g of H_2 gas
(d) 10 g of O_2 gas. *(2004)*

19. Which has maximum molecules?
(a) 7 g N_2 (b) 2 g H_2
(c) 16 g NO_2 (d) 16 g O_2 *(2002)*

20. Specific volume of cylindrical virus particle is 6.02×10^{-2} cc/g whose radius and length are 7 Å and 10 Å respectively. If $N_A = 6.02 \times 10^{23}$, find molecular weight of virus.
(a) 15.4 kg/mol (b) 1.54×10^4 kg/mol
(c) 3.08×10^4 kg/mol (d) 3.08×10^3 kg/mol
(2001)

21. The number of atoms in 4.25 g of NH_3 is approximately
(a) 4×10^{23} (b) 2×10^{23}
(c) 1×10^{23} (d) 6×10^{23} *(1999)*

22. Haemoglobin contains 0.334% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (Atomic weight of Fe is 56) present in one molecule of haemoglobin is
(a) 4 (b) 6
(c) 3 (d) 2 (1998)

23. The number of moles of oxygen in one litre of air containing 21% oxygen by volume, under standard conditions, is
(a) 0.0093 mol (b) 2.10 mol
(c) 0.186 mol (d) 0.21 mol *(1995)*

24. The total number of valence electrons in 4.2 g of N_3^- ion is (N_A is the Avogadro's number)
(a) 2.1 N_A (b) 4.2 N_A
(c) 1.6 N_A (d) 3.2 N_A *(1994)*

25. The number of gram molecules of oxygen in 6.02×10^{24} CO molecules is
(a) 10 g molecules (b) 5 g molecules
(c) 1 g molecule (d) 0.5 g molecules.
(1990)

26. Ratio of C_p and C_v of a gas '*X*' is 1.4. The number of atoms of the gas '*X*' present in 11.2 litres of it at NTP will be
(a) 6.02×10^{23} (b) 1.2×10^{23}
(c) 3.01×10^{23} (d) 2.01×10^{23} *(1989)*

27. The number of oxygen atoms in 4.4 g of CO_2 is
(a) 1.2×10^{23} (b) 6×10^{22}
(c) 6×10^{23} (d) 12×10^{23} *(1989)*

28. 1 cc N_2O at NTP contains
(a) $\frac{1.8}{224} \times 10^{22}$ atoms
(b) $\frac{6.02}{22400} \times 10^{23}$ molecules
(c) $\frac{1.32}{224} \times 10^{23}$ electrons
(d) all of the above. *(1988)*

1.9 Percentage Composition

29. An organic compound contains carbon, hydrogen and oxygen. Its elemental analysis gave C, 38.71% and H, 9.67%. The empirical formula of the compound would be
(a) CHO (b) CH_4O
(c) CH_3O (d) CH_2O *(2008)*

30. Percentage of Se in peroxidase anhydrous enzyme is 0.5% by weight (at. wt. = 78.4) then minimum molecular weight of peroxidase anhydrous enzyme is
(a) 1.568×10^4 (b) 1.568×10^3
(c) 15.68 (d) 2.136×10^4 *(2001)*

31. Which of the following fertilizers has the highest nitrogen percentage?
(a) Ammonium sulphate
(b) Calcium cyanamide
(c) Urea
(d) Ammonium nitrate *(1993)*

1.10 Stoichiometry and Stoichiometric Calculations

32. The number of moles of hydrogen molecules required to produce 20 moles of ammonia through Haber's process is
(a) 40 (b) 10
(c) 20 (d) 30 *(NEET 2019)*

33. The density of 2 M aqueous solution of NaOH is 1.28 g/cm^3. The molality of the solution is [Given that molecular mass of NaOH = 40 g mol^{-1}]
(a) 1.20 m (b) 1.56 m
(c) 1.67 m (d) 1.32 m
(Odisha NEET 2019)

34. A mixture of 2.3 g formic acid and 4.5 g oxalic acid is treated with conc. H_2SO_4. The evolved gaseous mixture is passed through KOH pellets. Weight (in g) of the remaining product at STP will be
(a) 1.4 (b) 3.0
(c) 2.8 (d) 4.4 *(NEET 2018)*

35. What is the mass of the precipitate formed when 50 mL of 16.9% solution of $AgNO_3$ is mixed with 50 mL of 5.8% NaCl solution?
(Ag = 107.8, N = 14, O = 16, Na = 23, Cl = 35.5)
(a) 3.5 g (b) 7 g
(c) 14 g (d) 28 g *(2015)*

36. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample?
(At. wt. of Mg = 24)
(a) 96 (b) 60
(c) 84 (d) 75 *(2015)*

37. When 22.4 litres of $H_{2(g)}$ is mixed with 11.2 litres of $Cl_{2(g)}$, each at STP, the moles of $HCl_{(g)}$ formed is equal to
(a) 1 mol of $HCl_{(g)}$ (b) 2 mol of $HCl_{(g)}$
(c) 0.5 mol of $HCl_{(g)}$ (d) 1.5 mol of $HCl_{(g)}$
(2014)

38. 1.0 g of magnesium is burnt with 0.56 g O_2 in a closed vessel. Which reactant is left in excess and how much? (At. wt. Mg = 24, O = 16)
(a) Mg, 0.16 g (b) O_2, 0.16 g
(c) Mg, 0.44 g (d) O_2, 0.28 g *(2014)*

39. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of solution is
(a) 0.001 M (b) 0.1 M
(c) 0.02 M (d) 0.01 M
(NEET 2013)

40. In an experiment it showed that 10 mL of 0.05 M solution of chloride required 10 mL of 0.1 M solution of $AgNO_3$, which of the following will be the formula of the chloride (*X* stands for the symbol of the element other than chlorine)?
(a) X_2Cl_2 (b) XCl_2
(c) XCl_4 (d) X_2Cl
(Karnataka NEET 2013)

41. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of sodium ion, Na^+ and carbonate ions, CO_3^{2-} are respectively
(Molar mass of Na_2CO_3 = 106 g mol^{-1})
(a) 0.955 M and 1.910 M
(b) 1.910 M and 0.955 M
(c) 1.90 M and 1.910 M
(d) 0.477 M and 0.477 M *(2010)*

42. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be
(a) 3 mol (b) 4 mol
(c) 1 mol (d) 2 mol *(2009)*

43. How many moles of lead(II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g HCl?
(a) 0.011 (b) 0.029
(c) 0.044 (d) 0.333 *(2008)*

44. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is
(a) 270 kg (b) 540 kg
(c) 90 kg (d) 180 kg
(Atomic mass : Al = 27) *(2005)*

45. Molarity of liquid HCl, if density of solution is 1.17 g/cc is
(a) 36.5 (b) 18.25
(c) 32.05 (d) 42.10 *(2001)*

46. Volume of CO_2 obtained by the complete decomposition of 9.85 g of $BaCO_3$ is
(a) 2.24 L (b) 1.12 L
(c) 0.84 L (d) 0.56 L *(2000)*

47. In the reaction,
$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(l)}$
when 1 mole of ammonia and 1 mole of O_2 are made to react to completion
(a) all the oxygen will be consumed
(b) 1.0 mole of NO will be produced
(c) 1.0 mole of H_2O is produced
(d) all the ammonia will be consumed. *(1998)*

48. The amount of zinc required to produce 224 mL of H_2 at STP on treatment with dilute H_2SO_4 will be
(a) 65 g (b) 0.065 g
(c) 0.65 g (d) 6.5 g *(1996)*

49. At STP the density of CCl_4 vapour in g/L will be nearest to
(a) 6.87 (b) 3.42
(c) 10.26 (d) 4.57 *(1988)*

ANSWER KEY

1.	(b)	**2.**	(d)	**3.**	(c)	**4.**	(a)	**5.**	(b)	**6.**	(c)	**7.**	(c)	**8.**	(d)	**9.**	(a)	**10.**	(d)
11.	(a)	**12.**	(a)	**13.**	(a)	**14.**	(c)	**15.**	(d)	**16.**	(c)	**17.**	(b)	**18.**	(a)	**19.**	(b)	**20.**	(a)
21.	(d)	**22.**	(a)	**23.**	(a)	**24.**	(c)	**25.**	(b)	**26.**	(a)	**27.**	(a)	**28.**	(d)	**29.**	(c)	**30.**	(a)
31.	(c)	**32.**	(d)	**33.**	(c)	**34.**	(c)	**35.**	(b)	**36.**	(c)	**37.**	(a)	**38.**	(a)	**39.**	(d)	**40.**	(b)
41.	(b)	**42.**	(b)	**43.**	(b)	**44.**	(c)	**45.**	(c)	**46.**	(b)	**47.**	(a)	**48.**	(c)	**49.**	(a)		

Hints & Explanations

1. **(b) :** Pressure $= \frac{\text{Force}}{\text{Area}}$

Therefore, dimensions of pressure $= \frac{MLT^{-2}}{L^2} = ML^{-1}T^{-2}$

and dimensions of energy per unit volume

$$= \frac{\text{Energy}}{\text{Volume}} = \frac{ML^2T^{-2}}{L^3} = ML^{-1}T^{-2}$$

2. **(d) :** Zeros placed left to the number are never significant, therefore the no. of significant figures for the numbers 161 cm, 0.161 cm and 0.0161 cm are same, *i.e.*, 3.

3. **(c) :** According to Avogadro's hypothesis, ratio of the volumes of gases will be equal to the ratio of their no. of moles.

So, no. of moles $= \frac{\text{Mass}}{\text{Mol. mass}}$

$$n_{H_2} = \frac{w}{2};\ n_{O_2} = \frac{w}{32};\ n_{CH_4} = \frac{w}{16}$$

So, the ratio is $\frac{w}{2} : \frac{w}{32} : \frac{w}{16}$ or $16:1:2$.

4. **(a) :** $\underset{1\text{ vol.}}{C_3H_8} + \underset{5\text{ vol.}}{5O_2} \longrightarrow \underset{3\text{ vol.}}{3CO_2} + \underset{4\text{ vol.}}{4H_2O}$

According to the above equation,
1 vol. or 1 litre of propane requires 5 vol. or 5 litres of O_2 to burn completely.

5. **(b) :** Weight of gas = 0.24 g,
Volume of gas = 45 mL = 0.045 litre and density of H_2 = 0.089 g/L
Weight of 45 mL of H_2 = density × volume
$= 0.089 \times 0.045 = 4.005 \times 10^{-3}$ g

Therefore, vapour density

$$= \frac{\text{Weight of certain volume of substance}}{\text{Weight of same volume of hydrogen}}$$

$$= \frac{0.24}{4.005 \times 10^{-3}} = 59.93$$

6. **(c) :** If 1 L of one gas contains N molecules, 2 L of any gas under the same conditions will contain $2N$ molecules.

7. **(c) :** $\underset{28\text{ g}}{C_2H_4} + \underset{96\text{ g}}{3O_2} \longrightarrow 2CO_2 + 2H_2O$

For complete combustion,

2.8 kg of C_2H_4 requires $= \frac{96}{28} \times 2.8 \times 10^3$ g
$= 9.6 \times 10^3$ g $= 9.6$ kg of O_2

8. **(d) :** Average isotopic mass of X

$$= \frac{200 \times 90 + 199 \times 8 + 202 \times 2}{90 + 8 + 2}$$

$$= \frac{18000 + 1592 + 404}{100} = 199.96 \text{ amu} \approx 200 \text{ amu}$$

9. **(a) :** Average atomic mass $= \frac{19 \times 10 + 81 \times 11}{100} = 10.81$

10. **(d) :** 1 mole of substance = N_A atoms

108 g of Ag = N_A atoms ⇒ 1 g of Ag $= \frac{N_A}{108}$ atoms

24 g of Mg = N_A atoms ⇒ 1 g of Mg $= \frac{N_A}{24}$ atoms

32 g of O_2 = N_A molecules = 2 N_A atoms

⇒ 1 g of $O_2 = \frac{N_A}{16}$ atoms

7 g of Li = N_A atoms $\Rightarrow$ $1\text{ g of Li} = \frac{N_A}{7}$ atoms

Therefore, 1 g of $Li_{(s)}$, has maximum number of atoms.

11. (a) : (a) Mass of water $= V \times d = 18 \times 1 = 18\text{ g}$

Molecules of water = mole × $N_A = \frac{18}{18} N_A = N_A$

(b) Molecules of water = mole × $N_A = \frac{0.18}{18} N_A$

$= 10^{-2}\, N_A$

(c) Moles of water $= \frac{0.00224}{22.4} = 10^{-4}$

Molecules of water = mole × $N_A = 10^{-4}\, N_A$

(d) Molecules of water = mole × $N_A = 10^{-3}\, N_A$

12. (a) : Let atomic weight of element X is x and that of element Y is y.

For XY_2, $n = \frac{w}{\text{Mol. wt.}}$

$$0.1 = \frac{10}{x+2y} \Rightarrow x + 2y = \frac{10}{0.1} = 100 \qquad \text{...(i)}$$

For X_3Y_2, $n = \frac{w}{\text{Mol. wt.}}$

$$0.05 = \frac{9}{3x+2y} \Rightarrow 3x + 2y = \frac{9}{0.05} = 180 \qquad \text{...(ii)}$$

On solving equations (i) and (ii), we get $x = 40$

$40 + 2y = 100 \Rightarrow 2y = 60 \Rightarrow y = 30$

13. (a) : Mass of 1 mol (6.022×10^{23} atoms) of carbon $= 12$ g

If Avogadro number is changed to 6.022×10^{20} atoms then mass of 1 mol of carbon

$$= \frac{12 \times 6.022 \times 10^{20}}{6.022 \times 10^{23}} = 12 \times 10^{-3}\text{ g}$$

14. (c) : 1.8 gram of water $= \frac{6.023 \times 10^{23}}{18} \times 1.8$

$= 6.023 \times 10^{22}$ molecules

18 gram of water $= 6.023 \times 10^{23}$ molecules

18 moles of water $= 18 \times 6.023 \times 10^{23}$ molecules

15. (d) : Number of moles of $H_2 = 1/2$

Number of moles of $O_2 = \frac{4}{32}$

Hence, molar ratio $= \frac{1}{2} : \frac{4}{32} = 4 : 1$

16. (c) : 8 g H_2 has 4 moles while the others has 1 mole each.

17. (b) : No. of atoms $= N_A \times$ No. of moles $\times 3$

$= 6.023 \times 10^{23} \times 0.1 \times 3 = 1.806 \times 10^{23}$

18. (a) : At STP, 22.4 L $= 6.023 \times 10^{23}$ molecules

$15\text{ L } H_2 = \frac{6.023 \times 10^{23} \times 15}{22.4} = 4.033 \times 10^{23}$ molecules

$5\text{ L } N_2 = \frac{6.023 \times 10^{23} \times 5}{22.4} = 1.344 \times 10^{23}$ molecules

2 g $H_2 = 6.023 \times 10^{23}$ molecules

$0.5\text{ g } H_2 = \frac{6.023 \times 10^{23} \times 0.5}{2} = 1.505 \times 10^{23}$ molecules

32 g $O_2 = 6.023 \times 10^{23}$ molecules

$10\text{ g of } O_2 = \frac{6.023 \times 10^{23} \times 10}{32} = 1.882 \times 10^{23}$ molecules

19. (b) : Number of molecules = moles × N_A

Molecules of $N_2 = \frac{7}{14}\, N_A = 0.5\, N_A$

Molecules of $H_2 = N_A$

Molecules of $NO_2 = \frac{16}{46}\, N_A = 0.35\, N_A$

Molecules of $O_2 = \frac{16}{32}\, N_A = 0.5\, N_A$

$\therefore$ 2 g H_2 (1 mole H_2) contains maximum molecules.

20. (a) : Specific volume (vol. of 1 g) of cylindrical virus particle $= 6.02 \times 10^{-2}$ cc/g

Radius of virus, $r = 7\text{ Å} = 7 \times 10^{-8}$ cm

Volume of virus $= \pi r^2 l$

$$= \frac{22}{7} \times (7 \times 10^{-8})^2 \times 10 \times 10^{-8} = 154 \times 10^{-23}\text{ cc}$$

$$\text{wt. of one virus particle} = \frac{\text{Volume (cc)}}{\text{Specific volume (cc/g)}}$$

$$= \frac{154 \times 10^{-23}}{6.02 \times 10^{-2}}\text{ g}$$

$\therefore$ Molecular wt. of virus = wt. of N_A particles

$$= \frac{154 \times 10^{-23}}{6.02 \times 10^{-2}} \times 6.02 \times 10^{23}\text{ g/mol}$$

$= 15400$ g/mol $= 15.4$ kg/mol

21. (d) : 17 g of $NH_3 = 4N_A$ atoms

$4.25\text{ g of } NH_3 = \frac{4N_A}{17} \times 4.25$ atoms

$= N_A$ atoms $= 6 \times 10^{23}$ atoms

22. (a) : Quantity of iron in one molecule

$$= \frac{67200}{100} \times 0.334 = 224.45\text{ amu}$$

No. of iron atoms in one molecule of haemoglobin

$$= \frac{224.45}{56} = 4$$

23. (a) : Volume of oxygen in one litre of air

$$= \frac{21}{100} \times 1000 = 210\text{ mL}$$

Therefore, no. of moles $= \frac{210}{22400} = 0.0093$ mol

24. (c) : Each nitrogen atom has 5 valence electrons, therefore total number of valence electrons in N_3^- ion is 16. Since the molecular mass of N_3^- is 42, therefore total number of valence electrons in 4.2 g of N_3^- ion

$$= \frac{4.2}{42} \times 16 \times N_A = 1.6\,N_A$$

25. (b) : Avogadro's no., $N_A = 6.02 \times 10^{23}$ molecules = 1 mole

∴ 6.02×10^{24} CO molecules = 10 moles CO

= 10 g atoms of O = 5 g molecules of O_2

26. (a) : Here, $C_p/C_v = 1.4$, which shows that the gas is diatomic.

22.4 L at NTP = 6.02×10^{23} molecules

∴ 11.2 L at NTP = 3.01×10^{23} molecules

Since gas is diatomic,

∴ 11.2 L at NTP = $2 \times 3.01 \times 10^{23}$ atoms

= 6.02×10^{23} atom

27. (a) : 1 mol of CO_2 = 44 g of CO_2

∴ 4.4 g CO_2 = 0.1 mol CO_2 = 6×10^{22} molecules

[Since, 1 mole CO_2 = 6×10^{23} molecules]

= $2 \times 6 \times 10^{22}$ atoms of O = 1.2×10^{23} atoms of O

28. (d) : As we know,

22400 cc of N_2O contain 6.02×10^{23} molecules

∴ 1 cc of N_2O contain $\frac{6.02 \times 10^{23}}{22400}$ molecules

Since in N_2O molecule there are 3 atoms

∴ 1 cc $N_2O = \frac{3 \times 6.02 \times 10^{23}}{22400}$ atoms $= \frac{1.8 \times 10^{22}}{224}$ atoms

No. of electrons in a molecule of N_2O = 7 + 7 + 8 = 22

Hence, no. of electrons in 1 cc of N_2O

$$= \frac{6.02 \times 10^{23}}{22400} \times 22 \text{ electrons} = \frac{1.32}{224} \times 10^{23} \text{ electrons}$$

29. (c) :

Element	%	Atomic mass	Mole	Simple ratio
C	38.71	12	$\frac{38.71}{12} = 3.22$	$\frac{3.22}{3.22} = 1$
H	9.67	1	$\frac{9.67}{1} = 9.67$	$\frac{9.67}{3.22} = 3$
O	51.62	16	$\frac{51.62}{16} = 3.22$	$\frac{3.22}{3.22} = 1$

Hence, empirical formula of the compound would be CH_3O.

30. (a) : In peroxidase anhydrous enzyme, 0.5% Se is present means, 0.5 g Se is present in 100 g of enzyme. In a molecule of enzyme one Se atom must be present. Hence, 78.4 g Se will be present in $\frac{100}{0.5} \times 78.4 = 1.568 \times 10^4$

∴ Minimum molecular weight of enzyme is 1.568×10^4.

31. (c) : Urea (NH_2CONH_2), % of N $= \frac{28}{60} \times 100 = 46.66\%$

Similarly, % of N in other compounds are :

$(NH_4)_2SO_4$ = 21.2%; $CaCN_2$ = 35.0% and NH_4NO_3 = 35.0%

32. (d) : Haber's process, $N_2 + 3H_2 \rightarrow 2NH_3$

2 moles of NH_3 are formed by 3 moles of H_2.

∴ 20 moles of NH_3 will be formed by 30 moles of H_2.

33. (c) : Density = 1.28 g/cc,

Conc. of solution = 2 M

Molar mass of NaOH = 40 g mol^{-1}

Volume of solution = 1 L = 1000 mL

Mass of solution = $d \times V$ = 1.28 × 1000 = 1280 g

Mass of solute = n × Molar mass = 2 × 40 = 80 g

Mass of solvent = (1280 – 80) g = 1200 g

Number of moles of solute $= \frac{80}{40} = 2$

∴ Molality $= \frac{2 \times 1000}{1200} = 1.67$ m

34. (c) : $HCOOH \xrightarrow[\text{conc. } H_2SO_4]{\text{Dehydrating agent}} CO + H_2O$

	HCOOH	CO	H_2O
n_i	$= \frac{2.3}{46} = \frac{1}{20}$	0	0
n_f	= 0	$\frac{1}{20}$	$\frac{1}{20}$

$H_2C_2O_4 \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$

	$H_2C_2O_4$	CO	CO_2	H_2O
n_i	$= \frac{4.5}{90} = \frac{1}{20}$	0	0	0
n_f	=0	$\frac{1}{20}$	$\frac{1}{20}$	$\frac{1}{20}$

H_2O gets absorbed by conc. H_2SO_4. Gaseous mixture (containing CO and CO_2) when passed through KOH pellets, CO_2 gets absorbed.

Moles of CO left (unabsorbed) $= \frac{1}{20} + \frac{1}{20} = \frac{1}{10}$

Mass of CO = moles × molar mass $= \frac{1}{10} \times 28 = 2.8$ g

35. (b) : 16.9% solution of $AgNO_3$ means 16.9 g of $AgNO_3$ in 100 mL of solution.

= 8.45 g of $AgNO_3$ in 50 mL solution.

Similarly, 5.8 g of NaCl in 100 mL solution

≡ 2.9 g of NaCl in 50 mL solution.

The reaction can be represented as :

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

	$AgNO_3$	NaCl	AgCl	$NaNO_3$
Initial mole	8.45/170 = 0.049	2.9/58.5 = 0.049	0	0
Final moles	0	0	0.049	0.049

∴ Mass of AgCl precipitated = 0.049 × 143.3

= 7.02 ≈ 7 g

36. **(c) :** $\underset{84\text{ g}}{MgCO_{3(s)}} \xrightarrow{\Delta} \underset{40\text{ g}}{MgO_{(s)}} + CO_{2(g)}$

84 g of $MgCO_3$ ≡ 40 g of MgO

$\therefore$ 20 g of $MgCO_3 \equiv \frac{40}{84} \times 20 = 9.52$ g of MgO

Actual yield = 8 g of MgO

$\therefore$ % purity $= \frac{8}{9.52} \times 100 = 84\%$

37. **(a) :** 1 mole ≡ 22.4 litres at STP.

$n_{H_2} = \frac{22.4}{22.4} = 1$ mol; $n_{Cl_2} = \frac{11.2}{22.4} = 0.5$ mol

Reaction is as,

	$H_{2(g)}$ +	$Cl_{2(g)}$ $\longrightarrow$	$2HCl_{(g)}$
Initial	1 mol	0.5 mol	0
Final	(1 – 0.5) = 0.5 mol	(0.5 – 0.5) = 0 mol	2 × 0.5 1 mol

Here, Cl_2 is limiting reagent. So, 1 mole of $HCl_{(g)}$ is formed.

38. **(a) :** $n_{Mg} = \frac{1}{24} = 0.0416$ moles

$n_{O_2} = \frac{0.56}{32} = 0.0175$ mole

The balanced equation is

	2Mg +	O_2 $\longrightarrow$	2MgO
Initial	0.0416 mole	0.0175 mole	0
Final	(0.0416 – 2 × 0.0175) = 0.0066 mole	0	2 × 0.0175

Here, O_2 is limiting reagent.

$\therefore$ Mass of Mg left in excess = 0.0066 × 24 = 0.16 g

39. **(d) :** Moles of urea $= \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}} = 0.001$

Concentration of solution $= \frac{0.001}{100} \times 1000 = 0.01$ M

40. **(b) :** Millimoles of solution of chloride

= 0.05 × 10 = 0.5

Millimoles of $AgNO_3$ solution = 10 × 0.1 = 1

So, the millimoles of $AgNO_3$ are double than the chloride solution.

$\therefore$ $XCl_2 + 2AgNO_3 \rightarrow 2AgCl + X(NO_3)_2$

41. **(b) :** Given that molar mass of Na_2CO_3 = 106 g

$\therefore$ Molarity of solution $= \frac{25.3 \times 1000}{106 \times 250} = 0.955$ M

$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$

$[Na^+] = 2[Na_2CO_3] = 2 \times 0.955 = 1.910$ M

$[CO_3^{2-}] = [Na_2CO_3] = 0.955$ M

42. **(b) :** $\underset{\substack{2\text{ g}\\1\text{ mol}}}{H_2} + \underset{\substack{16\text{ g}\\0.5\text{ mol}}}{1/2O_2} \rightarrow \underset{\substack{18\text{ g}\\1\text{ mol}}}{H_2O}$

10 g of H_2 = 5 mol and 64 g of O_2 = 2 mol

$\therefore$ In this reaction, oxygen is the limiting reagent so amount of H_2O produced depends on the amount of O_2.

Since 0.5 mol of O_2 gives 1 mol of H_2O

$\therefore$ 2 mol of O_2 will give 4 mol of H_2O

43. **(b) :** $\underset{\substack{\frac{6.5}{224}\text{ mol}\\= 0.029\text{ mol}}}{PbO} + \underset{\substack{\frac{3.2}{36.5}\text{ mol}\\= 0.087\text{ mol}}}{2HCl} \rightarrow PbCl_2 + H_2O$

Formation of moles of lead(II) chloride depends upon the no. of moles of PbO which acts as a limiting reagent here. So, no. of moles of $PbCl_2$ formed will be equal to the no. of moles of PbO *i.e.* 0.029.

44. **(c) :** $3C + \underset{\text{(From bauxite)}}{2Al_2O_3} \longrightarrow 4Al + 3CO_2$

4 moles of Al is produced by 3 moles of C.

1 mole of Al is produced by $\frac{3}{4}$ mole of C.

$\frac{270 \times 1000}{27} = 10^4$ moles of Al is produced by $\frac{3}{4} \times 10^4$ moles of C.

Amount of carbon used $= \frac{3}{4} \times 10^4 \times 12$ g

$= \frac{3}{4} \times 10 \times 12$ kg = 90 kg

45. **(c) :** Density = 1.17 g/cc.

⇒ 1 cc. solution contains 1.17 g of HCl

$\therefore$ Molarity $= \frac{1.17 \times 1000}{36.5 \times 1} = 32.05$

46. **(b) :** $\underset{\substack{197.3\text{ g}\\ \\9.85\text{ g}}}{BaCO_3} \rightarrow BaO + \underset{\substack{22.4\text{ L at N.T.P.}\\ \\ \frac{22.4}{197.3} \times 9.85\\= 1.118\text{ L}}}{CO_2}$

⇒ 9.85 g of $BaCO_3$ will produce 1.118 L of CO_2 at N.T.P. on the complete decomposition.

47. **(a) :** $\underset{4\text{ moles}}{4NH_{3(g)}} + \underset{5\text{ moles}}{5O_{2(g)}} \rightarrow \underset{4\text{ moles}}{4NO_{(g)}} + \underset{6\text{ moles}}{6H_2O_{(l)}}$

⇒ 1 mole of NH_3 requires = 5/4 = 1.25 mole of oxygen while 1 mole of O_2 requires =4/5 = 0.8 mole of NH_3.

Therefore, all oxygen will be consumed.

48. **(c) :** $\underset{65\text{ g}}{Zn} + H_2SO_4 \rightarrow ZnSO_4 + \underset{22400\text{ mL}}{H_2}$

Since 65 g of zinc reacts to liberate 22400 mL of H_2 at STP, therefore amount of zinc needed to produce 224 mL of H_2 at STP $= \frac{65}{22400} \times 224 = 0.65$ g

49. **(a) :** Weight of 1 mol of CCl_4 vapour

= 12 + 4 × 35.5 = 154 g

$\therefore$ Density of CCl_4 vapour $= \frac{154}{22.4}$ g L^{-1} = 6.875 g L^{-1}

* * *

CHAPTER

2

Structure of Atom

2.2 Atomic Models

1. The number of protons, neutrons and electrons in $^{175}_{71}Lu$, respectively, are

(a) 71, 104 and 71 (b) 104, 71 and 71
(c) 71, 71 and 104 (d) 175, 104 and 71

(NEET 2020)

2. Be^{2+} is isoelectronic with which of the following ions?

(a) H^+ (b) Li^+
(c) Na^+ (d) Mg^{2+} *(2014)*

3. Isoelectronic species are

(a) CO, CN^-, NO^+, C_2^{2-}
(b) CO^-, CN, NO, C_2^-
(c) CO^+, CN^+, NO^-, C_2
(d) CO, CN, NO, C_2 *(2000)*

4. The ion that is isoelectronic with CO is

(a) CN^- (b) N_2^+
(c) O^{2-} (d) N_2^- *(1997)*

5. Which one of the following is not isoelectronic with O^{2-}?

(a) Tl^+ (b) Na^+
(c) N^{3-} (d) F^- *(1994)*

2.3 Developments Leading to the Bohr's Model of Atom

6. Which of the following series of transitions in the spectrum of hydrogen atom falls in visible region?

(a) Brackett series (b) Lyman series
(c) Balmer series (d) Paschen series

(NEET 2019)

7. Calculate the energy in joule corresponding to light of wavelength 45 nm.
(Planck's constant, $h = 6.63 \times 10^{-34}$ J s, speed of light, $c = 3 \times 10^8$ m s^{-1})

(a) 6.67×10^{15} (b) 6.67×10^{11}
(c) 4.42×10^{-15} (d) 4.42×10^{-18} *(2014)*

8. The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s^{-1}. Which value is closest to the wavelength in nanometer of a quantum of light with frequency of 6×10^{15} s^{-1}?

(a) 50 (b) 75
(c) 10 (d) 25 *(NEET 2013)*

9. According to law of photochemical equivalence the energy absorbed (in ergs/mole) is given as ($h = 6.62 \times 10^{-27}$ ergs, $c = 3 \times 10^{10}$ cm s^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})

(a) $\dfrac{1.196\times10^8}{\lambda}$ (b) $\dfrac{2.859\times10^5}{\lambda}$
(c) $\dfrac{2.859\times10^{16}}{\lambda}$ (d) $\dfrac{1.196\times10^{16}}{\lambda}$

(Karnataka NEET 2013)

10. The energies E_1 and E_2 of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths *i.e.*, λ_1 and λ_2 will be

(a) $\lambda_1 = \lambda_2$ (b) $\lambda_1 = 2\lambda_2$
(c) $\lambda_1 = 4\lambda_2$ (d) $\lambda_1 = \frac{1}{2}\lambda_2$ *(2011)*

11. The value of Planck's constant is 6.63×10^{-34} J s. The velocity of light is 3.0×10^8 m s^{-1}. Which value is closest to the wavelength in nanometers of a quantum of light with frequency of 8×10^{15} s^{-1} ?

(a) 2×10^{-25} (b) 5×10^{-18}
(c) 4×10^1 (d) 3×10^7 *(2003)*

12. For given energy, $E = 3.03 \times 10^{-19}$ joules corresponding wavelength is
($h = 6.626 \times 10^{-34}$ J sec, $c = 3 \times 10^8$ m/sec)

(a) 65.6 nm (b) 6.56 nm
(c) 3.4 nm (d) 656 nm *(2000)*

13. What will be the longest wavelength line in Balmer series of spectrum?

(a) 546 nm (b) 656 nm
(c) 566 nm (d) 556 nm *(1996)*

2.4 Bohr's Model for Hydrogen Atom

14. Based on equation $E = -2.178 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$, certain conclusions are written. Which of them is not correct?

(a) Equation can be used to calculate the change in energy when the electron changes orbit.

(b) For $n = 1$, the electron has a more negative energy than it does for $n = 6$ which means that the electron is more loosely bound in the smallest allowed orbit.

(c) The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.

(d) Larger the value of n, the larger is the orbit radius. *(NEET 2013)*

15. According to the Bohr theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon?

(a) $n = 6$ to $n = 1$ (b) $n = 5$ to $n = 4$

(c) $n = 6$ to $n = 5$ (d) $n = 5$ to $n = 3$

(Mains 2011)

16. The energy of second Bohr orbit of the hydrogen atom is $-328\ \text{kJ mol}^{-1}$; hence the energy of fourth Bohr orbit would be

(a) $-41\ \text{kJ mol}^{-1}$ (b) $-82\ \text{kJ mol}^{-1}$

(c) $-164\ \text{kJ mol}^{-1}$ (d) $-1312\ \text{kJ mol}^{-1}$ *(2005)*

17. The frequency of radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionization energy of H $= 2.18 \times 10^{-18}\ \text{J atom}^{-1}$ and $h = 6.626 \times 10^{-34}\ \text{J s}$)

(a) $1.54 \times 10^{15}\ \text{s}^{-1}$ (b) $1.03 \times 10^{15}\ \text{s}^{-1}$

(c) $3.08 \times 10^{15}\ \text{s}^{-1}$ (d) $2.00 \times 10^{15}\ \text{s}^{-1}$ *(2004)*

18. In hydrogen atom, energy of first excited state is -3.4 eV. Then find out *K.E.* of same orbit of hydrogen atom.

(a) $+3.4$ eV (b) $+6.8$ eV

(c) -13.6 eV (d) $+13.6$ eV *(2002)*

19. Who modified Bohr's theory by introducing elliptical orbits for electron path?

(a) Rutherford (b) Thomson

(c) Hund (d) Sommerfeld *(1999)*

20. The Bohr orbit radius for the hydrogen atom ($n = 1$) is approximately 0.530 Å. The radius for the first excited state ($n = 2$) orbit is (in Å)

(a) 4.77 (b) 1.06

(c) 0.13 (d) 2.12 *(1998)*

21. In a Bohr's model of an atom, when an electron jumps from $n = 1$ to $n = 3$, how much energy will be emitted or absorbed?

(a) 2.389×10^{-12} ergs (b) 0.239×10^{-10} ergs

(c) 2.15×10^{-11} ergs (d) 0.1936×10^{-10} ergs

(1996)

22. The radius of hydrogen atom in the ground state is 0.53 Å. The radius of Li^{2+} ion (atomic number = 3) in a similar state is

(a) 0.53 Å (b) 1.06 Å

(c) 0.17 Å (d) 0.265 Å *(1995)*

23. The energy of an electron in the n^{th} Bohr orbit of hydrogen atom is

(a) $\frac{13.6}{n^4}$ eV (b) $\frac{13.6}{n^3}$ eV

(c) $\frac{13.6}{n^2}$ eV (d) $\frac{13.6}{n}$ eV *(1992)*

24. The spectrum of He is expected to be similar to that

(a) H (b) Li^+

(c) Na (d) He^+ *(1988)*

25. If r is the radius of the first orbit, the radius of n^{th} orbit of H-atom is given by

(a) rn^2 (b) rn

(c) r/n (d) r^2n^2 *(1988)*

2.5 Towards Quantum Mechanical Model of the Atom

26. In hydrogen atom, the de Broglie wavelength of an electron in the second Bohr orbit is [Given that Bohr radius, $a_0 = 52.9$ pm]

(a) 211.6 pm (b) 211.6 π pm

(c) 52.9 π pm (d) 105.8 pm

(Odisha NEET 2019)

27. A 0.66 kg ball is moving with a speed of 100 m/s. The associated wavelength will be ($h = 6.6 \times 10^{-34}$ J s)

(a) 6.6×10^{-32} m (b) 6.6×10^{-34} m

(c) 1.0×10^{-35} m (d) 1.0×10^{-32} m

(Mains 2010)

28. If uncertainty in position and momentum are equal, then uncertainty in velocity is

(a) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{\pi}}$ (c) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (d) $\sqrt{\frac{h}{2\pi}}$

(2008)

29. The measurement of the electron position is associated with an uncertainty in momentum, which is equal to $1 \times 10^{-18}\ \text{g cm s}^{-1}$. The uncertainty in electron velocity is (mass of an electron is 9×10^{-28} g)

(a) 1×10^5 cm s^{-1} (b) 1×10^{11} cm s^{-1}
(c) 1×10^9 cm s^{-1} (d) 1×10^6 cm s^{-1} *(2008)*

30. Given : The mass of electron is 9.11×10^{-31} kg, Planck constant is 6.626×10^{-34} J s, the uncertainty involved in the measurement of velocity within a distance of 0.1 Å is
(a) 5.79×10^5 m s^{-1} (b) 5.79×10^6 m s^{-1}
(c) 5.79×10^7 m s^{-1} (d) 5.79×10^8 m s^{-1}
(2006)

31. The uncertainty in momentum of an electron is 1×10^{-5} kg m/s. The uncertainty in its position will be ($h = 6.62 \times 10^{-34}$ kg m^2/s)
(a) 5.27×10^{-30} m (b) 1.05×10^{-26} m
(c) 1.05×10^{-28} m (d) 5.25×10^{-28} m *(1999)*

32. The de Broglie wavelength of a particle with mass 1 g and velocity 100 m/s is
(a) 6.63×10^{-35} m (b) 6.63×10^{-34} m
(c) 6.63×10^{-33} m (d) 6.65×10^{-35} m *(1999)*

33. The position of both, an electron and a helium atom is known within 1.0 nm. Further the momentum of the electron is known within 5.0×10^{-26} kg m s^{-1}. The minimum uncertainty in the measurement of the momentum of the helium atom is
(a) 8.0×10^{-26} kg m s^{-1} (b) 80 kg m s^{-1}
(c) 50 kg m s^{-1} (d) 5.0×10^{-26} kg m s^{-1}
(1998)

34. Uncertainty in position of an electron (Mass = 9.1×10^{-28} g) moving with a velocity of 3×10^4 cm/s accurate upto 0.001% will be
(Use $h/(4\pi)$ in uncertainty expression where $h = 6.626 \times 10^{-27}$ erg second)
(a) 5.76 cm (b) 7.68 cm
(c) 1.93 cm (d) 3.84 cm *(1995)*

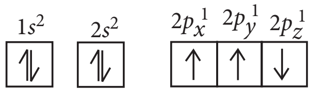
35. Which of the following statements do not form a part of Bohr's model of hydrogen atom?
(a) Energy of the electrons in the orbits are quantized.
(b) The electron in the orbit nearest the nucleus has the lowest energy.
(c) Electrons revolve in different orbits around the nucleus.
(d) The position and velocity of the electrons in the orbit cannot be determined simultaneously.
(1989)

2.6 Quantum Mechanical Model of Atom

36. 4*d*, 5*p*, 5*f* and 6*p* orbitals are arranged in the order of decreasing energy. The correct option is
(a) $5f > 6p > 4d > 5p$ (b) $5f > 6p > 5p > 4d$
(c) $6p > 5f > 5p > 4d$ (d) $6p > 5f > 4d > 5p$
(NEET 2019)

37. Orbital having 3 angular nodes and 3 total nodes is
(a) 5*p* (b) 3*d* (c) 4*f* (d) 6*d*
(Odisha NEET 2019)

38. Which one is a wrong statement?
(a) Total orbital angular momentum of electron in *s*-orbital is equal to zero.
(b) An orbital is designated by three quantum numbers while an electron in an atom is designated by four quantum numbers.
(c) The electronic configuration of N atom is



(d) The value of *m* for d_{z^2} is zero. *(NEET 2018)*

39. Which one is the wrong statement?
(a) The uncertainty principle is $\Delta E \times \Delta t \geq \dfrac{h}{4\pi}$
(b) Half filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement.
(c) The energy of 2*s*-orbital is less than the energy of 2*p*-orbital in case of hydrogen like atoms.
(d) de-Broglie's wavelength is given by $\lambda = \dfrac{h}{mv}$, where m = mass of the particle, v = group velocity of the particle. *(NEET 2017)*

40. How many electrons can fit in the orbital for which $n = 3$ and $l = 1$?
(a) 2 (b) 6
(c) 10 (d) 14 *(NEET-II 2016)*

41. Which of the following pairs of *d*-orbitals will have electron density along the axes?
(a) d_{z^2}, d_{xz} (b) d_{xz}, d_{yz}
(c) $d_{z^2}, d_{x^2-y^2}$ (d) $d_{xy}, d_{x^2-y^2}$
(NEET-II 2016)

42. Two electrons occupying the same orbital are distinguished by
(a) azimuthal quantum number
(b) spin quantum number
(c) principal quantum number
(d) magnetic quantum number. *(NEET-I 2016)*

43. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium?
(At. no. $Z = 22$)
(a) 4*s* 3*s* 3*p* 3*d* (b) 3*s* 3*p* 3*d* 4*s*
(c) 3*s* 3*p* 4*s* 3*d* (d) 3*s* 4*s* 3*p* 3*d* *(2015)*

44. The number of *d*-electrons in Fe^{2+} ($Z = 26$) is not equal to the number of electrons in which one of the following?
(a) *d*-electrons in Fe ($Z = 26$)
(b) *p*-electrons in Ne ($Z = 10$)

(c) *s*-electrons in Mg ($Z = 12$)
(d) *p*-electrons in Cl ($Z = 17$) *(2015, Cancelled)*

45. The angular momentum of electron in '*d*' orbital is equal to

(a) $2\sqrt{3}\,\hbar$ (b) $0\,\hbar$ (c) $\sqrt{6}\,\hbar$ (d) $\sqrt{2}\,\hbar$ *(2015, Cancelled)*

46. What is the maximum number of orbitals that can be identified with the following quantum numbers?

$n = 3, l = 1, m_l = 0$

(a) 1 (b) 2
(c) 3 (d) 4 *(2014)*

47. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers?

$n = 3$, $l = 1$ and $m = -1$

(a) 4 (b) 2
(c) 10 (d) 6 *(NEET 2013)*

48. The outer electronic configuration of Gd (At. No. 64) is

(a) $4f^5 5d^4 6s^1$ (b) $4f^7 5d^1 6s^2$
(c) $4f^3 5d^5 6s^2$ (d) $4f^4 5d^5 6s^1$ *(Karnataka NEET 2013)*

49. Maximum number of electrons in a subshell with $l = 3$ and $n = 4$ is

(a) 14 (b) 16
(c) 10 (d) 12 *(2012)*

50. The correct set of four quantum numbers for the valence electron of rubidium atom ($Z = 37$) is

(a) 5, 1, 1, +1/2 (b) 6, 0, 0, +1/2
(c) 5, 0, 0, +1/2 (d) 5, 1, 0, +1/2 *(2012)*

51. The orbital angular momentum of a *p*-electron is given as

(a) $\frac{h}{\sqrt{2}\,\pi}$ (b) $\sqrt{3}\,\frac{h}{2\pi}$

(c) $\sqrt{\frac{3}{2}}\,\frac{h}{\pi}$ (d) $\sqrt{6}\,\frac{h}{2\pi}$ *(Mains 2012)*

52. The total number of atomic orbitals in fourth energy level of an atom is

(a) 8 (b) 16
(c) 32 (d) 4 *(2011)*

53. If $n = 6$, the correct sequence for filling of electrons will be

(a) $ns \to (n-2)f \to (n-1)d \to np$
(b) $ns \to (n-1)d \to (n-2)f \to np$
(c) $ns \to (n-2)f \to np \to (n-1)d$
(d) $ns \to np \to (n-1)d \to (n-2)f$ *(2011)*

54. Maximum number of electrons in a subshell of an atom is determined by the following

(a) $2l + 1$ (b) $4l - 2$
(c) $2n^2$ (d) $4l + 2$ *(2009)*

55. Which of the following is not permissible arrangement of electrons in an atom?

(a) $n = 5, l = 3, m = 0, s = +1/2$
(b) $n = 3, l = 2, m = -3, s = -1/2$
(c) $n = 3, l = 2, m = -2, s = -1/2$
(d) $n = 4, l = 0, m = 0, s = -1/2$ *(2009)*

56. Consider the following sets of quantum numbers:

	n	***l***	***m***	***s***
(i)	3	0	0	+1/2
(ii)	2	2	1	+1/2
(iii)	4	3	−2	−1/2
(iv)	1	0	−1	−1/2
(v)	3	2	3	+1/2

Which of the following sets of quantum number is not possible?

(a) (i), (ii), (iii) and (iv)
(b) (ii), (iv) and (v)
(c) (i) and (iii)
(d) (ii), (iii) and (iv) *(2007)*

57. The orientation of an atomic orbital is governed by

(a) principal quantum number
(b) azimuthal quantum number
(c) spin quantum number
(d) magnetic quantum number. *(2006)*

58. The following quantum numbers are possible for how many orbitals?

$n = 3, l = 2, m = +2$

(a) 1 (b) 2
(c) 3 (d) 4 *(2001)*

59. For which of the following sets of four quantum numbers, an electron will have the highest energy?

	n	***l***	***m***	***s***
(a)	3	2	1	+1/2
(b)	4	2	− 1	+1/2
(c)	4	1	0	−1/2
(d)	5	0	0	−1/2

(1994)

60. Electronic configuration of calcium atom can be written as

(a) $[\mathrm{Ne}]4p^2$ (b) $[\mathrm{Ar}]4s^2$
(c) $[\mathrm{Ne}]4s^2$ (d) $[\mathrm{Kr}]4p^2$ *(1992)*

61. In a given atom no two electrons can have the same values for all the four quantum numbers. This is called

(a) Hund's Rule
(b) Aufbau principle
(c) Uncertainty principle
(d) Pauli's Exclusion principle. *(1991)*

62. For azimuthal quantum number $l = 3$, the maximum number of electrons will be
(a) 2 (b) 6
(c) 0 (d) 14 *(1991)*

63. The order of filling of electrons in the orbitals of an atom will be
(a) 3*d*, 4*s*, 4*p*, 4*d*, 5*s* (b) 4*s*, 3*d*, 4*p*, 5*s*, 4*d*
(c) 5*s*, 4*p*, 3*d*, 4*d*, 5*s* (d) 3*d*, 4*p*, 4*s*, 4*d*, 5*s* *(1991)*

64. The electronic configuration of Cu (atomic number 29) is
(a) $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2 3d^9$
(b) $1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^1$
(c) $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2 4p^6\ 5s^2 5p^1$
(d) $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2 4p^6 3d^3$ *(1991)*

65. The total number of electrons that can be accommodated in all the orbitals having principal quantum number 2 and azimuthal quantum number 1 are
(a) 2 (b) 4
(c) 6 (d) 8 *(1990)*

66. An ion has 18 electrons in the outermost shell, it is
(a) Cu^+ (b) Th^{4+}
(c) Cs^+ (d) K^+ *(1990)*

67. Number of unpaired electrons in N^{2+} is/are
(a) 2 (b) 0
(c) 1 (d) 3 *(1989)*

68. The maximum number of electrons in a subshell is given by the expression
(a) $4l - 2$ (b) $4l + 2$
(c) $2l + 2$ (d) $2n^2$ *(1989)*

69. The number of spherical nodes in 3*p* orbitals are/is
(a) one (b) three
(c) none (d) two *(1988)*

ANSWER KEY

1.	(a)	**2.**	(b)	**3.**	(a)	**4.**	(a)	**5.**	(a)	**6.**	(c)	**7.**	(d)	**8.**	(a)	**9.**	(a)	**10.**	(b)
11.	(c)	**12.**	(d)	**13.**	(b)	**14.**	(b)	**15.**	(c)	**16.**	(b)	**17.**	(c)	**18.**	(a)	**19.**	(d)	**20.**	(d)
21.	(d)	**22.**	(c)	**23.**	(c)	**24.**	(b)	**25.**	(a)	**26.**	(b)	**27.**	(c)	**28.**	(c)	**29.**	(c)	**30.**	(b)
31.	(a)	**32.**	(c)	**33.**	(d)	**34.**	(c)	**35.**	(d)	**36.**	(b)	**37.**	(c)	**38.**	(c)	**39.**	(c)	**40.**	(a)
41.	(c)	**42.**	(b)	**43.**	(c)	**44.**	(d)	**45.**	(c)	**46.**	(a)	**47.**	(b)	**48.**	(b)	**49.**	(a)	**50.**	(c)
51.	(a)	**52.**	(b)	**53.**	(a)	**54.**	(d)	**55.**	(b)	**56.**	(b)	**57.**	(d)	**58.**	(a)	**59.**	(b)	**60.**	(b)
61.	(d)	**62.**	(d)	**63.**	(b)	**64.**	(b)	**65.**	(c)	**66.**	(a)	**67.**	(c)	**68.**	(b)	**69.**	(a)		

Hints & Explanations

1. **(a) :** $^{175}_{71}Lu$, Number of protons = Number of electrons = Atomic number = 71
Number of neutrons = Mass number – Atomic number
= 175 – 71 = 104

2. **(b) :**

Species	**No. of electrons**
Be^{2+}	2
H^+	0
Li^+	2
Na^+	10
Mg^{2+}	10

3. **(a) :** Species having same no. of electrons are called isoelectronic species.
The no. of electrons in $CO = CN^- = NO^+ = C_2^{2-} = 14$. So, these are isoelectronic species.

4. **(a) :** Since both CO and CN^- have 14 electrons, therefore these are isoelectronic species (*i.e.* having same number of electrons).

5. **(a) :** The number of electrons in O^{2-}, N^{3-}, F^- and Na^+ is 10 each, but number of electrons in Tl^+ is 80.

6. **(c) :**
Lyman series : UV region
Balmer series : Visible region
Paschen series : IR region
Brackett series : IR region

7. **(d) :** $E = \dfrac{hc}{\lambda}$ [Given, $\lambda = 45\text{ nm} = 45 \times 10^{-9}\text{ m}$]

On putting the given values in the equation, we get

$$E = \frac{6.63\times10^{-34}\times3\times10^{8}}{45\times10^{-9}} = 4.42\times10^{-18}\ \text{J}$$

8. **(a) :** $c = \upsilon\lambda$

$$\lambda = \frac{c}{\upsilon} = \frac{3\times10^{17}}{6\times10^{15}} = 50\ \text{nm}$$

9. **(a) :** We know that, $E = \dfrac{hcN_A}{\lambda}$

$$= \frac{6.62\times10^{-27}\times3\times10^{10}\times6.02\times10^{23}}{\lambda}$$

$$= \frac{1.1955\times10^{8}}{\lambda} = \frac{1.196\times10^{8}}{\lambda}\ \text{ergs mol}^{-1}$$

10. **(b) :** $E_1 = \dfrac{hc}{\lambda_1}$ and $E_2 = \dfrac{hc}{\lambda_2}$;

$$\frac{E_1}{E_2} = \frac{hc}{\lambda_1}\times\frac{\lambda_2}{hc} = \frac{\lambda_2}{\lambda_1}$$

or $\dfrac{25}{50} = \dfrac{\lambda_2}{\lambda_1}$ or $\dfrac{1}{2} = \dfrac{\lambda_2}{\lambda_1} \Rightarrow \lambda_1 = 2\lambda_2$

11. **(c) :** Applying $\upsilon = c/\lambda$,

$$\lambda = \frac{c}{\upsilon} = \frac{3\times10^{8}}{8\times10^{15}} = 37.5\times10^{-9}\ \text{m}$$

$= 37.5$ nm $\approx 4\times10^{1}$ nm

12. **(d) :** $E = \dfrac{hc}{\lambda} \Rightarrow \lambda = \dfrac{6.626\times10^{-34}\times3\times10^{8}}{3.03\times10^{-19}}$

$= 656$ nm

13. **(b) :** The longest wavelength means the lowest energy. We know that relation for wavelength

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

(R_H, Rydberg constant = 109677 cm^{-1})
For $n_1 = 2$, $n_2 = 3$

$$\frac{1}{\lambda} = 109677\left(\frac{1}{(2)^2} - \frac{1}{(3)^2}\right) = 15233$$

or, $\lambda = \dfrac{1}{15233} = 6.56\times10^{-5}$ cm

$= 6.56\times10^{-7}$ m = 656 nm

14. **(b) :** The electron is more tightly bound in the smallest allowed orbit.

15. **(c) :** We know that

$$\Delta E \propto \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right],\ \text{where } n_2 > n_1$$

$\therefore$ $n = 6$ to $n = 5$ will give least energetic photon.

16. **(b) :** $E_n = -K\left(\dfrac{Z}{n}\right)^2$

$Z = 1$ for hydrogen; $n = 2$

$E_2 = \dfrac{-K\times1}{4} \Rightarrow E_2 = -328$ kJ mol^{-1}; $K = 4\times328$

$E_4 = \dfrac{-K\times1}{16} \Rightarrow E_4 = -4\times328\times\dfrac{1}{16} = -82$ kJ mol^{-1}

17. **(c) :** $E = h\upsilon$ or $\upsilon = E/h$

For H atom, $E = \dfrac{-21.8\times10^{-19}}{n^2}$ J atom^{-1}

$$\Delta E = -21.8\times10^{-19}\left(\frac{1}{4^2} - \frac{1}{1^2}\right) = 20.44\times10^{-19}\ \text{J atom}^{-1}$$

$$\upsilon = \frac{20.44\times10^{-19}}{6.626\times10^{-34}} = 3.08\times10^{15}\ \text{s}^{-1}$$

18. **(a) :** Kinetic energy $= \dfrac{1}{2}mv^2 = \left(\dfrac{\pi e^2}{nh}\right)^2\times2m$

$$\left[\because\ v = \frac{2\pi e^2}{nh}\right]$$

Total energy, $E_n = -\dfrac{2\pi^2me^4}{n^2h^2} = -\left(\dfrac{\pi e^2}{nh}\right)^2\times2m = -K.E.$

$\therefore$ Kinetic energy $= -E_n$
Energy of first excited state is -3.4 eV.
$\therefore$ Kinetic energy of same orbit ($n = 2$) will be $+3.4$ eV.

19. **(d) :** Sommerfeld modified Bohr's theory considering that in addition to circular orbits electrons also move in elliptical orbits.

20. **(d) :** For n^{th} orbit of 'H' atom, $r_n = n^2\times r_1$
$\Rightarrow$ radius of 2nd Bohr's orbit.
$r_2 = 4\times r_1 = 4\times0.53 = 2.12$ Å

21. **(d) :** Energy of an atom when $n = 1$

$E_1 = -\dfrac{1312}{(1)^2} = -1312$ kJ mol^{-1}

Similarly energy when $n = 3$, $(E_3) = -\dfrac{1312}{(3)^2}$

$= -145.7$ kJ mol^{-1}

The energy absorbed when an electron jumps from $n = 1$ to $n = 3$,

$E_3 - E_1 = -145.7 - (-1312) = 1166.3$ kJ mol^{-1}

$= \dfrac{1166.3}{6.023\times10^{23}} = 193.6\times10^{-23}$ kJ

$= 193.6\times10^{-20}$ J [1 joule = 10^7 ergs]

$\Rightarrow$ 193.6×10^{-13} ergs $= 0.1936\times10^{-10}$ ergs

22. **(c) :** Due to ground state, state of hydrogen atom $(n) = 1$; Radius of hydrogen atom $(r) = 0.53$ Å
Atomic no. of Li $(Z) = 3$

Now, radius of Li^{2+} ion $= r\times\dfrac{n^2}{Z} = 0.53\times\dfrac{(1)^2}{3} = 0.17$Å

23. **(c) :** Energy of an electron in n^{th} Bohr orbit of hydrogen atom $= \dfrac{-13.6}{n^2}$ eV.

24. **(b) :** Both He and Li^+ contain 2 electrons each.

25. **(a) :** Radius of n^{th} orbit of H-atom $= r_0n^2$
where r_0 = radius of the first orbit.

26. (b) : Bohr radius, $a_0 = 52.9$ pm

$n = 2, r_n = n^2 a_0 = (2)^2 a_0 = 4 \times 52.9$ pm $= 211.6$ pm

The angular momentum of an electron in a given stationary state can be expressed as in equation,

$$mvr = n \cdot \frac{h}{2\pi} = 2 \times \frac{h}{2\pi} = \frac{h}{\pi} \Rightarrow mvr\pi = h \quad \text{... (i)}$$

de-Broglie equation,

$$\lambda = \frac{h}{mv}; \ \lambda mv = h \quad \text{... (ii)}$$

From equations (i) and (ii), we get $\lambda = \pi r$

Putting the value of r, $\lambda = 211.6\,\pi$ pm

27. (c) : According to de-Broglie equation, $\lambda = \dfrac{h}{mv}$

Given, $h = 6.6 \times 10^{-34}$ J s ; $m = 0.66$ kg ; $v = 100$ m s^{-1}

$$\therefore \ \lambda = \frac{6.6 \times 10^{-34}}{0.66 \times 100} = 1 \times 10^{-35}\,\text{m}$$

28. (c) : From Heisenberg uncertainty principle,

$$\Delta p \cdot \Delta x \ge \frac{h}{4\pi} \quad \text{or} \quad m\Delta v \times \Delta x \ge \frac{h}{4\pi}$$

$$\text{or} \quad (m\Delta v)^2 \ge \frac{h}{4\pi} \qquad (\because \Delta x = \Delta p)$$

$$\text{or} \quad \Delta v \ge \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

29. (c) : Uncertainty in momentum $(m\Delta v)$

$= 1 \times 10^{-18}$ g cm s^{-1}

Uncertainty in velocity (Δv)

$$= \frac{1 \times 10^{-18}}{9 \times 10^{-28}} = 1.1 \times 10^{9}\,\text{cm s}^{-1}$$

30. (b) : $\Delta x \cdot m\Delta v = h/4\pi$

$$0.1 \times 10^{-10} \times 9.11 \times 10^{-31} \times \Delta v = \frac{6.626 \times 10^{-34}}{4 \times 3.143}$$

$$\therefore \ \Delta v = \frac{6.626 \times 10^{-34}}{0.1 \times 10^{-10} \times 9.11 \times 10^{-31} \times 4 \times 3.143}$$

$= 5.79 \times 10^6$ m s^{-1}

31. (a) : $\Delta x \times \Delta p = \dfrac{h}{4\pi}$

(Heisenberg uncertainty principle)

$$\Rightarrow \ \Delta x = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 10^{-5}} = 5.27 \times 10^{-30}\,\text{m}$$

32. (c) : $$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-27}\,\text{erg sec}}{1\,\text{g} \times 10^4\,\text{cm/s}}$$

$= 6.63 \times 10^{-31}$ cm $= 6.63 \times 10^{-33}$ m

33. (d) : According to uncertainty principle the product of uncertainty in position and uncertainty in momentum is constant for a particle.

i.e., $\Delta x \times \Delta p = \dfrac{h}{4\pi}$

As, $\Delta x = 1.0$ nm for both electron and helium atom, so Δp is also same for both the particles.

Thus, uncertainty in momentum of the helium atom is also 5.0×10^{-26} kg m s^{-1}.

34. (c) : Mass of an electron $(m) = 9.1 \times 10^{-28}$ g

Velocity of electron $(v) = 3 \times 10^4$ cm/s

Accuracy $= 0.001\% = \dfrac{0.001}{100}$ and

Planck's constant $(h) = 6.626 \times 10^{-27}$ erg-second.

We know that actual velocity of the electron

$(\Delta v) = 3 \times 10^4 \times \dfrac{0.001}{100} = 0.3$ cm/s

Therefore, uncertainty in the position of the electron,

$$(\Delta x) = \frac{h}{4\pi m\Delta v} = \frac{6.626 \times 10^{-27}}{4\pi \times (9.1 \times 10^{-28}) \times 0.3} = 1.93\,\text{cm}$$

35. (d) : It is Heisenberg's uncertainty principle and not Bohr's postulate.

36. (b) : Higher the value of $(n + l)$ for an orbital, higher is its energy. However, if two different types of orbitals have same value of $(n + l)$, the orbital with lower value of n has lower energy. Therefore, decreasing order of energy of the given orbitals is $5f > 6p > 5p > 4d$.

37. (c) : Number of spherical/radial nodes in any orbital $= n - l - 1$

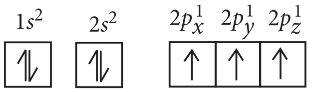
Number of planar/angular nodes in orbital $= l = 3$

$\therefore$ Total number of nodes in any orbital $= n - 1 = 3$

$\therefore$ $n = 4$

Thus, the orbital is $4f$.

38. (c) : According to Hund's rule of maximum multiplicity, the correct configuration of 'N' is



39. (c) : In case of hydrogen like atoms, energy depends on the principal quantum number only. Hence, $2s$-orbital will have energy equal to $2p$-orbital.

40. (a) : For $n = 3$ and $l = 1$, the subshell is $3p$ and a particular $3p$ orbital can accommodate only 2 electrons.

41. (c) : $d_{x^2-y^2}$ and d_{z^2} orbitals have electron density along the axes while d_{xy}, d_{yz} and d_{xz} orbitals have electron density in between the axes.

42. (b) : For the two electrons occupying the same orbital values of n, l and m_l are same but m_s is different, *i.e.*, $+\dfrac{1}{2}$ and $-\dfrac{1}{2}$.

43. (c) : Ti(22) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

$\therefore$ Order of increasing energy is $3s, 3p, 4s, 3d$.

44. (d) : Number of d-electrons in $Fe^{2+} = 6$
Number of p-electrons in Cl = 11

45. (c) : Angular momentum $= \sqrt{l(l+1)}\,\hbar$
For d-orbital, $l = 2$
Angular momentum $= \sqrt{2(2+1)}\,\hbar = \sqrt{6}\,\hbar$

46. (a) : Only one orbital, $3p_z$ has following set of quantum numbers, $n = 3, l = 1$ and $m_l = 0$.

47. (b) : The orbital associated with $n = 3, l = 1$ is $3p$. One orbital (with $m = -1$) of $3p$-subshell can accommodate maximum 2 electrons.

48. (b) : The electronic configuration of $_{64}Gd$ is $[Xe]4f^7 5d^1 6s^2$.

49. (a) : $l = 3$ and $n = 4$ represents $4f$. So, total number of electrons in a subshell $= 2(2l + 1) = 2(2 \times 3 + 1) = 14$ electrons. Hence, f-subshell can contain maximum 14 electrons.

50. (c) : Rb(37) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^1$
For $5s$, $n = 5, l = 0, m = 0, s = +1/2$ or $-1/2$

51. (a) : Orbital angular momentum (m)

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi}$$

For p-electrons; $l = 1$

$$\text{Thus, } m = \sqrt{1(1+1)}\,\frac{h}{2\pi} = \frac{\sqrt{2}\,h}{2\pi} = \frac{h}{\sqrt{2}\,\pi}$$

52. (b) : Total number of atomic orbitals in any energy level is given by n^2.

53. (a)

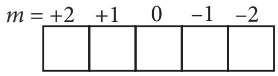
54. (d) : For a given shell, l,
the number of subshells, $m_l = (2l + 1)$
Since each subshell can accommodate 2 electrons of opposite spin, so maximum number of electrons in a subshell $= 2(2l + 1) = 4l + 2$.

55. (b) : In an atom, for any value of n, the values of $l = 0$ to $(n - 1)$.
For a given value of l, the values of $m_l = -l$ to 0 to $+l$ and the value of $s = +1/2$ or $-1/2$.
In option (b), $l = 2$ and $m_l = -3$
This is not possible, as values of m_l which are possible for $l = 2$ are $-2, -1, 0, +1$ and $+2$ only.

56. (b) : (i) represents an electron in $3s$ orbital.
(ii) is not possible as value of l varies from $0, 1, \ldots (n - 1)$.
(iii) represents an electron in $4f$ orbital.
(iv) is not possible as value of m varies from $-l \ldots +l$.
(v) is not possible as value of m varies from $-l \ldots +l$, it can never be greater than l.

57. (d) : Principal quantum number represents the name, size and energy of the shell to which the electron belongs. Azimuthal quantum number describes the spatial distribution of electron cloud and angular momentum. Magnetic quantum number describes the orientation or distribution of electron cloud. Spin quantum number represents the direction of electron spin around its own axis.

58. (a) : $n = 3, l = 2, m = +2$
It symbolises one of the five d-orbitals ($3d$).

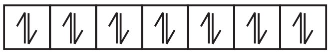


59. (b) : Energy of electron depends on the value of $(n + l)$. The subshell are $3d$, $4d$, $4p$ and $5s$, out of which $4d$ has highest energy.

60. (b) : Atomic no. of Ca = 20
$\therefore$ Electronic configuration of Ca $= [Ar]4s^2$

61. (d) : This is a Pauli's exclusion principle.

62. (d) : $l = 3$ means f-subshell
Maximum no. of electrons in f-subshell = 14

f-subshell =


63. (b) : Higher the value of $(n + l)$ for an orbital, higher is its energy. However, if two different types of orbitals have same value of $(n + l)$, the orbital with lower value of n has lower energy.

64. (b) : Electronic configuration of Cu is
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$.

65. (c) : $n = 2, l = 1$
It means $2p$-orbitals.
Total no. of electrons that can be accommodated in all the $2p$ orbitals = 6

66. (a) : Cu^+ ion has 18 electrons in its outermost shell.
Electronic configuration of Cu^+ is $1s^2 2s^2 2p^6\,3s^2 3p^6 3d^{10}$.

67. (c) : $N^{2+} = 1s^2 2s^2 2p^1$
$\therefore$ No. of unpaired electrons = 1

68. (b) : No. of orbitals in a subshell $= 2l + 1$
$\Rightarrow$ No. of electrons $= 2(2l + 1) = 4l + 2$

69. (a) : No. of radial nodes in $3p$-orbital $= n - l - 1$
$= 3 - 1 - 1 = 1$

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CHAPTER
3

Classification of Elements and Periodicity in Properties

3.4 Nomenclature of Elements with Atomic Numbers > 100

1. Identify the incorrect match.

Name	IUPAC Official Name
(A) Unnilunium	(i) Mendelevium
(B) Unniltrium	(ii) Lawrencium
(C) Unnilhexium	(iii) Seaborgium
(D) Unununnium	(iv) Darmstadtium

(a) (A), (i) (b) (B), (ii)
(c) (C), (iii) (d) (D), (iv)
(NEET 2020)

3.5 Electronic Configurations of Elements and The Periodic Table

2. The element $Z = 114$ has been discovered recently. It will belong to which of the following family/group and electronic configuration?
(a) Carbon family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^2$
(b) Oxygen family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^4$
(c) Nitrogen family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$
(d) Halogen family, [Rn] $5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$
(NEET 2017)

3. An atom has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$, you will place it in
(a) fifth group (b) fifteenth group
(c) second group (d) third group. *(2002)*

4. The electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$. What is the atomic number of the element, which is just below the above element in the periodic table?
(a) 36 (b) 49
(c) 33 (d) 34 *(1995)*

5. If the atomic number of an element is 33, it will be placed in the periodic table in the
(a) first group (b) third group
(c) fifth group (d) seventh group. *(1993)*

6. The electronic configuration of four elements are given below. Which elements does not belong to the same family as others?
(a) $[Xe]4f^{14}5d^{10}4s^2$ (b) $[Kr]4d^{10}5s^2$
(c) $[Ne]3s^2 3p^5$ (d) $[Ar]3d^{10}4s^2$ *(1989)*

3.7 Periodic Trends in Properties of Elements

7. For the second period elements the correct increasing order of first ionization enthalpy is
(a) Li < Be < B < C < O < N < F < Ne
(b) Li < Be < B < C < N < O < F < Ne
(c) Li < B < Be < C < O < N < F < Ne
(d) Li < B < Be < C < N < O < F < Ne *(NEET 2019)*

8. Match the oxide given in column I with its property given in column II.

Column I	Column II
(i) Na_2O	A. Neutral
(ii) Al_2O_3	B. Basic
(iii) N_2O	C. Acidic
(iv) Cl_2O_7	D. Amphoteric

Which of the following options has all correct pairs?
(a) (i)-B, (ii)-A, (iii)-D, (iv)-C
(b) (i)-C, (ii)-B, (iii)-A, (iv)-D
(c) (i)-A, (ii)-D, (iii)-B, (iv)-C
(d) (i)-B, (ii)-D, (iii)-A, (iv)-C *(Odisha NEET 2019)*

9. Which of the following oxides is most acidic in nature?
(a) MgO (b) BeO
(c) BaO (d) CaO *(NEET 2018)*

10. In which of the following options the order of arrangement does not agree with the variation of property indicated against it?
(a) I < Br < Cl < F (increasing electron gain enthalpy)
(b) Li < Na < K < Rb (increasing metallic radius)
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)
(d) B < C < N < O (increasing first ionisation enthalpy) *(NEET-I 2016)*

11. The formation of the oxide ion, $O^{2-}_{(g)}$ from oxygen atom requires first an exothermic and then an endothermic step as shown below :

$$O_{(g)} + e^- \rightarrow O^-_{(g)}; \Delta_f H° = -141 \text{ kJ mol}^{-1}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}; \Delta_f H° = +780 \text{ kJ mol}^{-1}$$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,

(a) O^- ion has comparatively smaller size than oxygen atom
(b) oxygen is more electronegative
(c) addition of electron in oxygen results in larger size of the ion
(d) electron repulsion outweighs the stability gained by achieving noble gas configuration. *(2015)*

12. Which of the following orders of ionic radii is correctly represented?

(a) $H^- > H^+ > H$
(b) $Na^+ > F^- > O^{2-}$
(c) $F^- > O^{2-} > Na^+$
(d) $Al^{3+} > Mg^{2+} > N^{3-}$
(2014)

13. Which one of the following arrangements represents the correct order of least negative to most negative electron gain enthalpy for C, Ca, Al, F and O?

(a) Al < Ca < O < C < F
(b) Al < O < C < Ca < F
(c) C < F < O < Al < Ca
(d) Ca < Al < C < O < F *(Karnataka NEET 2013)*

14. In which of the following arrangements the given sequence is not strictly according to the property indicated against it?

(a) HF < HCl < HBr < HI : increasing acidic strength
(b) $H_2O < H_2S < H_2Se < H_2Te$: increasing pK_a values
(c) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing acidic character
(d) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power *(Mains 2012)*

15. Identify the wrong statement in the following.

(a) Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius.
(b) Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius.
(c) Atomic radius of the elements increases as one moves down the first group of the periodic table.
(d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table. *(2012)*

16. What is the value of electron gain enthalpy of Na^+ if IE_1 of Na = 5.1 eV?

(a) –5.1 eV
(b) –10.2 eV
(c) +2.55 eV
(d) +10.2 eV *(Mains 2011)*

17. Which of the following oxides is amphoteric?

(a) SnO_2
(b) CaO
(c) SiO_2
(d) CO_2 *(Mains 2011)*

18. The correct order of the decreasing ionic radii among the following isoelectronic species is

(a) $Ca^{2+} > K^+ > S^{2-} > Cl^-$
(b) $Cl^- > S^{2-} > Ca^{2+} > K^+$
(c) $S^{2-} > Cl^- > K^+ > Ca^{2+}$
(d) $K^+ > Ca^{2+} > Cl^- > S^{2-}$ *(2010)*

19. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl?

(a) Cl < F < O < S
(b) O < S < F < Cl
(c) F < S < O < Cl
(d) S < O < Cl < F
(2010, 2005)

20. Among the elements Ca, Mg, P and Cl, the order of increasing atomic radii is

(a) Mg < Ca < Cl < P
(b) Cl < P < Mg < Ca
(c) P < Cl < Ca < Mg
(d) Ca < Mg < P < Cl
(Mains 2010)

21. Among the following which one has the highest cation to anion size ratio?

(a) CsI
(b) CsF
(c) LiF
(d) NaF *(Mains 2010)*

22. Amongst the elements with following electronic configurations, which one of them may have the highest ionisation energy?

(a) Ne $[3s^2\ 3p^2]$
(b) Ar $[3d^{10}\ 4s^2\ 4p^3]$
(c) Ne $[3s^2\ 3p^1]$
(d) Ne $[3s^2\ 3p^3]$ *(2009)*

23. Identify the correct order of the size of the following.

(a) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(b) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
(c) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$
(d) $Ca^{2+} < K^+ < Ar < S^{2-} < Cl^-$ *(2007)*

24. With which of the following electronic configuration an atom has the lowest ionisation enthalpy?

(a) $1s^2\ 2s^2\ 2p^3$
(b) $1s^2\ 2s^2\ 2p^5\ 3s^1$
(c) $1s^2\ 2s^2\ 2p^6$
(d) $1s^2\ 2s^2\ 2p^5$ *(2007)*

25. Which one of the following ionic species has the greatest proton affinity to form stable compound?

(a) NH_2^-
(b) F^-
(c) I^-
(d) HS^- *(2007)*

26. Which of the following is the most basic oxide?
(a) SeO_2 (b) Al_2O_3
(c) Sb_2O_3 (d) Bi_2O_3 *(2006)*

27. What is the correct relationship between the pH of isomolar solutions of sodium oxide, Na_2O (pH_1), sodium sulphide, Na_2S (pH_2), sodium selenide, Na_2Se (pH_3) and sodium telluride Na_2Te (pH_4)?
(a) $pH_1 > pH_2 > pH_3 > pH_4$
(b) $pH_1 > pH_2 \approx pH_3 > pH_4$
(c) $pH_1 < pH_2 < pH_3 < pH_4$
(d) $pH_1 < pH_2 < pH_3 \approx pH_4$ *(2005)*

28. Ionic radii are
(a) inversely proportional to effective nuclear charge
(b) inversely proportional to square of effective nuclear charge
(c) directly proportional to effective nuclear charge
(d) directly proportional to square of effective nuclear charge. *(2004)*

29. The ions O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show
(a) a significant increase from O^{2-} to Al^{3+}
(b) a significant decrease from O^{2-} to Al^{3+}
(c) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}
(d) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}. *(2003)*

30. Which of the following order is wrong?
(a) $NH_3 < PH_3 < AsH_3$ – acidic
(b) Li < Be < B < C – 1st IP
(c) $Al_2O_3 < MgO < Na_2O < K_2O$ – basic
(d) $Li^+ < Na^+ < K^+ < Cs^+$ – ionic radius. *(2002)*

31. Correct order of 1st ionisation potential among following elements Be, B, C, N, O is
(a) B < Be < C < O < N
(b) B < Be < C < N < O
(c) Be < B < C < N < O
(d) Be < B < C < O < N *(2001)*

32. Which of the following elements has the maximum electron affinity?
(a) I (b) Br
(c) Cl (d) F *(1999)*

33. The first ionization potentials (eV) of Be and B respectively are
(a) 8.29, 8.29 (b) 9.32, 9.32
(c) 8.29, 9.32 (d) 9.32, 8.29 *(1998)*

34. Which one of the following is correct order of the size of iodine species?
(a) $I^+ > I^- > I$ (b) $I^- > I > I^+$
(c) $I > I^- > I^+$ (d) $I > I^+ > I^-$ *(1997)*

35. Which of the following ions is the largest in size?
(a) K^+ (b) Ca^{2+}
(c) Cl^- (d) S^{2-} *(1996)*

36. Which of the following has the smallest size?
(a) Al^{3+} (b) F^-
(c) Na^+ (d) Mg^{2+} *(1996)*

37. Among the following oxides, the one which is most basic is
(a) ZnO (b) MgO
(c) Al_2O_3 (d) N_2O_5 *(1994)*

38. Which of the following has largest size?
(a) Na (b) Na^+
(c) Na^- (d) Can't be predicted.
(1993)

39. Na^+, Mg^{2+}, Al^{3+} and Si^{4+} are isoelectronic. The order of their ionic size is
(a) $Na^+ > Mg^{2+} < Al^{3+} < Si^{4+}$
(b) $Na^+ < Mg^{2+} > Al^{3+} > Si^{4+}$
(c) $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$
(d) $Na^+ < Mg^{2+} > Al^{3+} < Si^{4+}$ *(1993)*

40. In the periodic table from left to right in a period, the atomic volume
(a) decreases
(b) increases
(c) remains same
(d) first decreases then increases. *(1993)*

41. Which electronic configuration of an element has abnormally high difference between second and third ionization energy?
(a) $1s^2, 2s^2, 2p^6, 3s^1$
(b) $1s^2, 2s^2, 2p^6, 3s^1, 3p^1$
(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
(d) $1s^2, 2s^2, 2p^6, 3s^2$ *(1993)*

42. One of the characteristic properties of non-metals is that they
(a) are reducing agents
(b) form basic oxides
(c) form cations by electron gain
(d) are electronegative. *(1993)*

43. Which one of the following has minimum value of cation/anion ratio?
(a) NaCl (b) KCl
(c) $MgCl_2$ (d) CaF_2 *(1993)*

44. Which of the following sets has strongest tendency to form anions?
(a) Ga, Ni, Tl
(b) Na, Mg, Al
(c) N, O, F
(d) V, Cr, Mn *(1993)*

45. Elements of which of the following groups will form anions most readily?
(a) Oxygen family (b) Nitrogen family
(c) Halogens (d) Alkali metals *(1992)*

46. In the periodic table, with the increase in atomic number, the metallic character of an element
(a) decreases in a period and increases in a group
(b) increases in a period and decreases in a group
(c) increases both in a period and the group
(d) decreases in a period and the group. *(1989)*

47. Which of the following atoms will have the smallest size?
(a) Mg (b) Na
(c) Be (d) Li *(1989)*

ANSWER KEY

1.	(d)	**2.**	(a)	**3.**	(a)	**4.**	(c)	**5.**	(c)	**6.**	(c)	**7.**	(c)	**8.**	(d)	**9.**	(b)	**10.**	(a,d)
11.	(d)	**12.**	(None)			**13.**	(d)	**14.**	(b)	**15.**	(a)	**16.**	(a)	**17.**	(a)	**18.**	(c)	**19.**	(b)
20.	(b)	**21.**	(b)	**22.**	(d)	**23.**	(a)	**24.**	(b)	**25.**	(a)	**26.**	(d)	**27.**	(a)	**28.**	(a)	**29.**	(b)
30.	(b)	**31.**	(a)	**32.**	(c)	**33.**	(d)	**34.**	(b)	**35.**	(d)	**36.**	(a)	**37.**	(b)	**38.**	(c)	**39.**	(c)
40.	(d)	**41.**	(d)	**42.**	(d)	**43.**	(c)	**44.**	(c)	**45.**	(c)	**46.**	(a)	**47.**	(c)				

Hints & Explanations

1. (d) : Unnilunium – Mendelevium ⇒ (a)-(i)
Unniltrium – Lawrencium ⇒ (b)-(ii)
Unnilhexium – Seaborgium ⇒ (c)-(iii)
Unununnium – Roentgenium ⇒ (d)∗(iv)

2. (a) : The electronic configuration of the element with $Z = 114$ (Flerovium) is $[Rn]5f^{14}\,6d^{10}7s^2 7p^2$.
Hence, it belongs to carbon family which has the same outer electronic configuration.

3. (a) : The electronic configuration of an atom : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3\,4s^2$
In the configuration, the last electron of the atom is filled in *d*-subshell as $3d^3$. Thus, this element belongs to *d*-block of the periodic table with group no. VB or 5.

4. (c) : Atomic number of the given element is 15 and it belongs to group 15. Therefore atomic number of the element below the above element = 15 + 18 = 33.

5. (c) : Electronic configuration of an element with $Z = 33$ is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$.
Hence, it lies in VA or 15th group.

6. (c) : Elements (a), (b) and (d) belong to the same group since each one of them has two electrons in valence shell. In contrast, element (c) has seven electrons in the valence shell, and hence it lies in other group.

7. (c) : As we move across a period, ionisation enthalpy increases, because of increased nuclear charge and decrease in atomic radii. However, abnormal values are observed for Be, N and Ne due to extra stability of half filled and fully filled orbitals. Thus, the actual order is, Li < B < Be < C < O < N < F < Ne.

8. (d) : Na_2O - Basic oxide, Al_2O_3 - Amphoteric oxide, N_2O - Neutral oxide, Cl_2O_7 - Acidic oxide.

9. (b) : In metals, on moving down the group, metallic character increases, so basic nature increases hence most acidic will be BeO.

10. (a, d) : The correct order of increasing negative electron gain enthalpy is : I < Br < F < Cl due to electron-electron repulsion in small sized F atom and the correct order of increasing first ionisation enthalpy is B < C < O < N due to extra stability of half-filled orbitals in N-atom.

11. (d)

12. (None) : Cations lose electrons and are smaller in size than the parent atom, whereas anions add electrons and are larger in size than the parent atom. Hence, the order is $H^- > H > H^+$.
For isoelectronic species, the ionic radii decreases with increase in atomic number *i.e.*, nuclear charge. Hence, the correct orders are
$O^{2-} > F^- > Na^+$ and $N^{3-} > Mg^{2+} > Al^{3+}$.

13. (d) Electron gain enthalpy becomes less negative from top to bottom in a group while it becomes more negative from left to right within a period.

14. (b) : Acidic strength of hydrides increase with increase in molecular mass.

Thus, order of acidic strength is

$HF < HCl < HBr < HI$

$H_2O < H_2S < H_2Se < H_2Te$

$NH_3 < PH_3 < AsH_3 < SbH_3$

and as acidic strength increases, pK_a decreases. Thus order of pK_a

$H_2O > H_2S > H_2Se > H_2Te$

15. (a) : As positive charge on the cation increases, effective nuclear charge increases. Thus, atomic size decreases.

16. (a) : $Na \longrightarrow Na^+ + e^-; \Delta H = 5.1$ eV

$Na^+ + e^- \longrightarrow Na ; \Delta H = -5.1$ eV

17. (a) : SnO_2 reacts with acid as well as base. So, SnO_2 is an amphoteric oxide.

$SnO_2 + 4HCl \longrightarrow SnCl_2 + 2H_2O$

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

CaO is basic in nature while SiO_2 and CO_2 are acidic in nature.

18. (c) : $S^{2-} > Cl^- > K^+ > Ca^{2+}$

Among isoelectronic species, ionic radii increases with increase in negative charge. This happens because effective nuclear charge (Z_{eff}) decreases.

Similarly, ionic radii decreases with increase in positive charge as Z_{eff} increases.

19. (b) : Cl atom has the highest electron affinity in the periodic table. F being a member of group 17 has higher electron gain enthalpy than S which belongs to group 16. This in turn is higher than the electron affinity of O atom.

Thus, $Cl > F > S > O$

It is worth noting that the electron gain enthalpy of oxygen and fluorine, the members of the second period, have less negative values of electron gain enthalpy than the corresponding elements sulphur and chlorine of the third period.

This is due to small size of the atoms of oxygen and fluorine. As a result, there is a strong inter-electronic repulsion when extra electron is added to these atoms, *i.e.*, electron density is high and the addition of an extra electron is not easy.

20. (b) : The atomic radii decrease on moving from left to right in a period, thus order of sizes for Cl, P and Mg is $Cl < P < Mg$. Down the group size increases. Thus, overall order is $Cl < P < Mg < Ca$.

21. (b) : The cation to anion size ratio will be maximum when the cation is of largest size and the anion is of smallest size. Among the given species, Cs^+ has maximum size among given cations and F^- has smallest size among given anions, thus CsF has highest r_c/r_a ratio.

22. (d) : Among options (a), (c) and (d), option (d) has the highest ionisation energy because of extra stability associated with half-filled $3p$-orbital. In option (b), the presence of $3d^{10}$ electrons offers shielding effect, as a result the $4p^3$ electrons do not experience much nuclear charge and hence, the electrons can be removed easily.

23. (a) : Among isoelectronic ions, ionic radii of anions is more than that of cations. Further size of the anion increases with increase in negative charge and size of the cation decreases with increase in positive charge.

24. (b) : The larger the atomic size, smaller is the value of the ionisation enthalpy. Again higher the screening effect, lesser is the value of ionisation potential. Hence, option (b) has lowest ionisation enthalpy.

25. (a) : In going from left to right across a period in the periodic table, the basicity (*i.e.*, proton affinity) decreases as the electronegativity of the atom possessing the lone pair of electrons increases. Hence, basicity of NH_2^- is higher than F^-. On moving down a group, as the atomic size increases, basicity decreases. Hence, F^- is more basic than I^- and HO^- is more basic than HS^-. Hence, among the given ionic species, NH_2^- has maximum proton affinity.

26. (d) : $SeO_2 \longrightarrow$ acidic oxide,

Al_2O_3, $Sb_2O_3 \longrightarrow$ amphoteric,

$Bi_2O_3 \longrightarrow$ basic oxide.

27. (a) : Na_2O Basic character

Na_2S decreases down the group

Na_2Se

Na_2Te ↓

pH ∝ basic character

Hence, $pH_1 > pH_2 > pH_3 > pH_4$

28. (a)

29. (b) : Amongst isoelectronic ions, ionic radii of anions is more than that of cations. Further size of the anion increases with increase in –ve charge and size of cation decreases with increase in +ve charge. Hence, correct order is $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$.

30. (b) : Li, Be, B, C - these elements belong to the same period. Generally the value of 1st ionisation potential increases on moving from left to right in a period, since the nuclear charge of the elements also increase in the same direction. But the ionisation potential of boron ($B \longrightarrow 2s^2\,2p^1$) is lower than that of beryllium ($Be \longrightarrow 2s^2$), since in case of boron, $2p^1$ electron has to be removed to get B^+ while in case of Be ($2s^2$), s-electron has to be removed to get Be^+ ($2s^1$). p-electron can be removed more easily than *s*-electron so the energy required to remove electron will be less in case of boron. The order will be

$$Li < B < Be < C.$$

31. (a) : The energy required to remove the most loosely bound electron from an isolated gaseous atom is called the ionisation energy.

The ionisation potential increases as the size of the atom decreases. Atoms with fully or partly filled orbitals have high ionisation potential.

32. (c) : Among the halogens the electron affinity value of 'F' should be maximum. But due to small size there is inter-electronic repulsion thus, there is difficulty in entry of new electrons. Thus, the *E.A.* value is slightly lower than chlorine and the order is I < Br < F < Cl.

33. (d) : ${}_4Be \rightarrow 1s^2\ 2s^2$, ${}_5B \rightarrow 1s^2\ 2s^2\ 2p^1$

Due to stable fully-filled '*s*'-orbital arrangement of electrons in 'Be' atom, more energy is required to remove an electron from the valence shell than 'B'-atom. Therefore 'Be' has higher ionisation potential than 'B'.

34. (b) : Positive ion is always smaller and negative ion is always larger than the parent atom.

35. (d) : Since all of these ions contain 18 electrons each, so these are isoelectronic. For isoelectronic ions, the anion having large negative charge is the largest in size *i.e.*, S^{2-}.

36. (a) : These are isoelectronic ions (ions with same number of electrons) and for isoelectronic ions, greater the positive charge, greater is the force of attraction on the electrons by the nucleus and the smaller is the size of the ion. Thus, Al^{3+} has the smallest size.

37. (b) : Al_2O_3 and ZnO are amphoteric. N_2O_5 is strongly acidic. MgO is the most basic.

38. (c) : The cations are always smaller than the neutral atom and anions are always larger in size, $Na^- > Na > Na^+$.

39. (c) : In isoelectronic ions, the size of the cation decreases as the magnitude of the positive charge increases.

40. (d) : Within a period from left to right, atomic volume first decreases and then increases.

41. (d) : Abnormally high difference between 2nd and 3rd ionisation energy means that the element has two valence electrons, which is a case in configuration (d).

42. (d)

43. (c) : The order of ionic size for given ions will be $K^+ > Ca^{2+} > Mg^{2+}$ and that of $Cl^- > F^-$. Therefore, $MgCl_2$ has minimum value of cation/anion (Mg^{2+}/Cl^-) ratio.

44. (c) : N, O and F are highly electronegative non-metals and will have the strongest tendency to form anions by gaining electrons from metal atoms.

45. (c) : As halogens have seven electrons (ns^2np^5) in the valence shell, they have a strong tendency to acquire the nearest inert gas configuration by gaining an electron from the metallic atom and form halide ions easily.

46. (a) : Metallic character decreases in a period and increases in a group.

47. (c) : The atomic size decreases within a period from left to right, therefore Li > Be and Na > Mg. The size increases in a group from top to bottom. Hence, the size of Na is greater than Li. Overall order Na > Mg > Li > Be. Thus, Be has smallest size.

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CHAPTER
4

Chemical Bonding and Molecular Structure

4.1 Kössel-Lewis Approach to Chemical Bonding

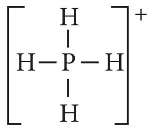
1. In PO_4^{3-} ion, the formal charge on each oxygen atom and P—O bond order respectively are

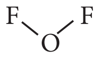
(a) –0.75, 1.25 (b) –0.75, 1.0
(c) –0.75, 0.6 (d) –3, 1.25 *(1998)*

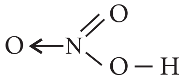
2. Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character follows the order

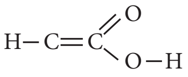
(a) $BeCl_2 > BCl_3 > CCl_4 < LiCl$
(b) $BeCl_2 < BCl_3 < CCl_4 < LiCl$
(c) $LiCl < BeCl_2 < BCl_3 < CCl_4$
(d) $LiCl > BeCl_2 > BCl_3 > CCl_4$ *(1990)*

3. Which one of the following formulae does not correctly represent the bonding capacities of the two atoms involved?

(a) 

(b) 

(c) 

(d) 

(1990)

4.2 Ionic or Electrovalent Bond

4. Among the following, which compound will show the highest lattice energy?

(a) KF (b) NaF
(c) CsF (d) RbF *(1993)*

4.3 Bond Parameters

5. Which of the following, set of molecules will have zero dipole moment?

(a) Ammonia, beryllium difluoride, water, 1, 4-dichlorobenzene
(b) Boron trifluoride, hydrogen fluoride, carbon dioxide, 1, 3-dichlorobenzene
(c) Nitrogen trifluoride, beryllium difluoride, water, 1, 3-dichlorobenzene
(d) Boron trifluoride, beryllium difluoride, carbon dioxide, 1, 4-dichlorobenzene *(NEET 2020)*

6. Which of the following is the correct order of dipole moment ?

(a) $NH_3 < BF_3 < NF_3 < H_2O$
(b) $BF_3 < NF_3 < NH_3 < H_2O$
(c) $BF_3 < NH_3 < NF_3 < H_2O$
(d) $H_2O < NF_3 < NH_3 < BF_3$ *(Odisha NEET 2019)*

7. The species, having bond angles of 120° is

(a) ClF_3 (b) NCl_3
(c) BCl_3 (d) PH_3 *(NEET 2017)*

8. Consider the molecules CH_4, NH_3 and H_2O. Which of the given statements is false?

(a) The H — O — H bond angle in H_2O is smaller than the H — N — H bond angle in NH_3.
(b) The H — C — H bond angle in CH_4 is larger than the H — N — H bond angle in NH_3.
(c) The H — C — H bond angle in CH_4, the H — N — H bond angle in NH_3, and the H — O — H bond angle in H_2O are all greater than 90°.
(d) The H — O — H bond angle in H_2O is larger than the H — C — H bond angle in CH_4.
(NEET-I 2016)

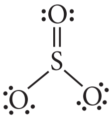
9. Which of the following molecules has the maximum dipole moment?

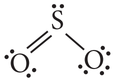
(a) CO_2 (b) CH_4
(c) NH_3 (d) NF_3 *(2014)*

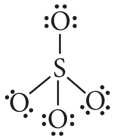
10. The correct order of increasing bond length of C – H, C – O, C – C and C = C is

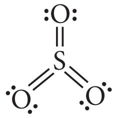
(a) $C-H < C=C < C-O < C-C$
(b) $C-C < C=C < C-O < C-H$
(c) $C-O < C-H < C-C < C=C$
(d) $C-H < C-O < C-C < C=C$ *(2011)*

11. Which of the following structures is the most preferred and hence of lowest energy for SO_3?

(a) 

(b) 

(c) 

(d) 

(Mains 2011)

12. The correct order of increasing bond angles in the following triatomic species is

(a) $NO_2^+ < NO_2 < NO_2^-$ (b) $NO_2^+ < NO_2^- < NO_2$

(c) $NO_2^- < NO_2^+ < NO_2$ (d) $NO_2^- < NO_2 < NO_2^+$

(2008)

13. The correct order of C – O bond length among CO, CO_3^{2-}, CO_2 is

(a) $CO < CO_3^{2-} < CO_2$ (b) $CO_3^{2-} < CO_2 < CO$

(c) $CO < CO_2 < CO_3^{2-}$ (d) $CO_2 < CO_3^{2-} < CO$

(2007)

14. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because

(a) in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3 these are in the same direction

(b) in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction

(c) in NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions

(d) in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in opposite directions. *(2006)*

15. The correct order in which the O – O bond length increases in the following is

(a) $O_2 < H_2O_2 < O_3$ (b) $O_3 < H_2O_2 < O_2$

(c) $H_2O_2 < O_2 < O_3$ (d) $O_2 < O_3 < H_2O_2$

(2005, 1995)

16. The correct sequence of increasing covalent character is represented by

(a) $LiCl < NaCl < BeCl_2$

(b) $BeCl_2 < LiCl < NaCl$

(c) $NaCl < LiCl < BeCl_2$

(d) $BeCl_2 < NaCl < LiCl$ *(2005)*

17. Which of the following would have a permanent dipole moment?

(a) SiF_4 (b) SF_4

(c) XeF_4 (d) BF_3 *(2005)*

18. H_2O is dipolar, whereas BeF_2 is not. It is because

(a) the electronegativity of F is greater than that of O

(b) H_2O involves hydrogen bonding whereas BeF_2 is a discrete molecule

(c) H_2O is linear and BeF_2 is angular

(d) H_2O is angular and BeF_2 is linear. *(2004)*

19. Which of the following molecules does not possess a permanent dipole moment?

(a) CS_2 (b) SO_3

(c) H_2S (d) SO_2 *(1994)*

20. The table shown below gives the bond dissociation energies (E_{diss}) for single covalent bonds of carbon (C) atoms with element *A*, *B*, *C* and *D*. Which element has the smallest atoms?

Bond	**E_{diss}(kJ mol^{-1})**
C-*A*	240
C-*B*	328
C-*C*	276
C-*D*	485

(a) *C* (b) *D*

(c) *A* (d) *B* *(1994)*

21. Strongest bond is in between

(a) CsF (b) NaCl

(c) both (a) and (b) (d) none of the above.

(1993)

22. Which of the following bonds will be most polar?

(a) N – Cl (b) O – F

(c) N – F (d) N – N *(1992)*

4.4 The Valence Shell Electron Pair Repulsion (VSEPR) Theory

23. In the structure of ClF_3, the number of lone pairs of electrons on central atom 'Cl' is

(a) one (b) two

(c) four (d) three *(NEET 2018)*

24. Predict the correct order among the following :

(a) bond pair - bond pair > lone pair - bond pair > lone pair - lone pair

(b) lone pair - bond pair > bond pair - bond pair > lone pair - lone pair

(c) lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

(d) lone pair - lone pair > bond pair - bond pair > lone pair - bond pair

(NEET-I 2016)

25. Which of the following species contains three bond pairs and one lone pair around the central atom?
(a) H_2O (b) BF_3
(c) NH_2^- (d) PCl_3 *(2012)*

26. Which of the following is not a correct statement?
(a) Multiple bonds are always shorter than corresponding single bonds.
(b) The electron-deficient molecules can act as Lewis acids.
(c) The canonical structures have no real existence.
(d) Every AB_5 molecule does in fact have square pyramid structure. *(2006)*

27. Which of the following is not isostructural with $SiCl_4$?
(a) NH_4^+ (b) SCl_4
(c) SO_4^{2-} (d) PO_4^{3-} *(2006)*

28. In which of the following molecules all the bonds are not equal?
(a) NF_3 (b) ClF_3
(c) BF_3 (d) AlF_3 *(2006)*

29. Which of the following molecules has trigonal planar geometry?
(a) BF_3 (b) NH_3
(c) PCl_3 (d) IF_3 *(2005)*

30. In a regular octahedral molecule, MX_6 the number of $X-M-X$ bonds at 180° is
(a) three (b) two
(c) six (d) four. *(2004)*

31. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimize
(a) lone pair - bond pair repulsion only
(b) bond pair - bond pair repulsion only
(c) lone pair - lone pair repulsion and lone pair - bond pair repulsion
(d) lone pair - lone pair repulsion only. *(2004)*

32. In NO_3^- ion, number of bond pair and lone pair of electrons on nitrogen atom are
(a) 2, 2 (b) 3, 1
(c) 1, 3 (d) 4, 0. *(2002)*

33. In which of the following bond angle is maximum?
(a) NH_3 (b) NH_4^+
(c) PCl_3 (d) SCl_2 *(2001)*

34. The BCl_3 is a planar molecule whereas NCl_3 is pyramidal because
(a) nitrogen atom is smaller than boron atom
(b) BCl_3 has no lone pair but NCl_3 has a lone pair of electrons
(c) B—Cl bond is more polar than N—Cl bond
(d) N—Cl bond is more covalent than B—Cl bond. *(1995)*

35. In compound X, all the bond angles are exactly 109°28′, X is
(a) chloromethane (b) carbon tetrachloride
(c) iodoform (d) chloroform. *(1991)*

4.5 Valence Bond Theory

36. Which of the following species contains equal number of σ and π-bonds?
(a) $(CN)_2$ (b) $(CH)_2(CN)_2$
(c) HCO_3^- (d) XeO_4,
(2015, Cancelled)

37. Which one of the following molecules contains no π bond?
(a) SO_2 (b) NO_2
(c) CO_2 (d) H_2O *(NEET 2013)*

38. Which one of the following statements is not correct for sigma- and pi- bonds formed between two carbon atoms?
(a) Sigma-bond is stronger than a pi-bond.
(b) Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively.
(c) Free rotation of atoms about a sigma-bond is allowed but not in case of a pi-bond.
(d) Sigma-bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard. *(2003)*

39. Main axis of a diatomic molecule is z, molecular orbital p_x and p_y overlap to form which of the following orbitals?
(a) π molecular orbital
(b) σ molecular orbital
(c) δ molecular orbital
(d) No bond will form. *(2001)*

40. Which statement is not correct?
(a) A sigma bond is weaker than a pi bond.
(b) A sigma bond is stronger than a pi bond.
(c) A double bond is stronger than a single bond.
(d) A double bond is shorter than a single bond.
(1990)

41. Linear combination of two hybridized orbitals belonging to two atoms and each having one electron leads to the formation of
(a) sigma bond
(b) double bond
(c) co-ordinate covalent bond
(d) pi bond. *(1990)*

42. Which of the following does not apply to metallic bond?
(a) Overlapping valence orbitals
(b) Mobile valence electrons

(c) Delocalized electrons
(d) Highly directed bonds *(1989)*

43. The angle between the overlapping of one *s*-orbital and one *p*-orbital is
(a) 180° (b) 120°
(c) 109°28′ (d) 120°, 60° *(1988)*

4.6 Hybridisation

44. Which of the following pairs of compounds is isoelectronic and isostructural?
(a) TeI_2, XeF_2 (b) IBr_2^-, XeF_2
(c) IF_3, XeF_2 (d) $BeCl_2$, XeF_2
(NEET 2017)

45. The hybridizations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are
(a) sp, sp^3 and sp^2 (b) sp^2, sp^3 and sp
(c) sp, sp^2 and sp^3 (d) sp^2, sp and sp^3
(NEET-II 2016)

46. Which of the following pairs of ions is isoelectronic and isostructural?
(a) CO_3^{2-}, NO_3^- (b) ClO_3^-, CO_3^{2-}
(c) SO_3^{2-}, NO_3^- (d) ClO_3^-, SO_3^{2-}
(NEET-II 2016)

47. The correct geometry and hybridization for XeF_4 are
(a) octahedral, sp^3d^2
(b) trigonal bipyramidal, sp^3d
(c) planar triangle, sp^3d^3
(d) square planar, sp^3d^2. *(NEET-II 2016)*

48. Among the following, which one is a wrong statement?
(a) PH_5 and $BiCl_5$ do not exist.
(b) $p\pi$-$d\pi$ bonds are present in SO_2.
(c) SeF_4 and CH_4 have same shape.
(d) I_3^+ has bent geometry. *(NEET-II 2016)*

49. In which of the following pairs, both the species are not isostructural?
(a) Diamond, Silicon carbide
(b) NH_3, PH_3
(c) XeF_4, XeO_4
(d) $SiCl_4$, PCl_4^+ *(2015)*

50. Maximum bond angle at nitrogen is present in which of the following?
(a) NO_2^+ (b) NO_3^-
(c) NO_2 (d) NO_2^-
(2015, Cancelled)

51. Which one of the following species has planar triangular shape?
(a) N_3 (b) NO_3^-
(c) NO_2^- (d) CO_2 *(2014)*

52. XeF_2 is isostructural with
(a) $SbCl_3$ (b) $BaCl_2$
(c) TeF_2 (d) ICl_2^- *(NEET 2013)*

53. Which of the following is a polar molecule?
(a) SiF_4 (b) XeF_4
(c) BF_3 (d) SF_4 *(NEET 2013)*

54. The outer orbitals of C in ethene molecule can be considered to be hybridized to give three equivalent sp^2 orbitals. The total number of sigma (σ) and pi (π) bonds in ethene molecule is
(a) 3 sigma (σ) and 2 pi (π) bonds
(b) 4 sigma (σ) and 1 pi (π) bonds
(c) 5 sigma (σ) and 1 pi (π) bonds
(d) 1 sigma (σ) and 2 pi (π) bonds.
(Karnataka NEET 2013)

55. In which of the following pairs both the species have sp^3 hybridization?
(a) SiF_4, BeH_2 (b) NF_3, H_2O
(c) NF_3, BF_3 (d) H_2S, BF_3
(Karnataka NEET 2013)

56. Which one of the following pairs is isostructural (*i.e.*, having the same shape and hybridization)?
(a) [BCl_3 and $BrCl_3$] (b) [NH_3 and NO_3^-]
(c) [NF_3 and BF_3] (d) [BF_4^- and NH_4^+]
(2012)

57. Which of the two ions from the list given below that have the geometry that is explained by the same hybridization of orbitals, NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^- ?
(a) NO_2^- and NO_3^- (b) NH_4^+ and NO_3^-
(c) SCN^- and NH_2^- (d) NO_2^- and NH_2^- *(2011)*

58. In which of the following pairs of molecules/ions, the central atoms have sp^2 hybridisation?
(a) NO_2^- and NH_3 (b) BF_3 and NO_2^-
(c) NH_2^- and H_2O (d) BF_3 and NH_2^- *(2010)*

59. In which one of the following species the central atom has the type of hybridization which is not the same as that present in the other three?
(a) SF_4 (b) I_3^-
(c) $SbCl_5^{2-}$ (d) PCl_5 *(2010)*

60. In which of the following molecules the central atom does not have sp^3 hybridization?
(a) CH_4 (b) SF_4
(c) BF_4^- (d) NH_4^+ *(Mains 2010)*

61. Some of the properties of the two species, NO_3^- and H_3O^+ are described below. Which one of them is correct?
(a) Dissimilar in hybridization for the central atom with different structures.
(b) Isostructural with same hybridization for the central atom.
(c) Isostructural with different hybridization for the central atom.
(d) Similar in hybridization for the central atom with different structures. *(Mains 2010)*

62. In which of the following molecules/ions BF_3, NO_2^-, NH_2^- and H_2O, the central atom is sp^2 hybridised?
(a) NH_2^- and H_2O (b) NO_2^- and H_2O
(c) BF_3 and NO_2^- (d) NO_2^- and NH_2^- *(2009)*

63. In which of the following pairs, the two species are isostructural?
(a) SO_3^{2-} and NO_3^- (b) BF_3 and NF_3
(c) BrO_3^- and XeO_3 (d) SF_4 and XeF_4 *(2007)*

64. Which of the following species has a linear shape?
(a) O_3 (b) NO_2^-
(c) SO_2 (d) NO_2^+ *(2006)*

65. The correct order regarding the electronegativity of hybrid orbitals of carbon is
(a) $sp < sp^2 < sp^3$ (b) $sp > sp^2 < sp^3$
(c) $sp > sp^2 > sp^3$ (d) $sp < sp^2 > sp^3$ *(2006)*

66. Among the following, the pair in which the two species are not isostructural is
(a) SiF_4 and SF_4 (b) IO_3^- and XeO_3
(c) BH_4^- and NH_4^+ (d) PF_6^- and SF_6. *(2004)*

67. Which of the following has $p\pi - d\pi$ bonding?
(a) NO_3^- (b) SO_3^{2-}
(c) BO_3^{3-} (d) CO_3^{2-} *(2002)*

68. Which of the following two are isostructural?
(a) XeF_2, IF_2^- (b) NH_3, BF_3
(c) CO_3^{2-}, SO_3^{2-} (d) PCl_5, ICl_5 *(2001)*

69. The bond length between hybridised carbon atom and other carbon atom is minimum in
(a) propene (b) propyne
(c) propane (d) butane. *(1996)*

70. Which of the following has sp^2-hybridisation?
(a) $BeCl_2$ (b) C_2H_2
(c) C_2H_6 (d) C_2H_4 *(1996)*

71. When the hybridization state of carbon atom changes from sp^3 to sp^2 and finally to sp, the angle between the hybridized orbitals
(a) decreases gradually
(b) decreases considerably
(c) is not affected
(d) increases progressively. *(1993)*

72. Which one of the following has the shortest carbon carbon bond length?
(a) Benzene (b) Ethene
(c) Ethyne (d) Ethane *(1992)*

73. Which structure is linear?
(a) SO_2 (b) CO_2
(c) CO_3^{2-} (d) SO_4^{2-} *(1992)*

74. A sp^3 hybrid orbital contains
(a) 1/4 *s*-character (b) 1/2 *s*-character
(c) 1/3 *s*-character (d) 2/3 *s*-character. *(1991)*

75. The complex ion $[Co(NH_3)_6]^{3+}$ is formed by sp^3d^2 hybridisation. Hence the ion should possess
(a) octahedral geometry
(b) tetrahedral geometry
(c) square planar geometry
(d) tetragonal geometry. *(1990)*

76. Which of the following molecules does not have a linear arrangement of atoms?
(a) H_2S (b) C_2H_2
(c) BeH_2 (d) CO_2 *(1989)*

77. In which one of the following molecules the central atom can be said to adopt sp^2 hybridization?
(a) BeF_2 (b) BF_3
(c) C_2H_2 (d) NH_3 *(1989)*

78. Equilateral shape has
(a) *sp* hybridisation (b) sp^2 hybridisation
(c) sp^3 hybridisation (d) dsp^3 hybridisation. *(1988)*

4.7 Molecular Orbital Theory

79. Consider the following species : CN^+, CN^-, NO and CN. Which one of these will have the highest bond order?
(a) NO (b) CN^-
(c) CN^+ (d) CN *(NEET 2018)*

80. Which one of the following pairs of species have the same bond order?
(a) O_2, NO^+ (b) CN^-, CO
(c) N_2, O_2^- (d) CO, NO *(NEET 2017)*

81. Which of the following is paramagnetic?
(a) CN^- (b) NO^+
(c) CO (d) O_2^- *(NEET 2013)*

82. The pair of species that has the same bond order in the following is
(a) CO, NO^+ (b) NO^-, CN^-
(c) O_2, N_2 (d) O_2, B_2
(Karnataka NEET 2013)

83. In which of the following ionization processes the bond energy increases and the magnetic behaviour changes from paramagnetic to diamagnetic?
(a) $O_2 \rightarrow O_2^+$ (b) $C_2 \rightarrow C_2^+$
(c) $NO \rightarrow NO^+$ (d) $N_2 \rightarrow N_2^+$
(Karnataka NEET 2013)

84. The pair of species with the same bond order is
(a) O_2^{2-}, B_2 (b) O_2^+, NO^+
(c) NO, CO (d) N_2, O_2 *(2012)*

85. During change of O_2 to O_2^- ion, the electron adds on which one of the following orbitals?
(a) π^* orbital (b) π orbital
(c) σ^* orbital (d) σ orbital *(Mains 2012)*

86. Four diatomic species are listed below. Identify the correct order in which the bond order is increasing in them.
(a) $NO < O_2^- < C_2^{2-} < He_2^+$
(b) $O_2^- < NO < C_2^{2-} < He_2^+$
(c) $C_2^{2-} < He_2^+ < O_2^- < NO$
(d) $He_2^+ < O_2^- < NO < C_2^{2-}$ *(Mains 2012, 2008)*

87. Which of the following is isoelectronic?
(a) CO_2, NO_2 (b) NO_2^-, CO_2
(c) CN^-, CO (d) SO_2, CO_2 *(2002)*

88. Which species does not exhibit paramagnetism?
(a) N_2^+ (b) O_2^-
(c) CO (d) NO *(2000)*

89. The number of anti-bonding electron pairs in O_2^{2-} molecular ion on the basis of molecular orbital theory is (Atomic number of O is 8.)
(a) 3 (b) 2
(c) 5 (d) 4 *(1998)*

90. Which of the following species is paramagnetic?
(a) CO (b) CN^-
(c) O_2^{2-} (d) NO *(1995)*

4.8 Bonding in Some Homonuclear Diatomic Molecules

91. Identify a molecule which does not exist.
(a) He_2 (b) Li_2
(c) C_2 (d) O_2 *(NEET 2020)*

92. Which of the following diatomic molecular species has only π bonds according to Molecular Orbital Theory?
(a) Be_2 (b) O_2
(c) N_2 (d) C_2 *(NEET 2019)*

93. Which of the following is paramagnetic?
(a) N_2 (b) H_2
(c) Li_2 (d) O_2
(Odisha NEET 2019)

94. Decreasing order of stability of O_2, O_2^-, O_2^+ and O_2^{2-} is
(a) $O_2^{2-} > O_2^- > O_2 > O_2^+$
(b) $O_2 > O_2^+ > O_2^{2-} > O_2^-$
(c) $O_2^- > O_2^{2-} > O_2^+ > O_2$
(d) $O_2^+ > O_2 > O_2^- > O_2^{2-}$ *(2015)*

95. The correct bond order in the following species is
(a) $O_2^+ < O_2^- < O_2^{2+}$ (b) $O_2^- < O_2^+ < O_2^{2+}$
(c) $O_2^{2+} < O_2^+ < O_2^-$ (d) $O_2^{2+} < O_2^- < O_2^+$
(2015, Cancelled)

96. Bond order of 1.5 is shown by
(a) O_2^+ (b) O_2^-
(c) O_2^{2-} (d) O_2 *(2012)*

97. Which of the following has the minimum bond length?
(a) O_2^+ (b) O_2^-
(c) O_2^{2-} (d) O_2 *(2011)*

98. The pairs of species of oxygen and their magnetic behaviour are noted below. Which of the following presents the correct description?
(a) O_2^-, O_2^{2-} - Both diamagnetic
(b) O^+, O_2^{2-} - Both paramagnetic
(c) O_2^+, O_2 - Both paramagnetic
(d) O, O_2^{2-} - Both paramagnetic *(2011)*

99. Which one of the following species does not exist under normal conditions?
(a) Be_2^+ (b) Be_2
(c) B_2 (d) Li_2 *(2010)*

100. According to MO theory which of the lists ranks the nitrogen species in terms of increasing bond order?
(a) $N_2^{2-} < N_2^- < N_2$ (b) $N_2 < N_2^{2-} < N_2^-$
(c) $N_2^- < N_2^{2-} < N_2$ (d) $N_2^- < N_2 < N_2^{2-}$
(2009)

101. Right order of dissociation energy N_2 and N_2^+ is
(a) $N_2 > N_2^+$ (b) $N_2 = N_2^+$
(c) $N_2^+ > N_2$ (d) none. *(2000)*

102. N_2 and O_2 are converted into monocations, N_2^+ and O_2^+ respectively. Which is wrong?
(a) In O_2^+ paramagnetism decreases.
(b) N_2^+ becomes diamagnetic.
(c) In N_2^+, the N–N bond weakens.
(d) In O_2^+, the O–O bond order increases. *(1997)*

103. N_2 and O_2 are converted into monoanions N_2^- and O_2^- respectively, which of the following statements is wrong?
(a) In O_2^-, bond length increases.
(b) N_2^- becomes diamagnetic.
(c) In N_2^-, N–N bond weakens.
(d) In O_2^-, the O–O bond order decreases. *(1997)*

104. The ground state electronic configuration of valence shell electrons in nitrogen molecule (N_2) is written as $KK, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$. Hence the bond order in nitrogen molecule is
(a) 2 (b) 3
(c) 0 (d) 1 *(1995)*

105. Which of the following molecules has the highest bond order?
(a) O_2^- (b) O_2
(c) O_2^+ (d) O_2^{2-} *(1994)*

4.9 Hydrogen Bonding

106. Which one of the following compounds shows the presence of intramolecular hydrogen bond?
(a) H_2O_2
(b) HCN
(c) Cellulose
(d) Concentrated acetic acid *(NEET-II 2016)*

107. What is the dominant intermolecular force or bond that must be overcome in converting liquid CH_3OH to a gas?
(a) Dipole-dipole interaction
(b) Covalent bonds
(c) London dispersion force
(d) Hydrogen bonding *(2009)*

108. In $X - H \cdots\cdots Y$, X and Y both are electronegative elements. Then
(a) electron density on X will increase and on H will decrease
(b) in both electron density will increase
(c) in both electron density will decrease
(d) on X electron density will decrease and on H increases. *(2001)*

109. Strongest hydrogen bond is shown by
(a) water
(b) ammonia
(c) hydrogen fluoride
(d) hydrogen sulphide. *(1992)*

110. Which one shows maximum hydrogen bonding?
(a) H_2O (b) H_2Se
(c) H_2S (d) HF *(1990)*

ANSWER KEY

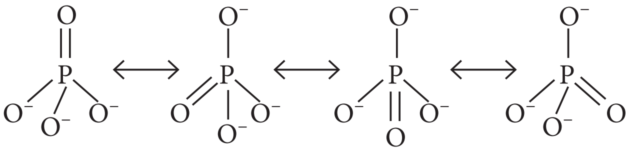
1. (a)	**2.** (c)	**3.** (d)	**4.** (b)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (d)	**9.** (c)	**10.** (a)
11. (d)	**12.** (d)	**13.** (c)	**14.** (c)	**15.** (d)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (a)	**20.** (b)
21. (a)	**22.** (c)	**23.** (b)	**24.** (c)	**25.** (d)	**26.** (d)	**27.** (b)	**28.** (b)	**29.** (a)	**30.** (a)
31. (d)	**32.** (d)	**33.** (b)	**34.** (b)	**35.** (b)	**36.** (d)	**37.** (d)	**38.** (b)	**39.** (a)	**40.** (a)
41. (a)	**42.** (d)	**43.** (a)	**44.** (None)		**45.** (c)	**46.** (a,d)	**47.** (a)	**48.** (c)	**49.** (c)
50. (a)	**51.** (b)	**52.** (d)	**53.** (d)	**54.** (c)	**55.** (b)	**56.** (d)	**57.** (a)	**58.** (b)	**59.** (c)
60. (b)	**61.** (a)	**62.** (c)	**63.** (c)	**64.** (d)	**65.** (c)	**66.** (a)	**67.** (b)	**68.** (a)	**69.** (b)
70. (d)	**71.** (d)	**72.** (c)	**73.** (b)	**74.** (a)	**75.** (a)	**76.** (a)	**77.** (b)	**78.** (b)	**79.** (b)
80. (b)	**81.** (d)	**82.** (a)	**83.** (c)	**84.** (a)	**85.** (a)	**86.** (d)	**87.** (c)	**88.** (c)	**89.** (d)
90. (d)	**91.** (a)	**92.** (d)	**93.** (d)	**94.** (d)	**95.** (b)	**96.** (b)	**97.** (a)	**98.** (c)	**99.** (b)
100. (a)	**101.** (a)	**102.** (b)	**103.** (b)	**104.** (b)	**105.** (c)	**106.** (c)	**107.** (d)	**108.** (a)	**109.** (c)
110. (a)									

Hints & Explanations

1. **(a) :** The total charge = –3

So, the average formal charge on each 'O' atom is –3/4

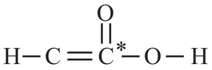
= –0.75



⇒ Average P—O bond order

$$= \frac{\text{Total no. of bonds}}{\text{Total no. of resonating structures}} = \frac{5}{4} = 1.25$$

2. **(c) :** Along the period, as we move from Li → Be → B → C, the electronegativity increases and hence the *EN* difference between the element and Cl decreases and accordingly, the covalent character increases. Thus $LiCl < BeCl_2 < BCl_3 < CCl_4$ is the correct order of covalent bond character.

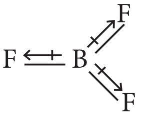
3. **(d) :** 

$H-C=\overset{\overset{O}{\|}}{C^*}-O-H$

The asterisk (*) marked carbon has a valency of 5 and hence, this formula is not correct because carbon has a maximum valency of 4.

4. **(b) :** For compounds containing ions of same charge, lattice energy increases as the size of ions decreases. Thus, NaF has highest lattice energy.

5. **(d) :**



Boron trifluoride

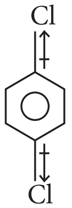
(μ = 0)

Beryllium difluoride

(μ = 0)

Carbon dioxide

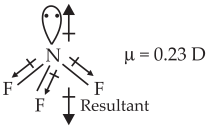
(μ = 0)

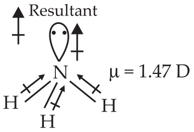


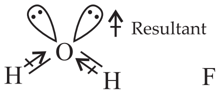
1, 4-Dichlorobenzene

(μ = 0)

6. **(b) :**

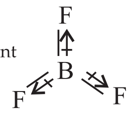






Water

μ = 1.85 D



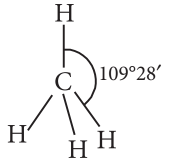
Boron trifluoride

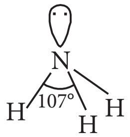
μ = 0 D

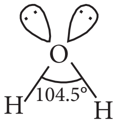
Symmetrical molecule

7. **(c) :** BCl_3-Trigonal planar, sp^2-hybridised, 120° angle.

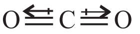
8. **(d) :**



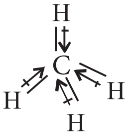




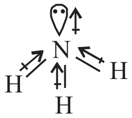
9. **(c) :**



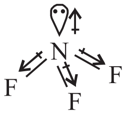
(μ = 0, symmetrical) ;



(μ = 0, symmetrical)



(μ ≠ 0, pyramidal)

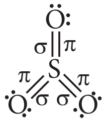


(μ ≠ 0, pyramidal)

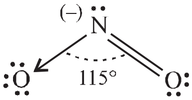
In NH_3, H is less electronegative than N and hence dipole moment of each N—H bond is towards N and create high net dipole moment whereas in NF_3, F is more electronegative than N, the dipole moment of each N—F bond is opposite to that of lone pair, hence reducing the net dipole moment.

10. **(a) :** Increasing order of bond length is

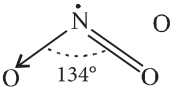
$$C-H < C=C < C-O < C-C$$

11. **(d) :**  has maximum number of covalent bonds involving *p*π – *d*π bonding also.

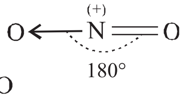
12. **(d) :** Structures of NO_2^-, NO_2 and NO_2^+ is given as



NO_2^-



NO_2

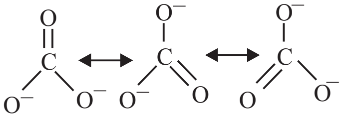


NO_2^+

The correct order of increasing bond angles in the following triatomic species is

$$NO_2^- < NO_2 < NO_2^+$$

13. **(c) :** $CO \Rightarrow :\bar{C}\equiv\overset{+}{O}: \longleftrightarrow :C=\ddot{O}:$

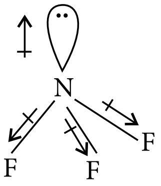
$CO_3^{2-} \Rightarrow$ 

$$CO_2 \Rightarrow :\ddot{O}=C=\ddot{O}: \longleftrightarrow :\overset{+}{O}\equiv C-\ddot{\bar{O}}: \longleftrightarrow :\ddot{\bar{O}}-C\equiv\overset{+}{O}:$$

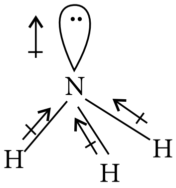
More single bond character in resonance hybrid, more is the bond length. Hence, the increasing bond length is

$CO < CO_2 < CO_3^{2-}$

14. (c) : The dipole moment of NF_3 is 0.24 D and of NH_3 is 1.48 D. The difference is due to fact that the dipole moment due to N – F bonds in NF_3 are in opposite directions to the direction of the dipole moment of the lone pair on N atom which partly cancel out. The dipole moment of N – H bonds in NH_3 are in the same direction of the dipole moment of the lone pair on N atom which adds up as shown :



NF_3



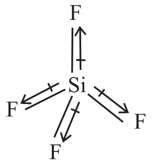
NH_3

15. (d) : Bond lengths of O – O in O_2 is 1.21 Å, in H_2O_2 is 1.48 Å and in O_3 is 1.28 Å. Therefore, correct order of the O – O bond length is $H_2O_2 > O_3 > O_2$.

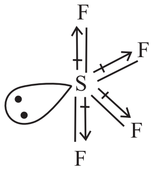
16. (c) : Covalent character in a compound is found by Fajan's rule.

Fajan's rule : The smaller the size of the cation and the larger the size of the anion, the greater is the covalent character of an ionic bond. The greater the charge on the cation, the greater is the covalent character of the ionic bond.

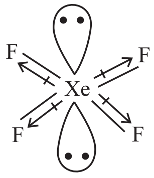
17. (b) : For dipole moment, we have to know the hybridisation and shape.



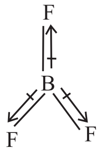
$\mu = 0$



$\mu \neq 0$

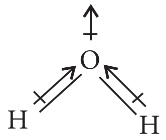


$\mu = 0$



$\mu = 0$

18. (d) : The overall value of the dipole moment of a polar molecule depends on its geometry and shape, *i.e.* vectorial addition of dipole moment of the constituent bonds. Water has angular structure with bond angle 105°, it has dipole moment. However BeF_2 is a linear molecule thus, dipole moment summation of all the bonds present in the molecule cancel each other.



$\mu \neq 0$

$\mu = 0$

19. (a) : The structure of CS_2 is linear and therefore it does not have permanent dipole moment. It is represented as S═C═S.

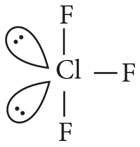
20. (b) : Smaller the atom, stronger is the bond and greater is the bond dissociation energy. Therefore, the bond C-*D* has the greatest energy or *D* has smallest atoms.

21. (a) : According to Fajans rule, ionic character increases with increase in size of the cation, (Cs > Rb > K > Na) and with decrease in size of the anion (F > Cl > Br > I). Thus, CsF has higher ionic character than NaCl and hence, bond in CsF is stronger than in NaCl.

22. (c) : Polarity of the bond depends upon the electronegativity difference of the two atoms forming the bond. Greater the electronegativity difference, more is the polarity of the bond.

N – Cl	O – F	N – F	N – N
3.04–3.16	3.5–4.0	3.04–4.0	3.04–3.04

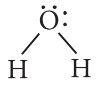
23. (b) : The structure of ClF_3 is



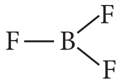
Hence, Cl has 2 lone pairs of electrons.

24. (c) : According to VSEPR theory, the repulsive forces between lone pair and lone pair are greater than between lone pair and bond pair which are further greater than bond pair and bond pair.

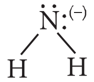
25. (d) :



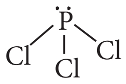
2 bond pairs, 2 lone pairs



3 bond pairs, 0 lone pair

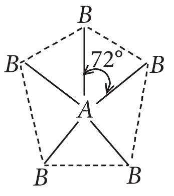


2 bond pairs, 2 lone pairs

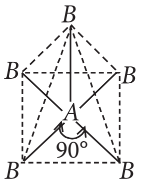


3 bond pairs, 1 lone pair

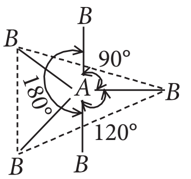
26. (d) : For AB_5 molecules, there are three possible geometries *i.e.* planar pentagonal, square pyramidal and trigonal bipyramidal.



planar pentagonal



square pyramidal



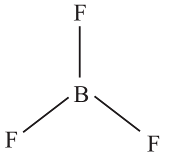
trigonal bipyramidal

Out of these three geometries, it is only trigonal bipyramidal shape in which bond pair-bond pair repulsions are minimum and hence, this geometry is the most probable geometry of AB_5 molecule.

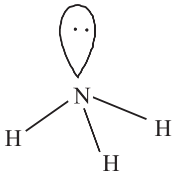
27. (b) : $SiCl_4$, NH_4^+, SO_4^{2-} and PO_4^{3-} ions are the examples of molecules/ions which are of AB_4 type and have tetrahedral structures. SCl_4 is AB_4 (lone pair) type species. Although the arrangement of five sp^3d hybrid orbitals in space is trigonal bipyramidal, due to the presence of one lone pair of electrons in the basal hybrid orbital, the shape of AB_4 (lone pair) species gets distorted and becomes distorted tetrahedral or see-saw.

28. (b) : The Cl – F (Cl – F_{eq}) bond length is equal to 1.60 Å while each of the two axial Cl – F (Cl – F_a) bond length is equal to 1.70 Å.

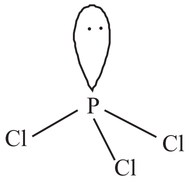
29. (a) :



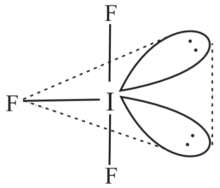
trigonal planar



pyramidal



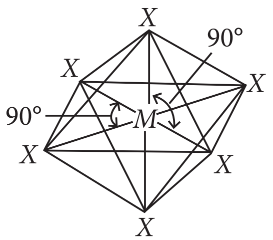
pyramidal



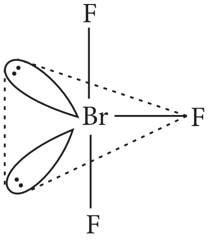
T-shape

30. (a) : In octahedral molecule, six hybrid orbitals directed towards the corners of a regular octahedron with a bond angle of 90°.

According to this geometry, the number of $X - M - X$ bonds at 180° must be three.

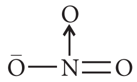


31. (d) :



Bent T-shaped geometry in which both lone pairs occupy the equatorial positions of the trigonal bipyramid. Here (*lp* - *lp*) repulsion = 0, (*lp* - *bp*) repulsion = 4 and (*bp* - *bp*) repulsion = 2.

32. (d) :



$\bar{O}-\overset{\overset{O}{\uparrow}}{N}=O$

In NO_3^- ion, nitrogen has 4 bond pairs of electrons and no lone pair of electrons.

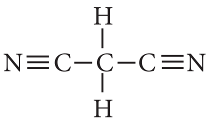
33. (b) : Bond angle is maximum in NH_4^+ tetrahedral molecule with bond angle 109°.

34. (b) : There is no lone pair on boron in BCl_3 hence, no repulsion takes place. There is a lone pair on nitrogen in NCl_3 hence, repulsion takes place. Therefore, BCl_3 is planar molecule but NCl_3 is pyramidal molecule.

35. (b) : As all C – Cl bonds are directed towards the corner of a regular tetrahedron.

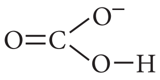
36. (d) : $(CN)_2$, $N\equiv C-C\equiv N$ $(3\sigma + 4\pi)$

$CH_2(CN)_2$,



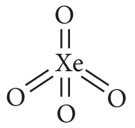
$N\equiv C-\underset{H}{\overset{H}{C}}-C\equiv N$ $(6\sigma + 4\pi)$

HCO_3^-,



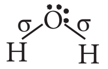
$(4\sigma + 1\pi)$

XeO_4,



$(4\sigma + 4\pi)$

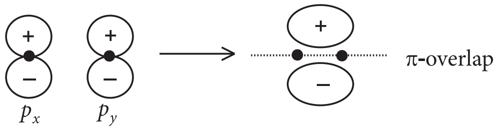
37. (d) :



38. (b) : Sigma bond dissociation energy = 347 kJ/mol

Pi-bond dissociation energy = 264 kJ/mol

39. (a) : For π overlap, the lobes of the atomic orbitals are perpendicular to the line joining the nuclei.



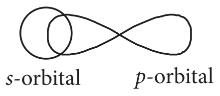
Hence, only sidewise overlapping takes place.

40. (a) : A σ-bond is stronger than a π-bond.

41. (a)

42. (d) : Metallic bonds have electrostatic attractions on all sides and hence, do not have directional characteristics.

43. (a) : The type of overlapping between *s* - and *p*-orbitals occurs along internuclear axis and hence, the angle is 180°.



s-p overlapping

44. (None) :

Species	No. of electrons	Structure
TeI_2 XeF_2	158 72	Bent Linear
IBr_2^- XeF_2	124 72	Linear Linear
IF_3 XeF_2	80 72	T-shaped Linear
$BeCl_2$ XeF_2	38 72	Linear Linear

Note : In this question, in place of isoelectronic there should be same number of valence electrons.

45. (c) : $X = \frac{1}{2}(VE + MA - c + a)$

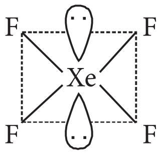
For NO_2^+, $X = \frac{1}{2}(5 + 0 - 1) = 2$ *i.e.*, *sp* hybridisation

For NO_3^-, $X = \frac{1}{2}(5 + 0 + 1) = 3$ *i.e.*, sp^2 hybridisation

For NH_4^+, $X = \frac{1}{2}(5 + 4 - 1) = 4$ *i.e.*, sp^3 hybridisation

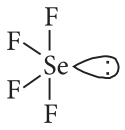
46. (a, d) : (a) CO_3^{2-} : 6 + 24 + 2 = 32; sp^2; trigonal planar
NO_3^- : 7 + 24 + 1 = 32; sp^2; trigonal planar
Hence, these are isoelectronic as well as isostructural.
(b) ClO_3^- : 17 + 24 + 1 = 42; sp^3, trigonal pyramidal
CO_3^{2-} : 6 + 24 + 2 = 32; sp^2, trigonal planar
Hence, these are neither isoelectronic nor isostructural.
(c) SO_3^{2-} : 16 + 24 + 2 = 42; sp^3, trigonal pyramidal
NO_3^- : 7 + 24 + 1 = 32; sp^2, trigonal planar
These are neither isoelectronic nor isostructural.
(d) ClO_3^- : 17 + 24 + 1 = 42; sp^3, trigonal pyramidal
SO_3^{2-} : 16 + 24 + 2 = 42; sp^3, trigonal pyramidal
Hence, these are isoelectronic as well as isostructural.

47. (a) :

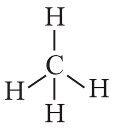


sp^3d^2 hybridisation
(octahedral geometry, square planar shape)

48. (c) :



sp^3d hybridisation
(see-saw shape)

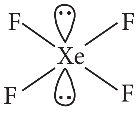


sp^3 hybridisation
(tetrahedral)

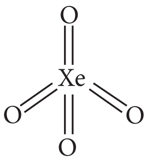
49. (c) : In diamond and silicon carbide, central atom is sp^3 hybridised and hence, both are isostructural.

NH_3 and PH_3, both are pyramidal and central atom in both cases is sp^3 hybridised. $SiCl_4$ and PCl_4^+, both are tetrahedral and central atom in both cases is sp^3 hybridised.

In XeF_4, Xe is sp^3d^2 hybridised and structure is square planar while in XeO_4, Xe is sp^3 hybridised and structure is tetrahedral.



XeF_4



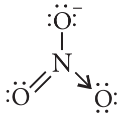
XeO_4

50. (a) :

Species	NO_3^-	NO_2	NO_2^-	NO_2^+
Hybridisation	sp^2	sp^2	sp^2	*sp*
Bond angle	120°	134°	115°	180°

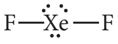
So, NO_2^+ has maximum bond angle.

51. (b) :



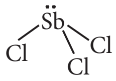
(sp^2-hybridised, trigonal planar)

52. (d) :

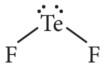


sp^3d, Linear

sp^3d, Linear

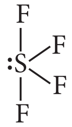


sp^3, Pyramidal



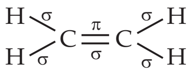
sp^3, V-shaped

53. (d) : SF_4 has sp^3d-hybridisation and see-saw shape with (4 *bp* + 1*lp*)



and resultant μ ≠ 0.

54. (c) :



5 σ-bond and 1 π-bond

55. (b) : NF_3 and H_2O are sp^3-hybridised.

56. (d) : BCl_3 ⇒ sp^2, trigonal planar
$BrCl_3$ ⇒ sp^3d, T-shaped
NH_3 ⇒ sp^3, pyramidal
NO_3^- ⇒ sp^2, trigonal planar
NF_3 ⇒ sp^3, pyramidal
BF_3 ⇒ sp^2, trigonal planar
BF_4^- ⇒ sp^3, tetrahedral
NH_4^+ ⇒ sp^3, tetrahedral

57. (a) :

Ions	**Hybridisation**
NO_2^-	sp^2
NO_3^-	sp^2
NH_2^-	sp^3
NH_4^+	sp^3
SCN^-	*sp*

58. (b) : The hybridisation of the central atom can be calculated as

$$H=\frac{1}{2}\left[\begin{pmatrix}\text{No. of electrons}\\ \text{in valence shell}\\ \text{of atom}\end{pmatrix}+\begin{pmatrix}\text{No. of monovalent}\\ \text{atoms around}\\ \text{central atom}\end{pmatrix}-\begin{pmatrix}\text{Charge on}\\ \text{cation}\end{pmatrix}+\begin{pmatrix}\text{Charge on}\\ \text{anion}\end{pmatrix}\right]$$

$\therefore$ For BF_3, $H=\frac{1}{2}[(3)+(3)-(0)+(0)]$

$= 3 \Rightarrow sp^2$ hybridisation.

For NO_2^-, $H=\frac{1}{2}[(5)+(0)-(0)+(1)]$

$= 3 \Rightarrow sp^2$ hybridisation.

59. (c) : Hybridisation of the central atom can be calculated as:

$$H=\frac{1}{2}\left[\begin{pmatrix}\text{No. of valence}\\ \text{electrons in the}\\ \text{central atom}\end{pmatrix}+\begin{pmatrix}\text{No. of monovalent}\\ \text{atoms around}\\ \text{central atom}\end{pmatrix}-\begin{pmatrix}\text{Charge on}\\ \text{cation}\end{pmatrix}+\begin{pmatrix}\text{Charge on}\\ \text{anion}\end{pmatrix}\right]$$

Applying this formula we find that all the given species except $[SbCl_5]^{2-}$ have central atom with sp^3d (corresponding to $H = 5$) hybridization. In $[SbCl_5]^{2-}$, Sb is sp^3d^2 hybridized.

60. (b) : For neutral molecules,

No. of electron pairs = No. of atoms bonded to it + 1/2[Gp. no. of central atom – Valency of central atom]

$\therefore$ For CH_4, no. of e^- pairs $=4+\frac{1}{2}[4-4]$

$= 4$ (sp^3 hybridisation)

For SF_4, no. of e^- pairs $=4+\frac{1}{2}[6-4]$

$= 5$ (sp^3d hybridisation)

For ions,

No. of electron pairs = No. of atoms bonded to it + 1/2[Gp. no. of central atom – Valency of central atom ± No. of electrons equals to the units of charge]

$\therefore$ For BF_4^-, no. of e^- pairs $=4+\frac{1}{2}[3-4+1]$

$= 4$ (sp^3 hybridisation)

For NH_4^+, no. of e^- pairs $=4+\frac{1}{2}[5-4-1]$

$= 4$ (sp^3 hybridisation)

61. (a) : No. of electron pairs at the central atom = No. of atoms bonded to it + 1/2[Group number of central atom – Valency of the central atom ± No. of electrons equals to the units of charge]

No. of electron pairs at the central atom in NO_3^-

$=3+\frac{1}{2}[5-6+1]=3$ (sp^2 hybridisation).

No. of electron pairs at the central atom in

$H_3O^+=3+\frac{1}{2}[6-3-1]=4$ (sp^3 hybridisation).

62. (c) : $BF_3\rightarrow sp^2$, $NO_2^-\rightarrow sp^2$, $NH_2^-\rightarrow sp^3$, $H_2O\rightarrow sp^3$

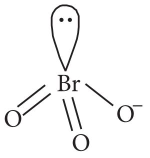
63. (c) : Hybridisation of Br in BrO_3^- :

$H = 1/2(7 + 0 - 0 + 1) = 4$ *i.e.* sp^3 hybridisation

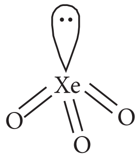
Hybridisation of Xe in XeO_3 :

$H=\frac{1}{2}(8+0-0+0)=4$ *i.e.* sp^3 hybridisation

In both BrO_3^- and XeO_3, the central atom is sp^3 hybridised and contains one lone pair of electrons, hence in both the cases, the structure is trigonal pyramidal.

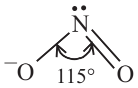


BrO_3^-

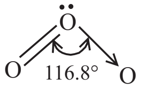


XeO_3

64. (d) : NO_2^- : Due to sp^2 hybridisation of N-atom and the presence of one lone pair on it, NO_2^- has angular shape.

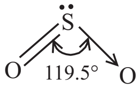


O_3 :



V-shaped

SO_2 : Due to the presence of one lone pair of electrons in one of the three sp^2-hybrid orbitals, SO_2 molecule has angular (V-shaped) structure.



NO_2^+ : Due to sp hybridisation of N^+, NO_2^+ ion has linear shape.

$$:\underset{\cdot\cdot}{\ddot{O}}\leftarrow\overset{+}{N}=\ddot{O}:$$

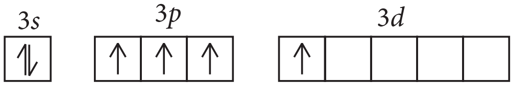
65. (c) : Electronegativity of carbon atom is not fixed. It varies with the state of hybridisation. Electronegativity of carbon increases as the *s*-character of the hybrid orbital increases.

C (sp) > C (sp^2) > C (sp^3)

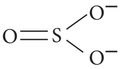
66. (a) : SiF_4 has symmetrical tetrahedral shape which is due to sp^3 hybridisation of the central silicon atom. SF_4 has distorted tetrahedral or see-saw geometry which arises due to sp^3d hybridisation of central sulphur atom and due to the presence of one lone pair of electrons in one of the equatorial hybrid orbital.

67. (b) : In sulphite ion, the central atom sulphur is sp^3 hybridised.

Electronic structure of S atom in excited state



The three *p* electrons form σ bonds with three oxygen atoms - with one position (of the tetrahedron) being occupied by a lone pair. The *d* electron (excluded from hybridisation) forms π bond with one oxygen atom. *i.e.* *p*π - *d*π bonding occurs.



68. (a) : Compounds having same shape with same hybridisation are known as isostructural.
XeF_2, IF_2^- → both are sp^3d hybridised linear molecules.

69. (b) : The C–C bond length = 1.54 Å, C = C bond length = 1.34 Å and C ≡ C bond length = 1.20 Å.
Since propyne has a triple bond, therefore it has minimum bond length.

70. (d) : $BeCl_2$ and C_2H_2 have *sp*-hybridisation and C_2H_6 has sp^3-hybridisation. C_2H_4 has sp^2 hybridisation.

71. (d) : Angle increases progressively,
sp^3 (109° 28′), sp^2 (120°), *sp* (180°).

72. (c) : There is a triple bond in ethyne molecule (H — C ≡ C — H) and due to this triple bond, carbon-carbon bond distance is shortest in ethyne.

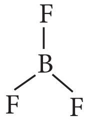
73. (b) : CO_2 molecule is *sp*-hybridised and thus, it is linear, while CO_3^{2-} is planar (sp^2 -hybridised), SO_2 is an angular molecule with sp^2 hybridisation and SO_4^{2-} is tetrahedral (sp^3-hybridised).

74. (a) : sp^3 orbital has 1/4 (25%) *s*-character.

75. (a) : According to VSEPR theory, a molecule with 6 bond pairs must be octahedral.

76. (a) : For linear arrangement of atoms the hybridisation is *sp* (bond angle = 180°).
Only H_2S has sp^3-hybridisation and hence it has angular shape while C_2H_2, BeH_2 and CO_2 all involve *sp*-hybridisation and hence, have linear arrangement of atoms.

77. (b) : BF_3 involves sp^2-hybridisation.



78. (b) : Equilateral or triangular planar shape involves sp^2 hybridisation, *e.g.*, BCl_3.

79. (b) : NO(15) : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^0$

$$\text{B.O.} = \frac{10-5}{2} = 2.5$$

$CN^-(14)$: $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2$

$$\text{B.O.} = \frac{10-4}{2} = 3$$

CN(13) : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^1$

$$\text{B.O.} = \frac{9-4}{2} = 2.5$$

CN^+ (12) : $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2$

$$\text{B.O.} = \frac{8-4}{2} = 2$$

Hence, CN^- has highest bond order.

80. (b) : Molecular orbital electronic configurations and bond order values are :

O_2 (16) : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2,$
$\pi^* 2p_x^1 = \pi^* 2p_y^1$

$$\text{B.O.} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-6) = 2$$

NO^+ (14) : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2$

$$\text{B.O.} = \frac{1}{2}(10-4) = 3$$

CN^- (14) : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$$\text{B.O.} = \frac{1}{2}(10-4) = 3$$

CO(14) : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$$\text{B.O.} = \frac{1}{2}(10-4) = 3$$

N_2 (14) : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$$\text{B.O.} = \frac{1}{2}(10-4) = 3$$

O_2^- (17) = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2,$
$\pi^* 2p_x^2 = \pi^* 2p_y^1$

$$\text{B.O.} = \frac{1}{2}(10-7) = 1.5$$

NO (15) : $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1$

$$\text{B.O.} = \frac{1}{2}(10-5) = 2.5$$

81. (d) : O_2^-(17) superoxide has one unpaired electron.
$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \ \pi^* 2p_x^2 = \pi^* 2p_y^1$

82. (a) : CO = 6 + 8 = 14 electrons
NO^+ = 7 + 8 – 1 = 14 electrons

Electronic configuration of NO^+:
$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2$

Electronic configuration of CO :
$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2$

So, both have bond order = $\frac{10-4}{2} = 3$

83. (c) : Molecular orbital configuration of
O_2 (16) : $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$
⇒ Paramagnetic

Bond order = $\frac{10-6}{2} = 2$

O_2^+ (15) : $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1$

$\Rightarrow$ Paramagnetic

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

$C_2\,(12):\ \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2$

$\Rightarrow$ Diamagnetic

$$\text{Bond order} = \frac{8-4}{2} = 2$$

$C_2^+\,(11):\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^1$

$\Rightarrow$ Paramagnetic

$$\text{Bond order} = \frac{7-4}{2} = 1.5$$

$NO(15):\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1$

$\Rightarrow$ Paramagnetic

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

$NO^+\,(14):\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2$

$\Rightarrow$ Diamagnetic

$$\text{Bond order} = \frac{10-4}{2} = 3$$

$N_2\,(14):\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2$

$\Rightarrow$ Diamagnetic

$$\text{Bond order} = \frac{10-4}{2} = 3$$

$N_2^+\,(13):\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^1$

$\Rightarrow$ Paramagnetic

$$\text{Bond order} = \frac{9-4}{2} = 2.5$$

Thus from NO $\rightarrow$ NO$^+$, bond order increases *i.e.*, bond energy increases and magnetic behaviour changes from paramagnetic to diamagnetic.

84. (a) : $O_2^{2-} \rightarrow 1.0$
$O_2^+ \rightarrow 2.5$
$NO \rightarrow 2.5$
$N_2 \rightarrow 3.0$
$B_2 \rightarrow 1.0$
$NO^+ \rightarrow 3.0$
$CO \rightarrow 3.0$
$O_2 \rightarrow 2.0$

85. (a) : Electronic configuration of $O_2(16)$

$$\sigma(1s)^2\ \sigma^*(1s)^2\ \sigma(2s)^2\ \sigma^*(2s)^2\ \sigma(2p_z)^2\,\pi(2p_x)^2 = \pi(2p_y)^2\ \pi^*(2p_x)^1 = \pi^*(2p_y)^1$$

Thus, the incoming electron will enter in $\pi^* 2p_x$ to form O_2^-.

86. (d) :

Diatomic species	Bond order
NO	2.5
O_2^-	1.5
C_2^{2-}	3.0
He_2^+	0.5

Thus, bond order increases as : $He_2^+ < O_2^- < NO < C_2^{2-}$

87. (c) : In CO, the number of electrons = 6 + 8 = 14

Molecular orbital electronic configuration of

$CO : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$

CN$^-$ have also get (6 + 7 + 1) 14 electrons and the configuration is similar to that of CO.

CN$^-$ and CO are isoelectronic species.

88. (c) : In 'CO' (14 electrons), there is no unpaired electron in its molecular orbital. Therefore, this does not exhibit paramagnetism.

89. (d) : $O_2^{2-}(18) : (\sigma 1s)^2, (\sigma^* 1s)^2(\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2, (\pi 2p_y)^2, (\pi^* 2p_x)^2, (\pi^* 2p_y)^2$

Thus, the no. of antibonding electrons in O_2^{2-} ion is 8(4 pairs).

90. (d) : As per their molecular orbital electronic configurations CO, CN$^-$ and O_2^{2-} are diamagnetic and NO is paramagnetic.

91. (a) : He_2 does not exist as it has zero bond order.

$He_2 : \sigma 1s^2, \sigma^* 1s^2$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2-2) = 0$$

92. (d) : $Be_2(8) : KK\ \sigma(2s)^2\ \sigma^*(2s)^2$

$O_2(16) : KK\sigma(2s)^2\ \sigma^*(2s)^2\ \sigma(2p_z)^2\pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^1\ \pi^*(2p_y)^1$

$N_2(14) : KK\ \sigma(2s)^2\ \sigma^*(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^2$

$C_2(12) : KK\ \sigma(2s)^2\ \sigma^*(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2$

Therefore, C_2 contains 2 π bonds as it has 4 electrons in two pi-molecular orbitals.

93. (d) : $N_2(14) : KK\ \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$; Diamagnetic

$H_2(2) : \sigma 1s^2$; Diamagnetic

$Li_2(6) : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2$; Diamagnetic

$O_2(16) : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$

$\pi^* 2p_x^1 = \pi^* 2p_y^1$; Paramagnetic

94. (d) : $O_2(16) : KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2$
$\pi^* 2p_x^1 = \pi^* 2p_y^1$

$$\text{Bond order} = \frac{1}{2}(8-4) = 2$$

$O_2^{2-}(18) : KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2$
$\pi^* 2p_x^2 = \pi^* 2p_y^2$

$$\text{Bond order} = \frac{1}{2}(8-6) = 1$$

$O_2^-(17) : KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2$
$\pi^* 2p_x^2 = \pi^* 2p_y^1$

$$\text{Bond order} = \frac{1}{2}(8-5) = 1.5$$

$O_2^+(15) : KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^1$

$$\text{Bond order} = \frac{1}{2}(8-3) = 2.5$$

As, bond order $\propto$ stability

The decreasing order of stability is

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

95. (b) : $O_2^- < O_2^+ < O_2^{2+}$

B.O. : 1.5 2.5 3.0

96. (b) : Configuration of O_2 (16) :

$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2\, \pi 2p_y^2\, \pi^* 2p_x^1\, \pi^* 2p_y^1$

$$\text{Bond order} = \frac{\begin{matrix}\text{No. of } e^- \text{ in} \\ \text{bonding M.O.}\end{matrix} - \begin{matrix}\text{No. of } e^- \text{ in} \\ \text{antibonding M.O.}\end{matrix}}{2}$$

$$\text{Bond order of } O_2^+ = \frac{10-5}{2} = 2.5$$

$$\text{Bond order of } O_2^- = \frac{10-7}{2} = 1.5$$

$$\text{Bond order of } O_2^{2-} = \frac{10-8}{2} = 1.0$$

$$\text{Bond order of } O_2 = \frac{10-6}{2} = 2$$

97. (a) : Electronic configuration

$O_2 : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^1$

$$\text{Bond order} = \frac{1}{2}(8-4) = 2$$

$$O_2^+ : \text{Bond order} = \frac{1}{2}(8-3) = 2\frac{1}{2}$$

$$O_2^- : \text{Bond order} = \frac{1}{2}(8-5) = 1\frac{1}{2}$$

$$O_2^{2-} : \text{Bond order} = \frac{1}{2}(8-6) = 1$$

As bond order increases, bond length decreases.

98. (c) : O_2^+ and O_2 are paramagnetic in nature as they contain one and two unpaired electrons respectively.

99. (b) : Be_2 does not exist.

Be_2 has an electronic configuration of :

$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2$

$$\therefore \quad \text{Bond order} = \frac{4-4}{2} = 0$$

Thus, Be_2 does not exist.

100. (a) : According to MOT, the molecular orbital electronic configuration of

N_2 (14) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$

$$\therefore \quad \text{B.O} = \frac{10-4}{2} = 3$$

N_2^- (15) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2 (\pi^* 2p_x)^1$

$$\therefore \quad \text{B.O} = \frac{10-5}{2} = 2.5$$

N_2^{2-} (16) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^1$

$$\therefore \quad \text{B.O.} = \frac{10-6}{2} = 2$$

Hence, bond order increases as : $N_2^{2-} < N_2^- < N_2$

101. (a) : $N_2(14) : (\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2 (\pi 2p_x)^2, (\pi 2p_y)^2, (\sigma 2p_z)^2$

$$\text{In } N_2, \text{ bond order} = \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$$

$$\text{In } N_2^+, \text{ bond order} = \frac{9-4}{2} = 2 \cdot 5$$

As the bond order in N_2 is more than N_2^+ so the dissociation energy of N_2 is higher than N_2^+.

102. (b) : Diamagnetism is caused due to the absence of unpaired electrons. But in N_2^+, there is unpaired electron. So, it is paramagnetic.

103. (b) : N_2^- becomes paramagnetic due to one unpaired electron in $\pi^* 2p_x$ orbital.

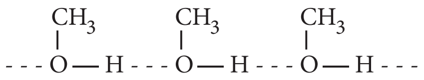
104. (b) : Number of electrons in bonding orbitals $N_b = 10$ and number of electrons in antibonding orbitals $N_a = 4$.

Therefore bond order = $1/2(N_b - N_a) = 1/2(10 - 4) = 3$

105. (c) : The bond order of $O_2^+ = 2.5$, $O_2^{2-} = 1$, $O_2^- = 1.5$ and that of $O_2 = 2$.

106. (c) : H_2O_2, HCN and conc. CH_3COOH form intermolecular hydrogen bonding while cellulose has intramolecular hydrogen bonding.

107. (d) : Methanol can undergo intermolecular association through H-bonding as the – OH group in alcohols is highly polarised.



$$\cdots \underset{\substack{|\\ CH_3}}{O} - H \cdots \underset{\substack{|\\ CH_3}}{O} - H \cdots \underset{\substack{|\\ CH_3}}{O} - H \cdots$$

As a result, in order to convert liquid CH_3OH to gaseous state, the strong hydrogen bonds must be broken.

108. (a) : $^{\delta-}X — H^{\delta+}$ ...... Y, the electrons of the covalent bond are shited towards the more electronegative atom. This partially positively charged H-atom forms hydrogen bond with the other more electronegative atom.

109. (c) : H – F shows strongest H-bonds because fluorine is most electronegative.

110. (a) : H_2O shows maximum H-bonding because each H_2O molecule is linked to four H_2O molecules through H-bonds.

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CHAPTER
5

States of Matter

5.1 Intermolecular Forces

1. Dipole-induced dipole interactions are present in which of the following pairs?
(a) HCl and He atoms (b) SiF_4 and He atoms
(c) H_2O and alcohol (d) Cl_2 and CCl_4
(NEET 2013)

2. Which one of the following is the correct order of interactions?
(a) Covalent < hydrogen bonding < van der Waals' < dipole-dipole
(b) van der Waals' < hydrogen bonding < dipole-dipole < covalent
(c) van der Waals' < dipole-dipole < hydrogen bonding < covalent
(d) Dipole-dipole < van der Waals' < hydrogen bonding < covalent. *(1993)*

5.4 The Gaseous State

3. Which of the following statements is wrong for gases?
(a) Confined gas exerts uniform pressure on the walls of its container in all directions.
(b) Volume of the gas is equal to volume of container confining the gas.
(c) Gases do not have a definite shape and volume.
(d) Mass of a gas cannot be determined by weighing a container in which it is enclosed. *(1999)*

5.5 The Gas Laws

4. At 25°C and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure?
(a) 569 mL (b) 365 mL
(c) 265 mL (d) 621 mL *(1999)*

5. Pressure remaining the same, the volume of a given mass of an ideal gas increases for every degree centrigrade rise in temperature by definite fraction of its volume at
(a) 0°C (b) its critical temperature
(c) absolute zero (d) its Boyle temperature.
(1989)

5.6 Ideal Gas Equation

6. A mixture of N_2 and Ar gases in a cylinder contains 7 g of N_2 and 8 g of Ar. If the total pressure of the mixture of the gases in the cylinder is 27 bar, the partial pressure of N_2 is
[Use atomic masses (in g mol^{-1}) : N = 14, Ar = 40]
(a) 9 bar (b) 12 bar
(c) 15 bar (d) 18 bar. *(NEET 2020)*

7. The volume occupied by 1.8 g of water vapour at 374°C and 1 bar pressure will be
[Use $R = 0.083$ bar L $K^{-1}mol^{-1}$]
(a) 96.66 L (b) 55.87 L
(c) 3.10 L (d) 5.37 L
(Odisha NEET 2019)

8. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
(a) 3/8 (b) 1/2
(c) 1/8 (d) 1/4 *(NEET-I 2016)*

9. What is the density of N_2 gas at 227°C and 5.00 atm pressure? ($R = 0.082$ L atm $K^{-1}mol^{-1}$)
(a) 1.40 g/mL (b) 2.81 g/mL
(c) 3.41 g/mL (d) 0.29 g/mL
(Karnataka NEET 2013)

10. 50 mL of each gas *A* and of gas *B* takes 150 and 200 seconds respectively for effusing through a pin hole under the similar conditions. If molecular mass of gas *B* is 36, the molecular mass of gas *A* will be
(a) 96 (b) 128
(c) 32 (d) 64 *(2012)*

11. A certain gas takes three times as long to effuse out as helium. Its molecular mass will be

(a) 27 u (b) 36 u
(c) 64 u (d) 9 u *(Mains 2012)*

12. Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49 u. Molecular mass of B will be
(a) 50.00 u (b) 12.25 u
(c) 6.50 u (d) 25.00 u *(2011)*

13. A gaseous mixture was prepared by taking equal moles of CO and N_2. If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen (N_2) in the mixture is
(a) 0.5 atm (b) 0.8 atm
(c) 0.9 atm (d) 1 atm *(2011)*

14. A bubble of air is underwater at temperature 15°C and the pressure 1.5 bar. If the bubble rises to the surface where the temperature is 25°C and the pressure is 1.0 bar, what will happen to the volume of the bubble?
(a) Volume will become greater by a factor of 1.6.
(b) Volume will become greater by a factor of 1.1.
(c) Volume will become smaller by a factor of 0.70.
(d) Volume will become greater by a factor of 2.5. *(Mains 2011)*

15. The pressure exerted by 6.0 g of methane gas in a 0.03 m^3 vessel at 129°C is (Atomic masses: C = 12.01, H = 1.01 and $R = 8.314$ J K^{-1} mol^{-1})
(a) 215216 Pa (b) 13409 Pa
(c) 41648 Pa (d) 31684 Pa *(Mains 2010)*

16. Which of the following mixtures of gases does not obey Dalton's law of partial pressure?
(a) Cl_2 and SO_2 (b) CO_2 and He
(c) O_2 and CO_2 (d) N_2 and O_2 *(1996)*

17. At what temperature, the rate of effusion of N_2 would be 1.625 times than the rate of SO_2 at 50°C?
(a) 373°C (b) 620°C
(c) 100°C (d) 173°C *(1996)*

18. 50 mL of hydrogen diffuses out through a small hole of a vessel, in 20 minutes. The time taken by 40 mL of oxygen to diffuse out is
(a) 32 minutes (b) 64 minutes
(c) 8 minutes (d) 12 minutes *(1994)*

19. Under what conditions will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of 1 mole $litre^{-1}$?
($R = 0.082$ litre atm mol^{-1} deg^{-1})
(a) At STP
(b) When $V = 22.4$ litres
(c) When $T = 12$ K
(d) Impossible under any conditions *(1993)*

20. The correct value of the gas constant 'R' is close to
(a) 0.082 litre-atmosphere K
(b) 0.082 litre-atmosphere K^{-1} mol^{-1}
(c) 0.082 $litre\text{-}atmosphere^{-1}$ K mol^{-1}
(d) 0.082 $litre^{-1}$ $atmosphere^{-1}$ K mol. *(1992)*

21. Select one correct statement. In the gas equation, $PV = nRT$
(a) n is the number of molecules of a gas
(b) V denotes volume of one mole of the gas
(c) n moles of the gas have a volume V
(d) P is the pressure of the gas when only one mole of gas is present. *(1992)*

22. At constant temperature, in a given mass of an ideal gas
(a) the ratio of pressure and volume always remains constant
(b) volume always remains constant
(c) pressure always remains constant
(d) the product of pressure and volume always remains constant. *(1991)*

23. If P, V, M, T and R are pressure, volume, molar mass, temperature and gas constant respectively, then for an ideal gas, the density is given by
(a) $\frac{RT}{PM}$ (b) $\frac{P}{RT}$ (c) $\frac{M}{V}$ (d) $\frac{PM}{RT}$ *(1989)*

24. Correct gas equation is
(a) $\frac{V_1T_2}{P_1} = \frac{V_2T_1}{P_2}$ (b) $\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$
(c) $\frac{P_1T_1}{V_1} = \frac{P_2V_2}{T_2}$ (d) $\frac{V_1V_2}{T_1T_2} = P_1P_2$ *(1989)*

5.7 Kinetic Energy and Molecular Speeds

25. By what factor does the average velocity of a gaseous molecule increase when the temperature (in Kelvin) is doubled?
(a) 2.0 (b) 2.8
(c) 4.0 (d) 1.4 *(2011)*

26. The temperature of a gas is raised from 27°C to 927°C. The root mean square speed of the gas
(a) remains same (b) gets $\sqrt{\frac{927}{27}}$ times
(c) gets halved (d) gets doubled. *(1994)*

27. The ratio among most probable velocity, mean velocity and root mean square velocity is given by
(a) 1 : 2 : 3 (b) $1 : \sqrt{2} : \sqrt{3}$
(c) $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$ (d) $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$ *(1993)*

28. The root mean square velocity at STP for the gases H_2, N_2, O_2 and HBr are in the order

(a) $H_2 < N_2 < O_2 < HBr$ (b) $HBr < O_2 < N_2 < H_2$
(c) $H_2 < N_2 = O_2 < HBr$ (d) $HBr < O_2 < H_2 < N_2$
(1991)

29. Root mean square velocity of a gas molecule is proportional to
(a) $m^{1/2}$ (b) m^0
(c) $m^{-1/2}$ (d) m *(1990)*

5.8 Kinetic Molecular Theory of Gases

30. The energy absorbed by each molecule (A_2) of a substance is 4.4×10^{-19} J and bond energy per molecule is 4.0×10^{-19} J. The kinetic energy of the molecule per atom will be
(a) 2.2×10^{-19} J (b) 2.0×10^{-19} J
(c) 4.0×10^{-20} J (d) 2.0×10^{-20} J *(2009)*

31. If a gas expands at constant temperature, it indicates that
(a) kinetic energy of molecules remains the same
(b) number of the molecules of gas increases
(c) kinetic energy of molecules decreases
(d) pressure of the gas increases. *(2008)*

32. Average molar kinetic energy of CO and N_2 at same temperature is
(a) $KE_1 = KE_2$
(b) $KE_1 > KE_2$
(c) $KE_1 < KE_2$
(d) can't say anything. Both volumes are not given.
(2000)

33. The average kinetic energy of an ideal gas, per molecule in S.I. units, at 25°C will be
(a) 6.17×10^{-20} J (b) 7.16×10^{-20} J
(c) 61.7×10^{-20} J (d) 6.17×10^{-21} J *(1996)*

34. At STP, 0.50 mol H_2 gas and 1.0 mol He gas
(a) have equal average kinetic energies
(b) have equal molecular speeds
(c) occupy equal volumes
(d) have equal effusion rates. *(1993)*

35. Internal energy and pressure of a gas per unit volume are related as
(a) $P = \frac{2}{3}E$ (b) $P = \frac{3}{2}E$
(c) $P = \frac{1}{2}E$ (d) $P = 2E$ *(1993)*

36. A closed flask contains water in all its three states solid, liquid and vapour at 0°C. In this situation, the average kinetic energy of water molecules will be
(a) the greatest in all the three states
(b) the greatest in vapour state
(c) the greatest in the liquid state
(d) the greatest in the solid state. *(1992)*

37. Which is not true in case of an ideal gas?
(a) It cannot be converted into a liquid.
(b) There is no interaction between the molecules.
(c) All molecules of the gas move with same speed.
(d) At a given temperature, PV is proportional to the amount of the gas. *(1992)*

5.9 Behaviour of Real Gases - Deviation from Ideal Gas Behaviour

38. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor (Z) is
(a) $Z < 1$ and repulsive forces are dominant
(b) $Z > 1$ and attractive forces are dominant
(c) $Z > 1$ and repulsive forces are dominant
(d) $Z < 1$ and attractive forces are dominant.
(NEET 2019)

39. A gas such as carbon monoxide would be most likely to obey the ideal gas law at
(a) low temperatures and high pressures
(b) high temperatures and high pressures
(c) low temperatures and low pressures
(d) high temperatures and low pressures. *(2015)*

40. Maximum deviation from ideal gas is expected from
(a) $CH_{4(g)}$ (b) $NH_{3(g)}$
(c) $H_{2(g)}$ (d) $N_{2(g)}$ *(NEET 2013)*

41. For real gases van der Waals' equation is written as $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$ where a and b are van der Waals' constants. Two sets of gases are
(I) O_2, CO_2, H_2 and He
(II) CH_4, O_2 and H_2
The gases given in set-I in increasing order of b and gases given in set-II in decreasing order of a, are arranged below. Select the correct order from the following :
(a) (I) $He < H_2 < CO_2 < O_2$ (II) $CH_4 > H_2 > O_2$
(b) (I) $O_2 < He < H_2 < CO_2$ (II) $H_2 > O_2 > CH_4$
(c) (I) $H_2 < He < O_2 < CO_2$ (II) $CH_4 > O_2 > H_2$
(d) (I) $H_2 < O_2 < He < CO_2$ (II) $O_2 > CH_4 > H_2$
(Mains 2012)

42. van der Waals' real gas, acts as an ideal gas, at which conditions?
(a) High temperature, low pressure
(b) Low temperature, high pressure
(c) High temperature, high pressure
(d) Low temperature, low pressure *(2002)*

43. When is deviation more in the behaviour of a gas from the ideal gas equation $PV = nRT$?
(a) At high temperature and low pressure
(b) At low temperature and high pressure
(c) At high temperature and high pressure
(d) At low temperature and low pressure *(1993)*

44. A gas is said to behave like an ideal gas when the relation PV/T = constant. When do you expect a real gas to behave like an ideal gas?
(a) When the temperature is low.
(b) When both the temperature and pressure are low.
(c) When both the temperature and pressure are high.
(d) When the temperature is high and pressure is low. *(1991)*

45. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular forces is
(a) $(V - b)$ (b) $(RT)^{-1}$
(c) $\left(P+\dfrac{a}{V^2}\right)$ (d) RT *(1990)*

5.10 Liquefaction of Gases

46. Given van der Waals' constant for NH_3, H_2, O_2 and CO_2 are respectively 4.17, 0.244, 1.36 and 3.59, which one of the following gases is most easily liquefied?
(a) NH_3 (b) H_2
(c) O_2 (d) CO_2 *(NEET 2018)*

47. An ideal gas, obeying kinetic theory of gases cannot be liquefied, because
(a) it solidifies before becoming a liquid
(b) forces acting between its molecules are negligible
(c) its critical temperature is above 0°C
(d) its molecules are relatively small in size. *(1995)*

5.11 Liquid State

48. The beans are cooked earlier in pressure cooker because
(a) boiling point increases with increasing pressure
(b) boiling point decreases with increasing pressure
(c) extra pressure of pressure cooker softens the beans
(d) internal energy is not lost while cooking in pressure cooker. *(2011)*

ANSWER KEY

1.	(a)	**2.**	(b)	**3.**	(d)	**4.**	(b)	**5.**	(a)	**6.**	(c)	**7.**	(d)	**8.**	(c)	**9.**	(c)	**10.**	(None)
11.	(b)	**12.**	(b)	**13.**	(a)	**14.**	(a)	**15.**	(c)	**16.**	(a)	**17.**	(c)	**18.**	(b)	**19.**	(c)	**20.**	(b)
21.	(c)	**22.**	(d)	**23.**	(d)	**24.**	(b)	**25.**	(d)	**26.**	(d)	**27.**	(d)	**28.**	(b)	**29.**	(c)	**30.**	(d)
31.	(a)	**32.**	(a)	**33.**	(d)	**34.**	(a)	**35.**	(a)	**36.**	(b)	**37.**	(c)	**38.**	(d)	**39.**	(d)	**40.**	(b)
41.	(c)	**42.**	(a)	**43.**	(b)	**44.**	(d)	**45.**	(c)	**46.**	(a)	**47.**	(b)	**48.**	(a)				

Hints & Explanations

1. (a) : HCl is polar ($\mu \neq 0$) and He is non-polar ($\mu = 0$) gives dipole-induced dipole interactions.

2. (b) : The strength of interaction follows the order : van der Waals' < hydrogen-bonding < dipole-dipole < covalent. It is so because bond length of H-bond is larger than that of a covalent bond.

And also covalent bond is strongest because, the greater the extent of overlapping, the stronger is the bond formed.

3. (d) : Mass of the gas = Mass of the cylinder including gas − Mass of empty cylinder.

So, mass of a gas can be determined by weighing the container in which it is enclosed.

Thus, the statement (d) is wrong for gases.

4. (b) : $V_1 = 380$ mL, $P_1 = 730$ mm, $V_2 = ?$, $P_2 = 760$ mm.

From Boyle's law, $P_1V_1 = P_2V_2$

$$\Rightarrow V_2 = \frac{P_1V_1}{P_2} = \frac{730 \times 380}{760} = 365 \text{ mL}$$

5. (a) : According to Charles' law which states that "The volume of the given mass of a gas increases or decreases by $\frac{1}{273}$ of its volume at 0°C for each degree rise or fall of temperature at constant pressure."

$$V_t = V_0\left(1+\frac{t}{273}\right) \text{ at constant } P \text{ and } n.$$

6. (c) : Number of moles of $N_2 = \frac{7}{28} = 0.25$ mol

Number of moles of Ar $= \frac{8}{40} = 0.2$ mol

Mole fraction of $N_2 = \frac{0.25}{0.25+0.2} = \frac{0.25}{0.45} = 0.55$

Partial pressure of N_2 gas = mole fraction × total pressure

$= 0.55 \times 27 = 14.85 \approx 15$ bar

7. (d) : $m = 1.8$ g $\Rightarrow n = \frac{m}{M} = \frac{1.8}{18} = 0.1$ mol

$T = 374°C = 647$ K, $P = 1$ bar, $R = 0.083$ bar L K^{-1} mol^{-1}

$$V = \frac{nRT}{P} = \frac{0.1 \times 0.083 \times 647}{1} = 5.37 \text{ L}$$

8. (c) : Let the number of moles of each gas $= x$

Fraction of hydrogen escaped $= \frac{1}{2}x$

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} \Rightarrow \frac{n_{O_2}/t}{\frac{x}{2}/t} = \sqrt{\frac{2}{32}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$\Rightarrow \frac{n_{O_2}/t}{\frac{x}{2}/t} = \frac{1}{4} \Rightarrow n_{O_2} = \frac{1}{8}x$$

Hence, fraction of oxygen escaped $= \frac{1}{8}$

9. (c) : $PV = nRT$

$$PV = \frac{w}{M}RT \left[n = \frac{\text{Weight of the gas taken } (W)}{\text{Mol. mass of gas } (M)}\right]$$

$$P = \frac{w}{M} \times \frac{RT}{V}$$

$$P = \frac{dRT}{M} \qquad \left[\text{Density} = \frac{\text{Mass}}{\text{Volume}}\right]$$

$$d = \frac{PM}{RT} = \frac{5 \times 28}{0.0821 \times 500} = 3.41 \text{ g/mL}$$

10. (None) : According to Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}},\ r_A = \frac{V_A}{T_A},\quad r_B = \frac{V_B}{T_B}$$

$$\frac{V_A/T_A}{V_B/T_B} = \sqrt{\frac{M_B}{M_A}}$$

$V_A = V_B$, $T_A = 150$ sec, $T_B = 200$ sec, $M_B = 36$, $M_A = ?$

$$\frac{T_B}{T_A} = \sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{200}{150} = \sqrt{\frac{36}{M_A}}$$

$$\frac{4}{3} = \sqrt{\frac{36}{M_A}} \text{ or } \frac{4\times4}{3\times3} = \frac{36}{M_A}$$

$$\text{or } M_A = \frac{36}{4\times4} \times 3 \times 3 = 20.25$$

11. (b) : According to Graham's law of diffusion,

$$r \propto \frac{1}{\sqrt{d}} \propto \frac{1}{\sqrt{M}} \Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused } (V)}{\text{Time taken } (t)}$$

$$\therefore \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{M_2}{M_1}}$$

If same volume of two gases diffuse, then $V_1 = V_2$

$$\therefore \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

Here $t_2 = 3t_1$, $M_1 = 4$ u, $M_2 = ?$

$$\therefore \frac{3t_1}{t_1} = \sqrt{\frac{M_2}{4}} \Rightarrow 3 = \sqrt{\frac{M_2}{4}}$$

$$\Rightarrow 9 = \frac{M_2}{4} \Rightarrow M_2 = 36 \text{ u}$$

12. (b) : We know that $\frac{r_A}{r_B} = \frac{V/t_A}{V/t_B} = \sqrt{\frac{M_B}{M_A}}$

$$\frac{t_B}{t_A} = \sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{10}{20} = \sqrt{\frac{M_B}{49}}$$

$$\Rightarrow \left(\frac{10}{20}\right)^2 = \frac{M_B}{49} \Rightarrow \frac{100}{400} = \frac{M_B}{49}$$

$$\Rightarrow M_B = \frac{49 \times 100}{400} = 12.25 \text{ u}$$

13. (a) : $p_{CO} + p_{N_2} = 1$ atm

$2p_{N_2} = 1$ $\quad [\because n_{CO} = n_{N_2}]$

$$p_{N_2} = \frac{1}{2} = 0.5 \text{ atm}$$

14. (a) : From ideal gas equation, $V \propto \frac{T}{P}$

Given $T_1 = 15 + 273 = 288$ K, $P_1 = 1.5$ bar

$T_2 = 25 + 273 = 298$ K, $P_2 = 1$ bar

$$V_1 \propto \frac{288}{1.5} \text{ i.e., } V_1 \propto 192 \text{ and } V_2 \propto \frac{298}{1}$$

$$\frac{V_2}{V_1} = \frac{298}{192} = 1.55 \approx 1.6$$

15. (c) : Given, mass of CH_4, $w = 6$ g

Volume of CH_4, $V = 0.03$ m^3

$T = 129°C = 129 + 273 = 402$ K

$R = 8.314$ J K^{-1} mol^{-1}

Molecular mass of CH_4, $M = 12.01 + 4 \times 1.01 = 16.05$

$$PV = nRT = \frac{w}{M}RT$$

$$\therefore P = \frac{w}{M}\frac{RT}{V} = \frac{6}{16.05} \times \frac{8.314 \times 402}{0.03}$$

$= 41647.7$ Pa ≈ 41648 Pa

16. (a) : $Cl_2 + SO_2 \xrightarrow{\text{Sunlight}} SO_2Cl_2$
(Sulphuryl chloride)

Dalton's law of partial pressure is applicable only in those cases where gases are non-reacting. As Cl_2 and SO_2 reacts to form SO_2Cl_2 so this law is not obeyed in given case.

17. (c) : $r_1 = 1.625r_2$ and $T_2 = 50°C = 323$ K

We know that $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1} \times \frac{T_1}{T_2}}$

or $1.625 = \sqrt{\frac{64}{28} \times \frac{T_1}{323}}$

or $T_1 = \frac{(1.625)^2 \times 28 \times 323}{64} = 373.15\text{ K} = 100.15°\text{C}$

18. (b) : Volume of hydrogen = 50 mL; Time for diffusion (t) = 20 min and volume of oxygen = 40 mL.

Rate of diffusion of hydrogen (r_1) = $\frac{50}{20}$ = 2.5 mL/min

Rate of diffusion of oxygen (r_2) = $\frac{40}{t}$ mL/min

Since the molecular mass of hydrogen (M_1) = 2 and that of oxygen (M_2) = 32, therefore

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{2.5}{40/t} = \sqrt{\frac{32}{2}} \Rightarrow \frac{t}{16} = 4 \Rightarrow t = 64 \text{ minutes}$$

19. (c) : $PV = nRT$ or $P = \frac{n}{V}RT = CRT$

Hence, $1 = 1 \times 0.082 \times T \Rightarrow T = \frac{1}{0.082} = 12$ K

20. (b)

21. (c) : In ideal gas equation, $PV = nRT$

n moles of the gas have volume V.

22. (d) : According to Boyle's law at constant temperature, $P \propto \frac{1}{V}$ or PV = constant

23. (d) : Ideal gas equation is

$$PV = nRT = \frac{m}{M}RT$$

or $PM = \frac{m}{V}RT = dRT$ [here d = density]

$\Rightarrow d = \frac{PM}{RT}$

24. (b) : $\frac{PV}{T}$ = constant or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$

25. (d) : Average velocity $= \sqrt{\frac{8RT}{\pi M}}$

When T becomes $2T$ then

average velocity $= \sqrt{\frac{8R(2T)}{\pi M}}$

i.e., $\sqrt{2}$ or 1.41 times increase.

26. (d) : $T_1 = 27°C = 300$ K and $T_2 = 927°C = 1200$ K

We know that root mean square speed $(v) \propto \sqrt{T}$.

Therefore root mean square speed of the gas, when its temperature is raised $= \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{1200}{300}} = 2$ times

27. (d) : Most probable velocity, $(u_{mp}) = \sqrt{\frac{2RT}{M}}$

Mean velocity, $(\bar{v}) = \sqrt{\frac{8RT}{\pi M}}$

Root mean square velocity, $(u_{r.m.s}) = \sqrt{\frac{3RT}{M}}$

$$\therefore u_{mp} : \bar{v} : u_{r.m.s} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

28. (b) : We know, $PV = \frac{1}{3}mnu^2 = \frac{1}{3}Mu^2$

or $u = \sqrt{3PV/M}$

At STP, $u \propto \sqrt{\frac{1}{M}}$

and molecular masses of H_2, N_2, O_2 and HBr are 2, 28, 32 and 81.

29. (c) : $PV = \frac{1}{3}mNu^2$,

here u = root mean square velocity.

Now $u^2 = \frac{3PV}{mN}$ or $u \propto \frac{1}{\sqrt{m}}$

30. (d) : Energy absorbed by each molecule

$= 4.4 \times 10^{-19}$ J

Energy required to break the bond $= 4.0 \times 10^{-19}$ J

Remaining energy to get converted to kinetic energy

$= (4.4 \times 10^{-19} - 4.0 \times 10^{-19})$ J $= 0.4 \times 10^{-19}$ J per molecule

$\therefore$ Kinetic energy per atom $= 0.2 \times 10^{-19}$ J or 2×10^{-20} J

31. (a) : The average translational *K.E.* of one molecule of an ideal gas will be given by

$$E_t = \frac{K.E.}{N_A} = \frac{3/2\,RT}{N_A} = \frac{3}{2}kT$$

where R/N_A = Boltzmann constant *i.e.* $E_t \propto T$

So, at constant temperature, *K.E.* of molecules remains the same.

32. (a) : $K.E. = \frac{3}{2}RT$ (for one mole of a gas)

As temperatures are same and KE is independent of molecular mass, so $KE_1 = KE_2$.

33. (d) : Temperature (T) = 25°C = 298 K.

Therefore, *K.E.* per molecule

$$= \frac{3RT}{2N_A} = \frac{3 \times 8.314 \times 298}{2 \times (6.02 \times 10^{23})} = 6.17 \times 10^{-21} \text{ J}$$

34. (a) : Because average kinetic energy depends only on temperature $K.E. = \frac{3}{2}kT$

35. (a) : $PV = \frac{1}{3}mnu^2 = \frac{1}{3}Mu^2$

$$= \frac{2}{3}\cdot\frac{1}{2}Mu^2 = \frac{2}{3}E \qquad \left\{\because \frac{1}{2}Mu^2 = E\right\}$$

or $\quad P = \frac{2}{3}E$ per unit volume.

36. (b) : Velocity and hence average *K.E.* of water molecules is maximum in the gaseous state.

37. (c) : Molecules in an ideal gas move with different speeds. Due to collision between the particles their speed changes.

38. (d) : $V_{\text{ideal}} = V$, $V_{\text{real}} = V - 0.2\text{ V} = 0.8\text{ V}$

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = 0.8$$

if value of $Z < 1$ then attractive forces are dominant.

39. (d) : Real gases show ideal gas behaviour at high temperatures and low pressures.

40. (b) : NH_3 is a polar molecule, thus more attractive forces between NH_3 molecules.

41. (c) : van der Waals' gas constant '*a*' represent intermolecular forces of attraction of gaseous molecules and van der Waals' gas constant '*b*' represent effective size of molecules. Therefore order should be

(I) $H_2 < He < O_2 < CO_2$ (II) $CH_4 > O_2 > H_2$

42. (a) : At low pressure and high temperature van der Waals real gas acts as ideal gas and observed to obey $PV = nRT$ relation. At very low pressure when the gas-volume is quite large the space occupied by the molecules themselves becomes negligible comparatively and because the molecules are then far apart, the force of mutual attraction becomes too feeble, the real gas would satisfy the postulates of kinetic theory. As temperature is raised, the volume of the gas increases and we can consider $\left(P + \frac{n^2a}{V^2}\right)$ term as P and at low pressure $(V - nb)$ term as V.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad \text{(van der Waals' equation)}$$

This equation becomes $PV = nRT$

This is an ideal gas equation.

43. (b) : At low temperature and high pressure, there is a deviation from the ideal behaviour in gases.

44. (d) : At high temperature and low pressure the effect of a/V^2 and b is negligible.

As we know, $PV = nRT$ (Ideal gas equation)

$$PV = RT \text{ or } \frac{PV}{RT} = 1$$

$\therefore \quad Z = 1$ [Z is compressibility factor]

Hence gas shows ideal behaviour.

45. (c) : van der Waals' equation for 1 mole is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Here, $\left(P + \frac{a}{V^2}\right)$ represents the intermolecular forces and $(V - b)$ is the correct volume.

46. (a) : van der Waals' constant '*a*' signifies the intermolecular forces of attraction between the particle of gas. So, higher the value of '*a*', easier will be the liquefaction of gas.

47. (b) : A gas can only be liquefied, if some forces of attraction are acting in its molecules. According to kinetic theory, an ideal gas is devoid of force of attraction in its molecules, therefore it cannot be liquefied.

48. (a) : More is the pressure, greater will be the boiling point.

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CHAPTER
6

Thermodynamics

6.1 Thermodynamic Terms

1. Which of the following are not state functions?

(I) $q + w$	(II) q
(III) w	(IV) $H - TS$
(a) (I), (II) and (III)	(b) (II) and (III)
(c) (I) and (IV)	(d) (II), (III) and (IV)

(2008)

2. In a closed insulated container a liquid is stirred with a paddle to increase the temperature, which of the following is true?

(a) $\Delta E = W \neq 0, q = 0$ (b) $\Delta E = W = q \neq 0$

(c) $\Delta E = 0, W = q \neq 0$ (d) $W = 0, \Delta E = q \neq 0$

(2002)

3. Which of the following is the correct equation?

(a) $\Delta U = \Delta W + \Delta Q$ (b) $\Delta U = \Delta Q - W$

(c) $\Delta W = \Delta U + \Delta Q$ (d) None of these *(1996)*

6.2 Applications

4. The correct option for free expansion of an ideal gas under adiabatic condition is

(a) $q = 0, \Delta T = 0$ and $w = 0$

(b) $q = 0, \Delta T < 0$ and $w > 0$

(c) $q < 0, \Delta T = 0$ and $w = 0$

(d) $q > 0, \Delta T > 0$ and $w > 0$ *(NEET 2020)*

5. Under isothermal conditions, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is [Given that 1 L bar = 100 J]

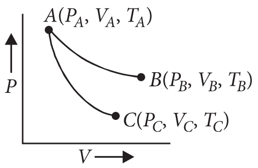
(a) 30 J (b) –30 J

(c) 5 kJ (d) 25 J *(NEET 2019)*

6. Reversible expansion of an ideal gas under isothermal and adiabatic conditions are as shown in the figure.

$AB \rightarrow$ Isothermal expansion

$AC \rightarrow$ Adiabatic expansion



Which of the following options is not correct ?

(a) $\Delta S_{\text{isothermal}} > \Delta S_{\text{adiabatic}}$

(b) $T_A = T_B$

(c) $W_{\text{isothermal}} > W_{\text{adiabatic}}$

(d) $T_c > T_A$ *(Odisha NEET 2019)*

7. An ideal gas expands isothermally from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 N m^{-2}. The work done on the gas is

(a) +270 kJ (b) –900 J

(c) +900 kJ (d) –900 kJ

(Odisha NEET 2019)

8. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be

(a) –500 J (b) –505 J

(c) +505 J (d) 1136.25 J

(NEET 2017)

9. Equal volumes of two monatomic gases, A and B at same temperature and pressure are mixed. The ratio of specific heats (C_P/C_V) of the mixture will be

(a) 0.83 (b) 1.50

(c) 3.3 (d) 1.67 *(2012)*

10. Which of the following is correct option for free expansion of an ideal gas under adiabatic condition?

(a) $q = 0, \Delta T \neq 0, w = 0$ (b) $q \neq 0, \Delta T = 0, w = 0$

(c) $q = 0, \Delta T = 0, w = 0$ (d) $q = 0, \Delta T < 0, w \neq 0$

(2011)

11. Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be

(a) infinite (b) 3 Joules

(c) 9 Joules (d) zero. *(Mains 2010)*

12. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?

(a) $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$

(b) $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$

(c) $C_{(s)} + 2H_2O_{(g)} \rightarrow 2H_{2(g)} + CO_{2(g)}$
(d) $PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$ *(2006)*

13. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is (1 L atm = 101.32 J)
(a) – 6 J (b) – 608 J
(c) + 304 J (d) – 304 J *(2004)*

14. For the reaction,
$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$
at constant temperature, $\Delta H - \Delta E$ is
(a) $+RT$ (b) $-3RT$
(c) $+3RT$ (d) $-RT$ *(2003)*

15. The molar heat capacity of water at constant pressure, C, is 75 J K^{-1} mol^{-1}. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is
(a) 1.2 K (b) 2.4 K
(c) 4.8 K (d) 6.6 K *(2003)*

16. When 1 mol of gas is heated at constant volume temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?
(a) $q = w = 500$ J, $\Delta E = 0$
(b) $q = \Delta E = 500$ J, $w = 0$
(c) $q = w = 500$ J, $\Delta E = 0$
(d) $\Delta E = 0$, $q = w = -500$ J *(2001)*

17. For the reaction,
$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$
which one is true?
(a) $\Delta H = \Delta E - RT$ (b) $\Delta H = \Delta E + RT$
(c) $\Delta H = \Delta E + 2RT$ (d) $\Delta H = \Delta E - 2RT$ *(2000)*

18. In an endothermic reaction, the value of ΔH is
(a) negative (b) positive
(c) zero (d) constant. *(1999)*

19. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is
(R = 2 cal mol^{-1} K^{-1})
(a) 1381.1 cal (b) zero
(c) 163.7 cal (d) 9 L atm *(1998)*

20. During isothermal expansion of an ideal gas, its
(a) internal energy increases
(b) enthalpy decreases
(c) enthalpy remains unaffected
(d) enthalpy reduces to zero. *(1994, 1991)*

21. For the reactionm, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, ΔH = ?
(a) $\Delta E + 2RT$ (b) $\Delta E - 2RT$
(c) $\Delta H = RT$ (d) $\Delta E - RT$ *(1991)*

22. If ΔH is the change in enthalpy and ΔE, the change in internal energy accompanying a gaseous reaction, then
(a) ΔH is always greater than ΔE
(b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of moles of the reactants
(c) ΔH is always less than ΔE
(d) $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants. *(1990)*

6.4 Enthalpy Change, $\Delta_r H$ of a Reaction - Reaction Enthalpy

23. Three thermochemical equations are given below :
(i) $C_{(\text{graphite})} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H^\circ = x$ kJ mol^{-1}
(ii) $C_{(\text{graphite})} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$; $\Delta_r H^\circ = y$ kJ mol^{-1}
(iii) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H^\circ = z$ kJ mol^{-1}
Based on the above equations, find out which of the relationship given below is correct.
(a) $z = x + y$ (b) $x = y + z$
(c) $y = 2z - x$ (d) $x = y - z$
(Karnataka NEET 2013)

24. Standard enthalpy of vaporisation $\Delta_{vap}H^\circ$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is
(a) +37.56 (b) – 43.76
(c) + 43.76 (d) + 40.66
(Assume water vapour to behave like an ideal gas) *(2012)*

25. Consider the following processes :

	ΔH (kJ/mol)
$1/2A \rightarrow B$	+150
$3B \rightarrow 2C + D$	–125
$E + A \rightarrow 2D$	+350

For $B + D \rightarrow E + 2C$, ΔH will be
(a) 525 kJ/mol (b) –175 kJ/mol
(c) –325 kJ/mol (d) 325 kJ/mol
(Mains 2011)

26. The following two reactions are known
$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$; $\Delta H = -26.8$ kJ
$FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$; $\Delta H = -16.5$ kJ
The value of ΔH for the following reaction
$Fe_2O_{3(s)} + CO_{(g)} \rightarrow 2FeO_{(s)} + CO_{2(g)}$ is
(a) + 10.3 kJ (b) – 43.3 kJ
(c) – 10.3 kJ (d) + 6.2 kJ *(Mains 2010)*

27. For which one of the following equations is $\Delta H^\circ_{\text{reaction}}$ equal to ΔH°_f for the product?
(a) $N_{2(g)} + O_{3(g)} \rightarrow N_2O_{3(g)}$
(b) $CH_{4(g)} + 2Cl_{2(g)} \rightarrow CH_2Cl_{2(l)} + 2HCl_{(g)}$
(c) $Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_{4(g)}$
(d) $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ *(2003)*

28. Heat of combustion ΔH for $C_{(s)}$, $H_{2(g)}$ and $CH_{4(g)}$ are –94, –68 and –213 kcal/mol, then ΔH for $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ is
(a) –17 kcal (b) –111 kcal
(c) –170 kcal (d) –85 kcal *(2002)*

29. Change in enthalpy for reaction,
$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$
if heat of formation of $H_2O_{2(l)}$ and $H_2O_{(l)}$ are –188 and –286 kJ/mol respectively, is
(a) –196 kJ/mol (b) +196 kJ/mol
(c) +948 kJ/mol (d) –948 kJ/mole *(2001)*

30. Enthalpy of $CH_4 + 1/2\ O_2 \rightarrow CH_3OH$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then which relation is correct?
(a) $x > y$ (b) $x < y$
(c) $x = y$ (d) $x \geq y$ *(2001)*

31. In the reaction : $S + 3/2O_2 \rightarrow SO_3 + 2x$ kcal and $SO_2 + 1/2\ O_2 \rightarrow SO_3 + y$ kcal, the heat of formation of SO_2 is
(a) $(2x + y)$ (b) $(x - y)$
(c) $(x + y)$ (d) $(2x - y)$ *(1999)*

32. Given that $C + O_2 \rightarrow CO_2$, $\Delta H^\circ = -x$ kJ
$2CO + O_2 \rightarrow 2CO_2$, $\Delta H^\circ = -y$ kJ
The enthalpy of formation of carbon monoxide will be
(a) $\dfrac{y-2x}{2}$ (b) $2x - y$
(c) $y - 2x$ (d) $\dfrac{2x-y}{2}$ *(1997)*

33. If enthalpies of formation for $C_2H_{4(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ at 25°C and 1 atm pressure are 52, – 394 and – 286 kJ/mol respectively, then enthalpy of combustion of $C_2H_{4(g)}$ will be
(a) + 141.2 kJ/mol (b) + 1412 kJ/mol
(c) – 141.2 kJ/mol (d) – 1412 kJ/mol *(1995)*

6.5 Enthalpies for Different Types of Reactions

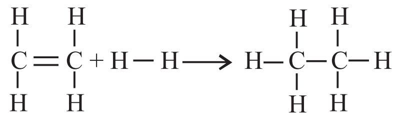
34. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be
(a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 800 kJ mol^{-1} (d) 400 kJ mol^{-1}
(NEET 2018)

35. The heat of combustion of carbon to CO_2 is –393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is
(a) + 315 kJ (b) – 630 kJ
(c) – 3.15 kJ (d) – 315 kJ *(2015)*

36. When 5 litres of a gas mixture of methane and propane is perfectly combusted at 0°C and 1 atmosphere, 16 litres of oxygen at the same temperature and pressure is consumed. The amount of heat released from this combustion in kJ (ΔH_{comb} (CH_4) = 890 kJ mol^{-1}, $\Delta H_{\text{comb.}}$ (C_3H_8) = 2220 kJ mol^{-1}) is
(a) 38 (b) 317 (c) 477 (d) 32
(Karnataka NEET 2013)

37. Enthalpy change for the reaction,
$4H_{(g)} \rightarrow 2H_{2(g)}$ is –869.6 kJ
The dissociation energy of H – H bond is
(a) – 434.8 kJ (b) – 869.6 kJ
(c) + 434.8 kJ (d) + 217.4 kJ *(2011)*

38. From the following bond energies :
H — H bond energy : 431.37 kJ mol^{-1}
C $=$ C bond energy : 606.10 kJ mol^{-1}
C — C bond energy : 336.49 kJ mol^{-1}
C — H bond energy : 410.50 kJ mol^{-1}
Enthalpy for the reaction,



$$\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} + H-H \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

will be
(a) – 243.6 kJ mol^{-1} (b) – 120.0 kJ mol^{-1}
(c) 553.0 kJ mol^{-1} (d) 1523.6 kJ mol^{-1}
(2009)

39. Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is
(a) –93 kJ mol^{-1} (b) 245 kJ mol^{-1}
(c) 93 kJ mol^{-1} (d) –245 kJ mol^{-1} *(2008)*

40. Consider the following reactions :
(i) $H^+_{(aq)} + OH^-_{(aq)} = H_2O_{(l)}$, $\Delta H = -X_1$ kJ mol^{-1}
(ii) $H_{2(g)} + 1/2O_{2(g)} = H_2O_{(l)}$, $\Delta H = -X_2$ kJ mol^{-1}
(iii) $CO_{2(g)} + H_{2(g)} = CO_{(g)} + H_2O_{(l)}$, $\Delta H = -X_3$ kJ mol^{-1}
(iv) $C_2H_{2(g)} + 5/2O_{2(g)} = 2CO_{2(g)} + H_2O_{(l)}$, $\Delta H = +X_4$ kJ mol^{-1}
Enthalpy of formation of $H_2O_{(l)}$ is
(a) $+X_3$ kJ mol^{-1} (b) $-X_4$ kJ mol^{-1}
(c) $+X_1$ kJ mol^{-1} (d) $-X_2$ kJ mol^{-1}. *(2007)*

41. Given that bond energies of H – H and Cl – Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is –90 kJ mol^{-1}, bond enthalpy of HCl is
(a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
(c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1} *(2007)*

42. The absolute enthalpy of neutralisation of the reaction :
$MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{(l)}$ will be
(a) –57.33 kJ mol^{-1}
(b) greater than –57.33 kJ mol^{-1}
(c) less than –57.33 kJ mol^{-1}
(d) 57.33 kJ mol^{-1} *(2005)*

43. If the bond energies of H–H, Br–Br, and H–Br are 433, 192 and 364 kJ mol^{-1} respectively, the $\Delta H°$ for the reaction $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$ is
(a) –261 kJ (b) +103 kJ
(c) +261 kJ (d) –103 kJ *(2004)*

6.6 Spontaneity

44. For the reaction, $2Cl_{(g)} \rightarrow Cl_{2(g)}$, the correct option is
(a) $\Delta_r H > 0$ and $\Delta_r S > 0$ (b) $\Delta_r H > 0$ and $\Delta_r S < 0$
(c) $\Delta_r H < 0$ and $\Delta_r S > 0$ (d) $\Delta_r H < 0$ and $\Delta_r S < 0$
(NEET 2020)

45. In which case change in entropy is negative?
(a) $2H_{(g)} \rightarrow H_{2(g)}$
(b) Evaporation of water
(c) Expansion of a gas at constant temperature
(d) Sublimation of solid to gas *(NEET 2019)*

46. For a given reaction, ΔH = 35.5 kJ mol^{-1} and ΔS = 83.6 J K^{-1} mol^{-1}. The reaction is spontaneous at (Assume that ΔH and ΔS do not vary with temperature.)
(a) $T > 425$ K (b) all temperatures
(c) $T > 298$ K (d) $T < 425$ K
(NEET 2017)

47. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by
(a) $\Delta S = nR\ln\left(\frac{p_f}{p_i}\right)$ (b) $\Delta S = nR\ln\left(\frac{p_i}{p_f}\right)$
(c) $\Delta S = nRT\ln\left(\frac{p_f}{p_i}\right)$ (d) $\Delta S = RT\ln\left(\frac{p_i}{p_f}\right)$
(NEET-II 2016)

48. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
(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 $\Delta S < 0$
(NEET-I 2016)

49. Consider the following liquid-vapour equilibrium.
Liquid $\rightleftharpoons$ Vapour
Which of the following relations is correct?
(a) $\frac{d\ln P}{dT^2} = \frac{-\Delta H_v}{T^2}$ (b) $\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$
(c) $\frac{d\ln G}{dT^2} = \frac{\Delta H_v}{RT^2}$ (d) $\frac{d\ln P}{dT} = \frac{-\Delta H_v}{RT}$
(NEET-I 2016)

50. Which of the following statements is correct for the spontaneous adsorption of a gas?
(a) ΔS is negative and, therefore ΔH should be highly positive.
(b) ΔS is negative and therefore, ΔH should be highly negative.
(c) ΔS is positive and therefore, ΔH should be negative.
(d) ΔS is positive and therefore, ΔH should also be highly positive. *(2014)*

51. For the reaction, $X_2O_{4(l)} \longrightarrow 2XO_{2(g)}$
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K
Hence, ΔG is
(a) 2.7 kcal (b) – 2.7 kcal
(c) 9.3 kcal (d) – 9.3 kcal *(2014)*

52. A reaction having equal energies of activation for forward and reverse reactions has
(a) $\Delta H = 0$ (b) $\Delta H = \Delta G = \Delta S = 0$
(c) $\Delta S = 0$ (d) $\Delta G = 0$ *(NEET 2013)*

53. In which of the following reactions, standard reaction entropy change ($\Delta S°$) is positive and standard Gibbs energy change ($\Delta G°$) decreases sharply with increasing temperature?
(a) $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$
(b) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$
(c) $Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)}$
(d) $\frac{1}{2}C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow \frac{1}{2}CO_{2(g)}$ *(2012)*

54. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is
(a) 10.52 cal/(mol K) (b) 21.04 cal/(mol K)
(c) 5.260 cal/(mol K) (d) 0.526 cal/(mol K)
(2012)

55. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy change for the process would be

(a) $10\ J\ mol^{-1}\ K^{-1}$ (b) $1.0\ J\ mol^{-1}\ K^{-1}$
(c) $0.1\ J\ mol^{-1}\ K^{-1}$ (d) $100\ J\ mol^{-1}\ K^{-1}$
(2011)

56. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 $J\ K^{-1}\ mol^{-1}$ respectively. For the reaction $1/2X_2 + 3/2Y_2 \rightleftharpoons XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature should be
(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K *(2010)*

57. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 $kJ\ mol^{-1}$ and 108.8 $J\ K^{-1}\ mol^{-1}$, respectively. The temperature when Gibbs' energy change (ΔG) for this transformation will be zero, is
(a) 273.4 K (b) 393.4 K
(c) 373.4 K (d) 293.4 K *(Mains 2010)*

58. The values of ΔH and ΔS for the reaction,
$C_{(graphite)} + CO_{2(g)} \rightarrow 2CO_{(g)}$
are 170 kJ and 170 $J\ K^{-1}$, respectively. This reaction will be spontaneous at
(a) 910 K (b) 1110 K
(c) 510 K (d) 710 K *(2009)*

59. For the gas phase reaction,
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
which of the following conditions are correct?
(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 $\Delta S > 0$
(2008)

60. Identify the correct statement for change of Gibbs' energy for a system (ΔG_{system}) at constant temperature and pressure.
(a) If $\Delta G_{system} < 0$, the process is not spontaneous.
(b) If $\Delta G_{system} > 0$, the process is spontaneous.
(c) If $\Delta G_{system} = 0$, the system has attained equilibrium.
(d) If $\Delta G_{system} = 0$, the system is still moving in a particular direction. *(2006)*

61. The enthalpy and entropy change for the reaction:
$Br_{2(l)} + Cl_{2(g)} \rightarrow 2BrCl_{(g)}$
are 30 $kJ\ mol^{-1}$ and 105 $J\ K^{-1}\ mol^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is
(a) 300 K (b) 285.7 K
(c) 273 K (d) 450 K *(2006)*

62. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
(a) Exothermic and increasing disorder
(b) Exothermic and decreasing disorder
(c) Endothermic and increasing disorder
(d) Endothermic and decreasing disorder *(2005)*

63. A reaction occurs spontaneously if
(a) $T\Delta S < \Delta H$ and both ΔH and ΔS are +ve
(b) $T\Delta S > \Delta H$ and ΔH is +ve and ΔS is –ve
(c) $T\Delta S > \Delta H$ and both ΔH and ΔS are +ve
(d) $T\Delta S = \Delta H$ and both ΔH and ΔS are +ve *(2005)*

64. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are $-382.64\ kJ\ mol^{-1}$ and $-145.6\ J\ mol^{-1}$, respectively. Standard Gibbs' energy change for the same reaction at 298 K is
(a) $-221.1\ kJ\ mol^{-1}$ (b) $-339.3\ kJ\ mol^{-1}$
(c) $-439.3\ kJ\ mol^{-1}$ (d) $-523.2\ kJ\ mol^{-1}$
(2004)

65. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is
(a) $\Delta S_{system} + \Delta S_{surroundings} > 0$
(b) $\Delta S_{system} - \Delta S_{surroundings} > 0$
(c) $\Delta S_{system} > 0$ only
(d) $\Delta S_{surroundings} > 0$ only. *(2004)*

66. What is the entropy change (in $J\ K^{-1}\ mol^{-1}$) when one mole of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 $kJ\ mol^{-1}$ at 0°C.)
(a) 20.13 (b) 2.013
(c) 2.198 (d) 21.98 *(2003)*

67. The densities of graphite and diamond at 298 K are 2.25 and 3.31 $g\ cm^{-3}$, respectively. If the standard free energy difference (ΔG°) is equal to 1895 $J\ mol^{-1}$, the pressure at which graphite will be transformed into diamond at 298 K is
(a) 9.92×10^8 Pa (b) 9.92×10^7 Pa
(c) 9.92×10^6 Pa (d) 9.92×10^5 Pa *(2003)*

68. Unit of entropy is
(a) $J\ K^{-1}\ mol^{-1}$ (b) $J\ mol^{-1}$
(c) $J^{-1}K^{-1}\ mol^{-1}$ (d) $J\ K\ mol^{-1}$ *(2002)*

69. 2 moles of ideal gas at 27°C temperature is expanded reversibly from 2 lit. to 20 lit. Find entropy change. (R = 2 cal/mol K)
(a) 92.1 (b) 0
(c) 4 (d) 9.2 *(2002)*

70. $PbO_2 \rightarrow PbO$; $\Delta G_{298} < 0$
$SnO_2 \rightarrow SnO$; $\Delta G_{298} > 0$
Most probable oxidation state of Pb and Sn will be

(a) Pb^{4+}, Sn^{4+} (b) Pb^{4+}, Sn^{2+}
(c) Pb^{2+}, Sn^{2+} (d) Pb^{2+}, Sn^{4+} *(2001)*

71. Cell reaction is spontaneous when
(a) ΔG° is negative (b) ΔG° is positive
(c) ΔE°_{red} is positive (d) ΔE°_{red} is negative.
(2000)

72. Identify the correct statement regarding entropy.
(a) At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero.
(b) At absolute zero of temperature, the entropy of a perfectly crystalline substance is +ve.
(c) At absolute zero of temperature, entropy of a perfectly crystalline substance is taken to be zero.
(d) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero. *(1998)*

6.7 Gibbs Energy Change and Equilibrium

73. Following reaction occurring in an automobile
$2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$
The sign of ΔH, ΔS and ΔG would be
(a) −, +, + (b) +, +, −
(c) +, −, + (d) −, +, − *(1994)*

ANSWER KEY

1.	(b)	**2.**	(a)	**3.**	(b)	**4.**	(a)	**5.**	(b)	**6.**	(d)	**7.**	(b)	**8.**	(b)	**9.**	(d)	**10.**	(c)
11.	(d)	**12.**	(b)	**13.**	(b)	**14.**	(b)	**15.**	(b)	**16.**	(b)	**17.**	(a)	**18.**	(b)	**19.**	(b)	**20.**	(c)
21.	(b)	**22.**	(d)	**23.**	(b)	**24.**	(a)	**25.**	(b)	**26.**	(d)	**27.**	(c)	**28.**	(a)	**29.**	(a)	**30.**	(a)
31.	(d)	**32.**	(a)	**33.**	(d)	**34.**	(c)	**35.**	(None)			**36.**	(b)	**37.**	(c)	**38.**	(b)	**39.**	(a)
40.	(d)	**41.**	(b)	**42.**	(c)	**43.**	(d)	**44.**	(d)	**45.**	(a)	**46.**	(a)	**47.**	(b)	**48.**	(a,c)	**49.**	(b)
50.	(b)	**51.**	(b)	**52.**	(a)	**53.**	(a)	**54.**	(c)	**55.**	(d)	**56.**	(a)	**57.**	(c)	**58.**	(b)	**59.**	(d)
60.	(c)	**61.**	(b)	**62.**	(a)	**63.**	(c)	**64.**	(b)	**65.**	(a)	**66.**	(d)	**67.**	(a)	**68.**	(a)	**69.**	(d)
70.	(d)	**71.**	(a)	**72.**	(c)	**73.**	(d)												

Hints & Explanations

1. (b) : State functions or state variables are those which depend only on the state of the system and not on how the state was reached.

$$\left.\begin{array}{r} q + w = \Delta E \text{ (internal energy)} \\ H - TS = G \text{ (free energy)} \end{array}\right\} \text{State functions}$$

Path function depends on the path followed during a process. Work and heat are the path functions.

2. (a) : The mathematical form of first law of thermodynamics : $q = \Delta E + W$
Since the system is closed and insulated, $q = 0$
Paddle work is done on system. ∴ $W \neq 0$.
Temperature and hence internal energy of the system increases. ∴ $\Delta E \neq 0$.

3. (b) : This is the mathematical relation of first law of thermodynamics. Here ΔU = change in internal energy; ΔQ = heat absorbed by the system and W = work done by the system.

4. (a) : For free expansion of an ideal gas, $P_{ex} = 0$,
$w = -P_{ex}\Delta V = 0$
For adiabatic process, $q = 0$
According to first law of thermodynamics,
$\Delta U = q + w = 0$
As internal energy of an ideal gas is a function of temperature, $\Delta U = 0$, ∴ $\Delta T = 0$

5. (b) : Expansion of a gas against a constant external pressure is an irreversible process. The work done in an irreversible process
$= -P_{ext}\,\Delta V = -P_{ext}\,(V_2 - V_1) = -2\,(0.25 - 0.1)$
$= -2 \times 0.15$ L bar $= -0.30 \times 100$ J $= -30$ J

6. (d) : For an ideal gas, internal energy is a function of temperature. Final temperature *i.e.*, T_C for adiabatic process is less than its initial temperature *i.e.*, T_A
∴ $T_C < T_A$

7. (b) : $w = -PdV = -P(V_2 - V_1)$
$= -10^5\ \text{N m}^{-2}\,(10^{-2} - 10^{-3})\ \text{m}^3 = -10^5\ \text{N m}^{-2}\,(9 \times 10^{-3})\ \text{m}^3$
$= -9 \times 10^2$ N m $= -900$ J ($\because$ 1 J = 1 N m)

8. (b) : $w = -P_{ext}\Delta V = -2.5(4.50 - 2.50)$
$= -5$ L atm $= -5 \times 101.325$ J $= -506.625$ J
$\Delta U = q + w$
As, the container is insulated, thus $q = 0$
Hence, $\Delta U = w = -506.625$ J

9. (d) : C_P for monoatomic gas mixture of same volume $= \dfrac{5}{2}R,\ C_V = \dfrac{3}{2}R$

$$\therefore\ \frac{C_P}{C_V}=\frac{\frac{5}{2}R}{\frac{3}{2}R}=\frac{5}{3}=1.67$$

10. (c) : For free expansion of an ideal gas under adiabatic condition $q = 0, \Delta T = 0, w = 0$.
For free expansion, $w = 0$, adiabatic process, $q = 0$
$\Delta U = q + w = 0$
Internal energy remain constant means $\Delta T = 0$.

11. (d) : Since the ideal gas expands spontaneously into vacuum, $P_{ext} = 0$, hence work done is also zero.

12. (b) : $\Delta H = \Delta E + \Delta n_g RT$
For $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$
$\Delta n_g = 2 - (1 + 1) = 0$. *i.e.* $\Delta H = \Delta E$

13. (b) : Work $= -P_{ext} \times$ volume change
$= -3 \times (6 - 4) \times 101.32 = 6 \times 101.32$
$= -607.92\ J \approx -608\ J$

14. (b) : $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$
$\Delta n_g = 3 - 6 = -3$
$\Delta H = \Delta E + P\Delta V$ or $\Delta H - \Delta E = P\Delta V$
$\Delta H - \Delta E = \Delta n_g RT = -3RT$

15. (b) : Molar heat capacity $= 75\ J\ K^{-1}\ mol^{-1}$
18 g of water = 1 mole $= 75\ J\ K^{-1}\ mol^{-1}$

$$1\text{ g of water} = \frac{75}{18}\ J\ K^{-1}$$

$$100\text{ g of water}=\frac{75}{18}\times 100\ J\ K^{-1}$$

$$Q = m \cdot C \cdot \Delta T \text{ or } 1000 = 100\times\frac{75}{18}\times\Delta T$$

$$\Rightarrow\ \Delta T=\frac{10\times 18}{75}=2.4\ K$$

16. (b) : $\Delta H = \Delta E + P\Delta V$
When $\Delta V = 0$; $w = 0$.
$\Delta H = \Delta E + 0$ or $\Delta H = \Delta E$
As $\Delta E = q + w$, $\Delta E = q$
In the present problem, $\Delta H = 500$ J,
$\Delta H = \Delta E = 500$ J, $q = 500$ J, $w = 0$

17. (a) : $\Delta H = \Delta E + P\Delta V$
also $PV = nRT$ (ideal gas equation)
or $P\Delta V = \Delta n_g RT$
Δn_g = Change in number of gaseous moles
$\therefore\ \Delta H = \Delta E + \Delta n_g RT \Rightarrow \Delta n_g = 2 - 3 = -1$
$\Rightarrow\ \Delta H = \Delta E - RT$

18. (b) : In endothermic reactions, energy of reactants is less than energy of products. Thus, $E_R < E_P$.
$\Delta H = E_P - E_R = +ve$

19. (b) : Change in internal energy depends upon temperature. At constant temperature, the internal energy of the gas remains constant, so $\Delta E = 0$.

20. (c) : During isothermal expansion of an ideal gas, $\Delta T = 0$, $\Delta E = 0$ $\therefore$ $\Delta H = 0$
$H = E + PV$
$\because\ \Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta(nRT)$
$\therefore\ \Delta H = \Delta E + nR\Delta T = 0 + 0 = 0$
Change in enthalpy is zero, means its enthalpy remains same or unaffected.

21. (b) : $\Delta n_g = 2 - 4 = -2$, $\Delta H = \Delta E - 2RT$

22. (d) : If $n_p < n_r$; $\Delta n_g = n_p - n_r = -ve$.
Hence, $\Delta H < \Delta E$.

23. (b) : According to Hess's law, equation (i) is equal to equations (ii) + (iii) *i.e.*, $x = y + z$

24. (a) : $\Delta_{vap}H^\circ = 40.66\ kJ\ mol^{-1}$
$T = 100 + 273 = 373\ K, \Delta E = ?$
$\Delta H = \Delta E + \Delta n_g RT \Rightarrow \Delta E = \Delta H - \Delta n_g RT$
Δn_g = number of gaseous moles of products − number of gaseous moles of reactants
$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
$\Delta n_g = 1 - 0 = 1$
$\Delta E = \Delta H - RT$
$\Delta E = (40.66 \times 10^3) - (8.314 \times 373)$
$= 37559$ J/mol or 37.56 kJ/mol

25. (b) : Adding all the equations, we get

	ΔH
$A \rightarrow 2B$	300 kJ/mol
$3B \rightarrow 2C + D$	−125 kJ/mol
$2D \rightarrow A + E$	−350 kJ/mol

$B + D \rightarrow E + 2C$; $\Delta H = (300 - 125 - 350)$
$= -175$ kJ/mol

26. (d) : $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$;
$\Delta H = -26.8$ kJ ...(i)
$FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$; $\Delta H = -16.5$ kJ ...(ii)
$Fe_2O_{3(s)} + CO_{(g)} \rightarrow 2FeO_{(s)} + CO_{2(g)}$; $\Delta H = ?$ ..(iii)
Eq. (iii) can be obtained as :
(i) − 2(ii) $= -26.8 - 2(-16.5) = -26.8 + 33.0 = +6.2$ kJ

27. (c) : For (c), $\Delta H^\circ_{reaction}$
$= \Delta H^\circ_f(XeF_4) - [\Delta H^\circ_f(Xe) + 2\Delta H^\circ_f(F_2)]$
Enthalpies of formation of elementary substances Xe and F_2 are taken as zero.
Thus, $\Delta H^\circ_{reaction} = \Delta H^\circ_f(XeF_4)$

28. (a) : (i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H_i = -94$ kcal/mole
(ii) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$; $\Delta H_{ii} = -68 \times 2$ kcal/mole
(iii) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$;
$\Delta H_{iii} = -213$ kcal/mole
(iv) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$; $\Delta H_{iv} = ?$
By applying Hess's law, we can compute ΔH_{iv}.
$\therefore\ \Delta H_{iv} = \Delta H_i + \Delta H_{ii} - \Delta H_{iii}$
$= (-94 - 68 \times 2 + 213)$ kcal $= -17$ kcal

29. (a) : $\Delta H^\circ_f = \Sigma H^\circ_{f\,(\text{products})} - \Sigma H^\circ_{f\,(\text{reactants})}$
For the given reaction,

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

$\Delta H^\circ_f = 2 \times \Delta H^\circ_{f(H_2O)} - 2 \times \Delta H^\circ_{f(H_2O_2)}$

$= 2 \times -286 \text{ kJ mol}^{-1} - 2 \times (-188) \text{ kJ mol}^{-1}$

$= -196 \text{ kJ mol}^{-1}$

30. (a) : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \Delta H_1 = -x$ ...(i)

$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O, \Delta H_2 = -y$ ...(ii)

Subtracting (ii) from (i), we get

$CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH, \Delta H_3 = -\text{ve}$

i.e., $-x - (-y) = -\text{ve}$

$y - x = -\text{ve}$. Hence, $x > y$.

31. (d) : $S + \frac{3}{2}O_2 \rightarrow SO_3 + 2x \text{ kcal}$ ...(i)

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 + y \text{ kcal}$ ....(ii)

By subtracting equation (ii) from (i) we get,

$S + O_2 \rightarrow SO_2 + (2x - y) \text{ kcal}$

The heat of formation of SO_2 is $(2x - y)$ kcal/mole.

32. (a) : $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}; \Delta H^\circ = -x \text{ kJ}$ ...(i)

$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}; \Delta H^\circ = \frac{-y}{2} \text{kJ}$ ...(ii)

By subtracting equation (ii) from (i) we get,

$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)};$

$$\Delta H^\circ = -x - \left(-\frac{y}{2}\right) = \frac{y - 2x}{2} \text{ kJ}$$

33. (d) : $C_2H_4 + 3O_2 \rightarrow 2\,CO_2 + 2H_2O$

$\Delta H^\circ = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}}$

$= 2 \times (-394) + 2 \times (-286) - (52 + 0) = -1412 \text{ kJ/mol}$

34. (c) : Let *B.E.* of X_2, Y_2 and XY are x kJ mol^{-1}, $0.5x$ kJ mol^{-1} and x kJ mol^{-1} respectively.

$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY\,;\, \Delta H = -200 \text{ kJ mol}^{-1}$

$\Delta H = \Sigma(B.E.)_{\text{Reactants}} - \Sigma(B.E.)_{\text{Products}}$

$$\therefore\ -200 = \left[\frac{1}{2} \times (x) + \frac{1}{2} \times (0.5x)\right] - [1 \times (x)]$$

B.E. of $X_2 = x = 800 \text{ kJ mol}^{-1}$

35. (None) : Given :

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}, \Delta H = -393.5 \text{ kJ/mol}$

$\Rightarrow$ Amount of heat released on formation of 44 g CO_2 = 393.5 kJ

$\therefore$ Amount of heat released on formation of

$$35.2 \text{ g of } CO_2 = \frac{393.5}{44} \times 35.2 = 314.8 \approx 315 \text{ kJ}$$

Note : –ve or +ve sign considering the reaction is exothermic or endothermic.

36. (b) : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

No. of moles in gaseous mixture

$$CH_4 + C_3H_8 = \frac{5}{22.4} = 0.22 \text{ moles}$$

No. of moles of $O_2 = \frac{16}{22.4} = 0.71$ moles

Let x moles of CH_4 is there in a gaseous mixture so, number of moles of C_3H_8 would be $0.22 - x$. Then moles of O_2 consumed,

$2x + (0.22 - x)5 = 0.71$ or $x = 0.13$

Total amount of heat liberated

$= 0.13 \times 890 + 0.09 \times 2220 = 315.5 \text{ kJ}$

37. (c) : The dissociation energy of H – H bond is $\frac{869.6}{2} = 434.8 \text{ kJ}$

38. (b) : For the given reaction, enthalpy of reaction can be calculated as

$= \Sigma B.E.(\text{reactants}) - \Sigma B.E.(\text{products})$

$= [B.E._{(C=C)} + B.E._{(H-H)} + 4 \times B.E._{(C-H)}]$
$\quad - [B.E._{(C-C)} + 6 \times B.E._{(C-H)}]$

$= [606.10 + 431.37 + 4 \times 410.50] - [336.49 + 6 \times 410.50]$

$= 2679.47 - 2799.49 = -120.02 \text{ kJ mol}^{-1}$

39. (a) : $H_2 + Cl_2 \rightarrow 2HCl$

$\Delta H_{\text{reaction}} = \Sigma(B.E)_{\text{reactants}} - \Sigma(B.E)_{\text{products}}$

$= [(B.E)_{H-H} + (B.E)_{Cl-Cl}] - [2B.E_{(H-Cl)}]$

$= 434 + 242 - (431) \times 2$

$\Delta H_{\text{reaction}} = -186 \text{ kJ}$

Heat of formation is the amount of heat absorbed or evolved when one mole of substance is directly obtained from its constituent elements.

Hence, enthalpy of formation of HCl $= \frac{-186}{2} = -93 \text{ kJ mol}^{-1}$

40. (d) : The amount of heat absorbed or released when 1 mole of a substance is directly obtained from its constituent elements is called the heat of formation or enthalpy of formation.

Equation (i) represents neutralisation reaction, (iii) represents hydrogenation reaction and (iv) represents combustion reaction.

Thus, enthalpy of formation of $H_2O_{(l)}$ is $-X_2$ kJ mol^{-1}.

41. (b) : $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$

$\Delta H = \Sigma\, B.E._{(\text{reactants})} - \Sigma\, B.E._{(\text{products})}$

$= \frac{1}{2}[B.E._{(H_2)} + B.E._{(Cl_2)}] - B.E._{(HCl)} = -90$

$\frac{1}{2}(430 + 240) - B.E._{(HCl)} = -90$

$B.E._{(HCl)} = \frac{1}{2}(430 + 240) + 90 = 425 \text{ kJ mol}^{-1}$

42. (c) : MgO is the oxide of weak base and we know that heat of neutralisation of 1 eq. of strong acid with strong base is –57.33 kJ/mol.

⇒ With weak base some heat is absorbed in dissociation of weak base.

⇒ Heat of neutralisation of weak base with strong acid will be less than –57.33 kJ/mol.

43. (d) : $H - H + Br - Br \rightarrow 2H - Br$

$$\begin{array}{cc} 433 + 192 & 2 \times 364 \\ = 625 & = 728 \\ \text{Energy absorbed} & \text{Energy released} \end{array}$$

Net energy released = 728 – 625 = 103 kJ

i.e. $\Delta H° = -103$ kJ

44. (d) : In the reaction, $2Cl_{(g)} \longrightarrow Cl_{2(g)}$, the randomness decreases as 2 moles of $Cl_{(g)}$ are converted to 1 mole of $Cl_{2(g)}$, thus, $\Delta_r S < 0$.

And this is an exothermic reaction, thus, $\Delta_r H < 0$.

45. (a) : If $\Delta n_g < 0$ then $\Delta S < 0$

46. (a) : For a spontaneous reaction,

$\Delta G < 0$ *i.e.*, $\Delta H - T\Delta S < 0$

$$T > \frac{\Delta H}{\Delta S}$$

$$T > \left(\frac{35.5 \times 1000}{83.6} = 424.6\right) \approx 425 \text{ K}$$

$\therefore \quad T > 425$ K

47. (b) : For an ideal gas undergoing reversible expansion, when temperature changes from T_i to T_f and pressure changes from p_i to p_f,

$$\Delta S = nC_p \ln \frac{T_f}{T_i} + nR \ln \frac{p_i}{p_f}$$

For an isothermal process, $T_i = T_f$ so, ln 1 = 0

$$\therefore \quad \Delta S = nR \ln \frac{p_i}{p_f}$$

48. (a, c) : $\Delta G = \Delta H - T\Delta S$

If $\Delta H < 0$ and $\Delta S > 0$

$\Delta G = (-\text{ve}) - T(+\text{ve})$

then at all temperatures, $\Delta G = -$ve, spontaneous reaction.

If $\Delta H < 0$ and $\Delta S = 0$

$\Delta G = (-\text{ve}) - T(0) = -$ve at all temperatures.

49. (b) : This is Clausius—Clapeyron equation.

50. (b) : Using Gibbs'-Helmholtz equation,

$\Delta G = \Delta H - T\Delta S$

During adsorption of a gas, entropy decreases *i.e.* $\Delta S < 0$

For spontaneous adsorption, ΔG should be negative, which is possible when ΔH is highly negative.

51. (b) : $\Delta H = \Delta U + \Delta n_g RT$

Given, $\Delta U = 2.1$ kcal, $\Delta n_g = 2$,

$R = 2 \times 10^{-3}$ kcal, $T = 300$ K

$\therefore \quad \Delta H = 2.1 + 2 \times 2 \times 10^{-3} \times 300 = 3.3$ kcal

Again, $\Delta G = \Delta H - T\Delta S$

Given, $\Delta S = 20 \times 10^{-3}$ kcal K^{-1}

On putting the values of ΔH and ΔS in the equation, we get $\Delta G = 3.3 - 300 \times 20 \times 10^{-3}$

$= 3.3 - 6 \times 10^3 \times 10^{-3} = -2.7$ kcal

52. (a) : $\Delta H = (E_a)_f - (E_a)_b = 0$

53. (a) : $C_{(\text{graphite})} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$

$$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$$

As amount of gaseous substance is increasing in the product side thus, ΔS is positive for this reaction.

And we know that $\Delta G = \Delta H - T\Delta S$

As ΔS is positive, thus increase in temperature will make the term $(-T\Delta S)$ more negative and ΔG will decrease.

54. (c) : $\Delta H_{fus} = 1.435$ kcal/mol

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}} = \frac{1.435 \times 10^3}{273} = 5.26 \text{ cal/(mol K)}$$

55. (d) : We know that $\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$ [$\because$ $\Delta G = 0$ as transition of $H_2O_{(l)} \rightleftharpoons H_2O_{(v)}$ is at equilibrium]

$$\Delta S = \frac{\Delta H}{T} = \frac{30 \times 10^3}{300} = 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

56. (a) : Given reaction is :

$$\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightleftharpoons XY_3$$

We know, $\Delta S° = \Sigma S°_{\text{products}} - \Sigma S°_{\text{reactants}}$

$$= 50 - \left(\frac{1}{2}(60) + \frac{3}{2}(40)\right)$$

$= 50 - (30 + 60) = -40$ J K^{-1} mol^{-1}

At equilibrium $\Delta G° = 0$

$\Delta H° = T\Delta S°$

$$\therefore \quad T = \frac{\Delta H°}{\Delta S°} = \frac{-30 \times 10^3 \text{ J mol}^{-1}}{-40 \text{ J K}^{-1} \text{ mol}^{-1}} = 750 \text{ K}$$

57. (c) : According to Gibbs equation,

$\Delta G = \Delta H - T\Delta S$

when $\Delta G = 0$, $\Delta H = T\Delta S$

Given, $\Delta H = 40.63$ kJ mol^{-1} = 40.63×10^3 J mol^{-1}

$\Delta S = 108.8$ J K^{-1} mol^{-1}

$$\therefore \quad T = \frac{\Delta H}{\Delta S} = \frac{40.63 \times 10^3}{108.8} = 373.43 \text{ K}$$

58. (b) : For the reaction to be spontaneous, $\Delta G = -$ve.

Given : $\Delta H = 170$ kJ = 170×10^3 J, $\Delta S = 170$ J K^{-1}

Applying, $\Delta G = \Delta H - T\Delta S$, the value of $\Delta G = -$ve only when $T\Delta S > \Delta H$, which is possible only when $T = 1110$ K.

$\therefore\quad \Delta G = 170 \times 10^3 - (1110 \times 170) = -18700$ J

Thus, reaction is spontaneous at $T = 1110$ K.

59. (d) : Gas phase reaction,

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

$$\Delta H = \Delta E + \Delta n_g RT$$

Δn_g = Change in number of moles of products and reactants species.

Since Δn_g = +ve, hence ΔH = +ve

also one mole of PCl_5 is dissociated into two moles of PCl_3 and Cl_2 in the same phase.

Therefore, $\Delta S = S_{\text{products}} - S_{\text{reactants}}$

ΔS = +ve.

60. (c) : The criteria for spontaneity of a process in terms of ΔG is as follows :

- If ΔG is negative, the process is spontaneous.
- If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.
- If ΔG is zero, the system is in equilibrium.

61. (b) : $Br_{2(l)} + Cl_{2(g)} \rightarrow 2BrCl_{(g)}$

$\Delta H = 30$ kJ mol^{-1}, $\Delta S = 105$ J K^{-1} mol^{-1}

$$\Delta S = \frac{\Delta H}{T} \quad i.e. \quad 105 = \frac{30}{T} \times 1000$$

$$\therefore\ T = \frac{30 \times 1000}{105} = 285.7\ \text{K}$$

62. (a) : For spontaneous reaction, ΔH = –ve, ΔS = +ve. Spontaneity depends upon both critical minimum energy and maximum randomness disorderness.

63. (c) : $\Delta G = \Delta H - T\Delta S$

ΔG = –ve for spontaneous reaction.

When ΔS = +ve, ΔH = +ve and $T\Delta S > \Delta H \Rightarrow \Delta G$ = –ve

64. (b) : $\Delta G = \Delta H - T\Delta S$

$$= -382.64 - 298\left(\frac{-145.6}{1000}\right)$$

$= -382.64 + 43.38 = -339.3$ kJ mol^{-1}

65. (a) : For spontaneous process, $\Delta S_{\text{total}} > 0$.

$\therefore\quad \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

66. (d) : $S = \dfrac{q_{rev}}{T} = \dfrac{6000}{273} = 21.978\ \text{J K}^{-1}\text{mol}^{-1}$

67. (a) : $\Delta G^\circ = -P\Delta V$ = Work done

$$\Delta V = \left(\frac{12}{3.31} - \frac{12}{2.25}\right) \times 10^{-3}\ \text{L} = -1.71 \times 10^{-3}\ \text{L}$$

ΔG° = Work done = $-(-1.71 \times 10^{-3}) \times P \times 101.3$ J

$$P = \frac{1895}{1.71 \times 10^{-3} \times 101.3} = 10.93 \times 10^3\ \text{atm}$$

$= 11.08 \times 10^8$ Pa $\approx 9.92 \times 10^8$ Pa $\quad (\because$ 1 atm = 101325 Pa)

68. (a) : Entropy change (ΔS) is given by $\Delta S = \dfrac{q_{rev}}{T}$

$\therefore\quad$ Unit of entropy = J K^{-1}mol^{-1}

69. (d) : The change of entropy $dS = \dfrac{q_{rev}}{T}$

From the first law of thermodynamics,

$dq = dU + PdV = C_V dT + PdV$

$$\Rightarrow \frac{dq}{T} = C_V \frac{dT}{T} + \frac{P}{T} dV$$

$$\Rightarrow \frac{dq}{T} = C_V \frac{dT}{T} + \frac{RdV}{V} \quad \left[\text{For 1 mole of a gas, } \frac{P}{T} = \frac{R}{V}\right]$$

$$\therefore\ dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

$$\Rightarrow \Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \quad \text{[for one mole of ideal gas]}$$

Here $T_2 = T_1 = 27°\text{C} = 300$ K $\therefore\ \ln\dfrac{T_2}{T_1} = 0$

$$\therefore\quad \Delta S = R\ln\frac{V_2}{V_1} = 2\ln\frac{20}{2} = 2\ln 10 = 4.605$$

$\therefore\quad \Delta S = 4.605$ cal/mol K

Entropy change for 2 moles of gas

$= 2 \times 4.605$ cal/K $= 9.2$ cal/K

70. (d) : The sign and magnitude of Gibbs free energy is a criterion of spontaneity for a process.

When $\Delta G > 0$ or +ve, it means $G_{\text{products}} > G_{\text{reactants}}$

as $\quad \Delta G = G_{\text{products}} - G_{\text{reactants}}$

the reaction will not take place spontaneously, *i.e.* the reaction should be spontaneous in reverse direction.

$$\underset{\text{(more favourable)}}{\overset{+4}{Sn}O_2} \rightarrow \overset{+2}{Sn}O;\quad \Delta G > 0$$

$\Delta G < 0$ or –ve, the reaction or change occurs spontaneously.

$$\overset{+4}{Pb}O_2 \rightarrow \underset{\text{(more favourable)}}{\overset{+2}{Pb}O};\quad \Delta G < 0$$

71. (a) : For a cell reaction to be spontaneous, ΔG° should be negative. As $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, so the value will be –ve only when E°_{cell} is +ve.

72. (c) : The entropy of a substance increases with increase in temperature. However at absolute zero the entropy of a perfectly crystalline substance is taken as zero, which is also called as third law of thermodynamics.

73. (d) : (i) The given reaction is a combustion reaction, therefore ΔH is less than 0. Hence, ΔH is negative.

(ii) Since there is increase in the number of moles of gaseous products, therefore ΔS is positive.

(iii) Since reaction is spontaneous, therefore ΔG is negative.

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CHAPTER
7

Equilibrium

7.1 Equilibrium in Physical Processes

1. In liquid-gas equilibrium, the pressure of vapours above the liquid is constant at
(a) constant temperature
(b) low temperature
(c) high temperature
(d) none of these. *(1995)*

7.3 Law of Chemical Equilibrium and Equilibrium Constant

2. The equilibrium constants of the following are

$N_2 + 3H_2 \rightleftharpoons 2NH_3; K_1$

$N_2 + O_2 \rightleftharpoons 2NO; K_2$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O; K_3$

The equilibrium constant (K) of the reaction :

$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$ will be

(a) $K_2K_3^3/K_1$
(b) K_2K_3/K_1
(c) $K_2^3K_3/K_1$
(d) $K_1K_3^3/K_2$
(NEET 2017, 2007, 2003)

3. If the equilibrium constant for

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ is K, the equilibrium constant for $\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{(g)}$ will be

(a) $\frac{1}{2}K$
(b) K
(c) K^2
(d) $K^{1/2}$ *(2015)*

4. Given that the equilibrium constant for the reaction,

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

has a value of 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature?

$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$

(b) 1.8×10^{-3}
(b) 3.6×10^{-3}
(c) 6.0×10^{-2}
(d) 1.3×10^{-5}
(Mains 2012)

5. Given the reaction between 2 gases represented by A_2 and B_2 to give the compound $AB_{(g)}$.

$A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$

At equilibrium, the concentration of
$A_2 = 3.0 \times 10^{-3}$ M, of $B_2 = 4.2 \times 10^{-3}$ M, of
$AB = 2.8 \times 10^{-3}$ M
If the reaction takes place in a sealed vessel at 527°C, then the value of K_c will be
(a) 2.0 (b) 1.9 (c) 0.62 (d) 4.5
(Mains 2012)

6. For the reaction, $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, the equilibrium constant is K_1. The equilibrium constant is K_2 for the reaction,

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

What is K for the reaction,

$NO_{2(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + O_{2(g)}$?

(a) $\frac{1}{2K_1K_2}$
(b) $\frac{1}{4K_1K_2}$
(c) $\left[\frac{1}{K_1K_2}\right]^{1/2}$
(d) $\frac{1}{K_1K_2}$ *(2011)*

7. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium,
$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ would be
(a) 3.0×10^{-5}
(b) 3.0×10^{-4}
(c) 3.0×10^{4}
(d) 3.0×10^{5} *(2009)*

8. The value of equilibrium constant of the reaction,

$HI_{(g)} \rightleftharpoons \frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)}$

is 8.0. The equilibrium constant of the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ will be

(a) 16 (b) 1/8
(c) 1/16 (d) 1/64 *(2008)*

9. Equilibrium constants K_1 and K_2 for the following equilibria :

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \xrightleftharpoons{K_1} NO_{2(g)} \text{ and}$$

$$2NO_{2(g)} \xrightleftharpoons{K_2} 2NO_{(g)} + O_{2(g)}$$

are related as

(a) $K_2 = 1/K_1^2$ (b) $K_2 = K_1^2$
(c) $K_2 = 1/K_1$ (d) $K_2 = K_1/2$ *(2005)*

10. If K_1 and K_2 are the respective equilibrium constants for the two reactions,

$XeF_{6(g)} + H_2O_{(g)} \rightarrow XeOF_{4(g)} + 2HF_{(g)}$
$XeO_{4(g)} + XeF_{6(g)} \rightarrow XeOF_{4(g)} + XeO_3F_{2(g)}$,
the equilibrium constant of the reaction,
$XeO_{4(g)} + 2HF_{(g)} \rightarrow XeO_3F_{2(g)} + H_2O_{(g)}$,
will be

(a) K_1/K_2 (b) $K_1 \cdot K_2$
(c) $K_1/(K_2)^2$ (d) K_2/K_1 *(1998)*

11. The equilibrium constant for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is K, then the equilibrium constant for the equilibrium $2NH_3 \rightleftharpoons N_2 + 3H_2$ is

(a) $\sqrt{K}$ (b) $\sqrt{\frac{1}{K}}$ (c) $\frac{1}{K}$ (d) $\frac{1}{K^2}$
(1996)

12. K_1 and K_2 are equilibrium constants for reactions (i) and (ii) respectively.

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ ....(i)

$NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$ ...(ii)

(a) $K_1 = \left(\frac{1}{K_2}\right)^2$ (b) $K_1 = K_2{}^2$

(c) $K_1 = \frac{1}{K_2}$ (d) $K_1 = (K_2)^0$ *(1989)*

7.4 Homogeneous Equilibrium

13. The reaction, $2A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$ is begun with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression

(a) $[(0.75)^3(0.25)] \div [(1.00)^2(1.00)]$
(b) $[(0.75)^3(0.25)] \div [(0.50)^2(0.75)]$
(c) $[(0.75)^3(0.25)] \div [(0.50)^2(0.25)]$
(d) $[(0.75)^3(0.25)] \div [(0.75)^2(0.25)]$ *(Mains 2010)*

14. The dissociation equilibrium of a gas AB_2 can be represented as :

$2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$

The degree of dissociation is x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is

(a) $(2K_p/P)^{1/2}$ (b) (K_p/P)
(c) $(2K_p/P)$ (d) $(2K_p/P)^{1/3}$ *(2008)*

15. The values of K_{p_1} and K_{p_2} for the reactions,

$X \rightleftharpoons Y + Z$ ...(i)
$A \rightleftharpoons 2B$ ...(ii)

are in the ratio 9 : 1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (i) and (ii) are in the ratio

(a) 36 : 1 (b) 1 : 1
(c) 3 : 1 (d) 1 : 9 *(2008)*

7.5 Heterogeneous Equilibrium

16. A 20 litre container at 400 K contains $CO_{2(g)}$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be

(Given that : $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}$, $K_p = 1.6$ atm)

(a) 10 litre (b) 4 litre
(c) 2 litre (d) 5 litre *(NEET 2017)*

17. In which of the following equilibrium K_c and K_p are not equal?

(a) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
(b) $SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$
(c) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
(d) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$ *(2010)*

18. If the concentration of OH^- ions in the reaction

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$

is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by

(a) 64 times (b) 4 times
(c) 8 times (d) 16 times. *(2008)*

19. Equilibrium constant K_p for following reaction

$MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$

(a) $K_p = p_{CO_2}$

(b) $K_p = p_{CO_2} \times \frac{p_{CO_2} \times p_{MgO}}{p_{MgCO_3}}$

(c) $K_p = \frac{p_{CO_2} + p_{MgO}}{p_{MgCO_3}}$ (d) $K_p = \frac{p_{MgCO_3}}{p_{CO_2} \times p_{MgO}}$

(2000)

7.6 Applications of Equilibrium Constant

20. If the value of equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain

(a) mostly products
(b) similar amounts of reactants and products
(c) all reactants
(d) mostly reactants. *(2015, Cancelled)*

21. In Haber process, 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end?

(a) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen
(b) 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
(c) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen
(d) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen *(2003)*

22. The reaction quotient (Q) for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is given by $Q = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed from right to left if

(a) $Q = K_c$ (b) $Q < K_c$
(c) $Q > K_c$ (d) $Q = 0$

where K_c is the equilibrium constant. *(2003)*

7.7 Relationship Between *K*, *Q*, and *G*

23. Hydrolysis of sucrose is given by the following reaction : Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose
If the equilibrium constant (K_C) is 2×10^{13} at 300 K, the value of $\Delta_rG°$ at the same temperature will be

(a) $-8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K} \times \ln(2 \times 10^{13})$
(b) $8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K} \times \ln(2 \times 10^{13})$
(c) $8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K} \times \ln(3 \times 10^{13})$
(d) $-8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K} \times \ln(4 \times 10^{13})$ *(NEET 2020)*

24. Which of the following statements is correct for a reversible process in a state of equilibrium?

(a) $\Delta G° = -2.30\ RT \log K$ (b) $\Delta G° = 2.30\ RT \log K$
(c) $\Delta G = -2.30\ RT \log K$ (d) $\Delta G = 2.30\ RT \log K$ *(2015, Cancelled)*

25. Match List I (Equations) with List II (Type of processes) and select the correct option.

List I (Equations)	List II (Type of processes)
A. $K_p > Q$	(i) Non- spontaneous
B. $\Delta G° < RT \ln Q$	(ii) Equilibrium
C. $K_p = Q$	(iii) Spontaneous and endothermic
D. $T > \dfrac{\Delta H}{\Delta S}$	(iv) Spontaneous

(a) A - (i), B - (ii), C - (iii), D - (iv)
(b) A - (iii), B - (iv), C - (ii), D - (i)
(c) A - (iv), B - (i), C - (ii), D - (iii)
(d) A - (ii), B - (i), C - (iv), D - (iii) *(Mains 2010)*

7.8 Factors Affecting Equilibrium

26. Which one of the following conditions will favour maximum formation of the product in the reaction
$A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}, \Delta_rH = -X$ kJ ?

(a) Low temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and high pressure
(d) High temperature and low pressure *(NEET 2018)*

27. For the reversible reaction,
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ + heat
The equilibrium shifts in forward direction

(a) by increasing the concentration of $NH_{3(g)}$
(b) by decreasing the pressure
(c) by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$
(d) by increasing pressure and decreasing temperature. *(2014)*

28. For a given exothermic reaction, K_p and K'_p are the equilibrium constants at temperatures T_1 and T_2, respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2, it is readily observed that

(a) $K_p > K'_p$ (b) $K_p < K'_p$
(c) $K_p = K'_p$ (d) $K_p = \dfrac{1}{K'_p}$ *(2014)*

29. $KMnO_4$ can be prepared from K_2MnO_4 as per the reaction,
$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$
The reaction can go to completion by removing OH^- ions by adding

(a) CO_2 (b) SO_2
(c) HCl (d) KOH *(NEET 2013)*

30. The value of ΔH for the reaction
$X_{2(g)} + 4Y_{2(g)} \rightleftharpoons 2XY_{4(g)}$ is less than zero.

Formation of $XY_{4(g)}$ will be favoured at
(a) high temperature and high pressure
(b) low pressure and low temperature
(c) high temperature and low pressure
(d) high pressure and low temperature. *(2011)*

31. For the reaction :
$CH_{4(g)} + 2O_{2(g)} \rightleftharpoons CO_{2(g)} + 2H_2O_{(l)}$,
$\Delta H_r = -170.8$ kJ mol^{-1}. Which of the following statements is not true?
(a) The reaction is exothermic.
(b) At equilibrium, the concentrations of $CO_{2(g)}$ and $H_2O_{(l)}$ are not equal.
(c) The equilibrium constant for the reaction is given by $K_p = \frac{[CO_2]}{[CH_4][O_2]}$.
(d) Addition of $CH_{4(g)}$ or $O_{2(g)}$ at equilibrium will cause a shift to the right. *(2006)*

32. Reaction $BaO_{2(s)} \rightleftharpoons BaO_{(s)} + O_{2(g)}$; $\Delta H = +$ve. In equilibrium condition, pressure of O_2 depends on
(a) increase mass of BaO_2
(b) increase mass of BaO
(c) increase temperature on equilibrium
(d) increase mass of BaO_2 and BaO both. *(2002)*

33. For any reversible reaction, if we increase concentration of the reactants, then effect on equilibrium constant
(a) depends on amount of concentration
(b) unchange
(c) decrease
(d) increase. *(2000)*

34. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the
(a) temperature to increase
(b) temperature to decrease
(c) amount of liquid to decrease
(d) amount of solid to decrease. *(1993)*

35. Which one of the following information can be obtained on the basis of Le Chatelier principle?
(a) Dissociation constant of a weak acid
(b) Entropy change in a reaction
(c) Equilibrium constant of a chemical reaction
(d) Shift in equilibrium position on changing value of a constraint *(1992)*

7.9 Ionic Equilibrium in Solution

36. Aqueous solution of which of the following compounds is the best conductor of electric current?
(a) Hydrochloric acid, HCl
(b) Ammonia, NH_3
(c) Fructose, $C_6H_{12}O_6$
(d) Acetic acid, $C_2H_4O_2$ *(2015)*

37. Aqueous solution of acetic acid contains
(a) CH_3COO^- and H^+
(b) CH_3COO^-, H_3O^+ and CH_3COOH
(c) CH_3COO^-, H_3O^+ and H^+
(d) CH_3COOH, CH_3COO^- and H^+ *(1991)*

7.10 Acids, Bases and Salts

38. Conjugate base for Bronsted acids H_2O and HF are
(a) H_3O^+ and H_2F^+, respectively
(b) OH^- and H_2F^+, respectively
(c) H_3O^+ and F^-, respectively
(d) OH^- and F^-, respectively. *(NEET 2019)*

39. Which of the following cannot act both as Bronsted acid and as Bronsted base ?
(a) HCO_3^- (b) NH_3
(c) HCl (d) HSO_4^-
(Odisha NEET 2019)

40. Which of the following fluoro-compounds is most likely to behave as a Lewis base?
(a) BF_3 (b) PF_3 (c) CF_4 (d) SiF_4
(NEET-II 2016)

41. Which of these is least likely to act as a Lewis base?
(a) BF_3 (b) PF_3 (c) CO (d) F^-
(NEET 2013)

42. Which is the strongest acid in the following?
(a) $HClO_4$ (b) H_2SO_3
(c) H_2SO_4 (d) $HClO_3$ *(NEET 2013)*

43. Which one of the following molecular hydrides acts as a Lewis acid?
(a) NH_3 (b) H_2O
(c) B_2H_6 (d) CH_4 *(2010)*

44. Which of the following molecules acts as a Lewis acid?
(a) $(CH_3)_2O$ (b) $(CH_3)_3P$
(c) $(CH_3)_3N$ (d) $(CH_3)_3B$ *(2009)*

45. Which one of the following statements is not true?
(a) Among halide ions, iodide is the most powerful reducing agent.
(b) Fluorine is the only halogen that does not show a variable oxidation state.
(c) HOCl is a stronger acid than HOBr.
(d) HF is a stronger acid than HCl. *(2003)*

46. Which one of the following compounds is not a protonic acid?

(a) $B(OH)_3$ (b) $PO(OH)_3$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$ *(2003)*

47. In HS^-, I^-, $R - NH_2$, NH_3 order of proton accepting tendency will be
(a) $I^- > NH_3 > R - NH_2 > HS^-$
(b) $NH_3 > R - NH_2 > HS^- > I^-$
(c) $R - NH_2 > NH_3 > HS^- > I^-$
(d) $HS^- > R - NH_2 > NH_3 > I^-$ *(2001)*

48. Conjugate acid of NH_2^- is
(a) NH_4OH (b) NH_4^+
(c) NH_2^- (d) NH_3 *(2000)*

49. Which compound is electron deficient?
(a) $BeCl_2$ (b) BCl_3
(c) CCl_4 (d) PCl_5 *(2000)*

50. The strongest conjugate base is
(a) SO_4^{2-} (b) Cl^-
(c) NO_3^- (d) CH_3COO^- *(1999)*

51. Which of the following is not a Lewis acid?
(a) SiF_4 (b) C_2H_4
(c) BF_3 (d) $FeCl_3$ *(1996)*

52. Repeated use of which one of the following fertilizers would increase the acidity of the soil?
(a) Ammonium sulphate
(b) Superphosphate of lime
(c) Urea
(d) Potassium nitrate *(1998)*

7.11 Ionization of Acids and Bases

53. Find out the solubility of $Ni(OH)_2$ in 0.1 M NaOH. Given that the ionic product of $Ni(OH)_2$ is 2×10^{-15}.
(a) 2×10^{-13} M (b) 2×10^{-8} M
(c) 1×10^{-13} M (d) 1×10^{8} M
(NEET 2020)

54. The pH of 0.01 M $NaOH_{(aq)}$ solution will be
(a) 7.01 (b) 2 (c) 12 (d) 9
(Odisha NEET 2019)

55. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations :

A. $60\text{ mL }\frac{M}{10}\text{ HCl} + 40\text{ mL }\frac{M}{10}\text{ NaOH}$

B. $55\text{ mL }\frac{M}{10}\text{ HCl} + 45\text{ mL }\frac{M}{10}\text{ NaOH}$

C. $75\text{ mL }\frac{M}{5}\text{ HCl} + 25\text{ mL }\frac{M}{5}\text{ NaOH}$

D. $100\text{ mL }\frac{M}{10}\text{ HCl} + 100\text{ mL }\frac{M}{10}\text{ NaOH}$

pH of which one of them will be equal to 1?
(a) *B* (b) *A* (c) *D* (d) *C*
(NEET 2018)

56. The percentage of pyridine (C_5H_5N) that forms pyridinium ion ($C_5H_5\overset{+}{N}H$) in a 0.10 M aqueous pyridine solution (K_b for $C_5H_5N = 1.7 \times 10^{-9}$) is
(a) 0.0060% (b) 0.013%
(c) 0.77% (d) 1.6% *(NEET-II 2016)*

57. What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed?
(a) 2.0 (b) 7.0
(c) 1.04 (d) 12.65 *(2015)*

58. Which of the following salts will give highest pH in water?
(a) KCl (b) NaCl
(c) Na_2CO_3 (d) $CuSO_4$ *(2014)*

59. Accumulation of lactic acid ($HC_3H_5O_3$), a monobasic acid in tissues leads to pain and a feeling of fatigue. In a 0.10 M aqueous solution, lactic acid is 3.7% dissociated. The value of dissociation constant, K_a, for this acid will be
(a) 1.4×10^{-5} (b) 1.4×10^{-4}
(c) 3.7×10^{-4} (d) 2.8×10^{-4}
(Karnataka NEET 2013)

60. At 100°C the K_w of water is 55 times its value at 25°C. What will be the pH of neutral solution? (log 55 = 1.74)
(a) 7.00 (b) 7.87 (c) 5.13 (d) 6.13
(Karnataka NEET 2013)

61. Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value?
(a) $BaCl_2$ (b) $AlCl_3$
(c) LiCl (d) $BeCl_2$ *(2012)*

62. What is $[H^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH? (K_a for $CH_3COOH = 1.8 \times 10^{-5}$)
(a) 3.5×10^{-4} (b) 1.1×10^{-5}
(c) 1.8×10^{-5} (d) 9.0×10^{-6} *(2010)*

63. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is
(a) 6.50×10^{-12} (b) 5.65×10^{-13}
(c) 5.65×10^{-12} (d) 5.65×10^{-10} *(2009)*

64. What is the $[OH^-]$ in the final solution prepared by mixing 20.0 mL of 0.050 M HCl with 30.0 mL of 0.10 M $Ba(OH)_2$?
(a) 0.40 M (b) 0.0050 M
(c) 0.12 M (d) 0.10 M *(2009)*

65. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

(a) 3.7×10^{-3} M (b) 1.11×10^{-3} M
(c) 1.11×10^{-4} M (d) 3.7×10^{-4} M *(2008)*

66. A weak acid, HA, has a K_a of 1.00×10^{-5}. If 0.100 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to

(a) 1.00% (b) 99.9%
(c) 0.100% (d) 99.0% *(2007)*

67. Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, *i.e.* H_3O^+.

(a) 4.000 (b) 9.000
(c) 1.000 (d) 7.000 *(2007)*

68. The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is

(a) 1.0×10^{-8} M (b) 1.0×10^{-6} M
(c) 1.0525×10^{-7} M (d) 9.525×10^{-8} M *(2006)*

69. At 25°C, the dissociation constant of a base, *B*OH, is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be

(a) 1.0×10^{-5} mol L^{-1} (b) 1.0×10^{-6} mol L^{-1}
(c) 2.0×10^{-6} mol L^{-1} (d) 1.0×10^{-7} mol L^{-1} *(2005)*

70. Which has highest pH?

(a) CH_3COOK (b) Na_2CO_3
(c) NH_4Cl (d) $NaNO_3$ *(2002)*

71. Ionisation constant of CH_3COOH is 1.7×10^{-5} and concentration of H^+ ions is 3.4×10^{-4}. Then find out initial concentration of CH_3COOH molecules.

(a) 3.4×10^{-4} (b) 3.4×10^{-3}
(c) 6.8×10^{-4} (d) 6.8×10^{-3} *(2001)*

72. Correct relation between dissociation constants of a dibasic acid is

(a) $K_{a_1} = K_{a_2}$ (b) $K_{a_1} > K_{a_2}$
(c) $K_{a_1} < K_{a_2}$ (d) $K_{a_1} = \frac{1}{K_{a_2}}$ *(2000)*

73. Which statement is wrong about pH and H^+?

(a) pH of neutral water is not zero.
(b) Adding 1 N solution of CH_3COOH and 1 N solution of NaOH, pH will be seven.
(c) $[H^+]$ of dilute and hot H_2SO_4 is more than concentrated and cold H_2SO_4.
(d) Mixing solution of CH_3COOH and HCl, pH will be less than 7. *(2000)*

74. The concentration of $[H^+]$ and concentration of $[OH^-]$ of a 0.1 aqueous solution of 2% ionised weak acid is [ionic product of water = 1×10^{-14}]

(a) 2×10^{-3} M and 5×10^{-12} M
(b) 1×10^{-3} M and 3×10^{-11} M
(c) 0.02×10^{-3} M and 5×10^{-11} M
(d) 3×10^{-2} M and 4×10^{-13} M *(1999)*

75. The hydride ion H^- is stronger base than its hydroxide ion OH^-. Which of the following reaction will occur if sodium hydride (NaH) is dissolved in water?

(a) $H^- + H_2O \rightarrow$ no reaction
(b) $H^-_{(aq)} + H_2O \rightarrow H_2O$
(c) $H^-_{(aq)} + H_2O_{(l)} \rightarrow OH^- + H_2$
(d) None of these. *(1997)*

76. The ionic product of water at 25°C is 10^{-14}. Its ionic product at 90°C will be,

(a) 1×10^{-14} (b) 1×10^{-16}
(c) 1×10^{-20} (d) 1×10^{-12} *(1996)*

77. If α is dissociation constant, then the total number of moles for the reaction, $2HI \rightarrow H_2 + I_2$ will be

(a) 1 (b) $1 - \alpha$
(c) 2 (d) $2 - \alpha$ *(1996)*

78. The pH value of N/10 NaOH solution is

(a) 12 (b) 13 (c) 10 (d) 11 *(1996)*

79. The pH value of a 10 M solution of HCl is

(a) equal to 1 (b) equal to 2
(c) less than 0 (d) equal to 0 *(1995)*

80. At 80°C, distilled water has $[H_3O^+]$ concentration equal to 1×10^{-6} mole/litre. The value of K_w at this temperature will be

(a) 1×10^{-12} (b) 1×10^{-15}
(c) 1×10^{-6} (d) 1×10^{-9} *(1994)*

81. 0.1 M solution of which one of these substances will act basic?

(a) Sodium borate (b) Ammonium chloride
(c) Calcium nitrate (d) Sodium sulphate *(1992)*

82. The compound whose water solution has the highest pH is

(a) NaCl (b) $NaHCO_3$
(c) Na_2CO_3 (d) NH_4Cl *(1988)*

7.12 Buffer Solutions

83. Which will make basic buffer?

(a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
(b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
(c) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
(d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH *(NEET 2019)*

84. Which one of the following pairs of solutions is not an acidic buffer?
(a) CH_3COOH and CH_3COONa
(b) H_2CO_3 and Na_2CO_3
(c) H_3PO_4 and Na_3PO_4
(d) $HClO_4$ and $NaClO_4$ *(2015)*

85. The dissociation constant of a weak acid is 1×10^{-4}. In order to prepare a buffer solution with a pH = 5, the [Salt]/[Acid] ratio should be
(a) 4 : 5 (b) 10 : 1 (c) 5 : 4 (d) 1 : 10
(Karnataka NEET 2013)

86. Buffer solutions have constant acidity and alkalinity because
(a) these give unionised acid or base on reaction with added acid or alkali
(b) acids and alkalies in these solutions are shielded from attack by other ions
(c) they have large excess of H^+ or OH^- ions
(d) they have fixed value of pH. *(2012)*

87. A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5}, what is the pH of this solution? (log 2.7 = 0.43)
(a) 9.08 (b) 9.43
(c) 11.72 (d) 8.73 *(2011)*

88. In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is
(a) 10 (b) 7 (c) 6 (d) 4 *(2010)*

89. Which of the following pairs constitutes a buffer?
(a) HCl and KCl (b) HNO_2 and $NaNO_2$
(c) NaOH and NaCl (d) HNO_3 and NH_4NO_3
(2006)

90. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression

(a) $\log\frac{[In^-]}{[HIn]} = pK_{In} - pH$

(b) $\log\frac{[HIn]}{[In^-]} = pK_{In} - pH$

(c) $\log\frac{[HIn]}{[In^-]} = pH - pK_{In}$

(d) $\log\frac{[In^-]}{[HIn]} = pH - pK_{In}$ *(2004)*

91. Solution of 0.1 N NH_4OH and 0.1 N NH_4Cl has pH 9.25. Then find out pK_b of NH_4OH.
(a) 9.25 (b) 4.75
(c) 3.75 (d) 8.25 *(2002)*

92. A physician wishes to prepare a buffer solution at pH = 3.85 that efficiently resists changes in pH yet contains only small concentration of the buffering agents. Which of the following weak acids together with its sodium salt would be best to use?
(a) 2, 5-Dihydroxybenzoic acid ($pK_a = 2.97$)
(b) Acetoacetic acid ($pK_a = 3.58$)
(c) *m*-Chlorobenzoic acid ($pK_a = 3.98$)
(d) *p*-Chlorocinnamic acid ($pK_a = 4.41$) *(1997)*

93. The pH value of blood does not appreciably change by a small addition of an acid or a base, because the blood
(a) can be easily coagulated
(b) contains iron as a part of the molecule
(c) is a body fluid
(d) contains serum protein which acts as buffer.
(1995)

7.13 Solubility Equilibrium of Sparingly Soluble Salts

94. pH of a saturated solution of $Ca(OH)_2$ is 9. The solubility product (K_{sp}) of $Ca(OH)_2$ is
(a) 0.5×10^{-10} (b) 0.5×10^{-15}
(c) 0.25×10^{-10} (d) 0.125×10^{-15}
(NEET 2019)

95. The molar solubility of CaF_2 ($K_{sp} = 5.3 \times 10^{-11}$) in 0.1 M solution of NaF will be
(a) 5.3×10^{-11} mol L^{-1} (b) 5.3×10^{-8} mol L^{-1}
(c) 5.3×10^{-9} mol L^{-1} (d) 5.3×10^{-10} mol L^{-1}
(Odisha NEET 2019)

96. The solubility of $BaSO_4$ in water is 2.42×10^{-3} g L^{-1} at 298 K. The value of its solubility product (K_{sp}) will be
(Given molar mass of $BaSO_4$ = 233 g mol^{-1})
(a) 1.08×10^{-10} mol^2 L^{-2}
(b) 1.08×10^{-12} mol^2 L^{-2}
(c) 1.08×10^{-14} mol^2 L^{-2}
(d) 1.08×10^{-8} mol^2 L^{-2} *(NEET 2018)*

97. Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol L^{-1}. Solubility product of $Ag_2C_2O_4$ is
(a) 2.66×10^{-12} (b) 4.5×10^{-11}
(c) 5.3×10^{-12} (d) 2.42×10^{-8}
(NEET 2017)

98. The solubility of $AgCl_{(s)}$ with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be

(a) 1.26×10^{-5} M (b) 1.6×10^{-9} M
(c) 1.6×10^{-11} M (d) zero. *(NEET-II 2016)*

99. MY and NY_3, two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3?

(a) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.
(b) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.
(c) The molar solubilities of MY and NY_3 in water are identical.
(d) The molar solubility of MY in water is less than that of NY_3. *(NEET-I 2016)*

100. The K_{sp} of Ag_2CrO_4, AgCl, AgBr and AgI are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}. Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of NaCl, NaBr, NaI and Na_2CrO_4?

(a) AgBr (b) Ag_2CrO_4
(c) AgI (d) AgCl
(2015, Cancelled)

101. Using the Gibbs' energy change, $\Delta G° = +63.3$ kJ, for the following reaction,

$$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO^{2-}_{3\,(aq)}$$

the K_{sp} of $Ag_2CO_{3(s)}$ in water at 25 °C is
($R = 8.314$ J K^{-1} mol^{-1})

(a) 3.2×10^{-26} (b) 8.0×10^{-12}
(c) 2.9×10^{-3} (d) 7.9×10^{-2} *(2014)*

102. The values of K_{sp} of $CaCO_3$ and CaC_2O_4 are 4.7×10^{-9} and 1.3×10^{-9} respectively at 25°C. If the mixture of these two is washed with water, what is the concentration of Ca^{2+} ions in water?

(a) 5.831×10^{-5} M (b) 6.856×10^{-5} M
(c) 3.606×10^{-5} M (d) 7.746×10^{-5} M
(Karnataka NEET 2013)

103. Identify the correct order of solubility in aqueous medium.

(a) $Na_2S > CuS > ZnS$ (b) $Na_2S > ZnS > CuS$
(c) $CuS > ZnS > Na_2S$ (d) $ZnS > Na_2S > CuS$
(NEET 2013)

104. pH of a saturated solution of $Ba(OH)_2$ is 12. The value of solubility product (K_{sp}) of $Ba(OH)_2$ is

(a) 3.3×10^{-7} (b) 5.0×10^{-7}
(c) 4.0×10^{-6} (d) 5.0×10^{-6} *(2012, 2010)*

105. In qualitative analysis, the metals of group I can be separated from other ions by precipitating them as chloride salts. A solution initially contains Ag^+ and Pb^{2+} at a concentration of 0.10 M. Aqueous HCl is added to this solution until the Cl^- concentration is 0.10 M. What will the concentrations of Ag^+ and Pb^{2+} be at equilibrium? (K_{sp} for AgCl = 1.8×10^{-10}, K_{sp} for $PbCl_2$ $= 1.7 \times 10^{-5}$)

(a) $[Ag^+] = 1.8 \times 10^{-7}$ M, $[Pb^{2+}] = 1.7 \times 10^{-6}$ M
(b) $[Ag^+] = 1.8 \times 10^{-11}$ M, $[Pb^{2+}] = 8.5 \times 10^{-5}$ M
(c) $[Ag^+] = 1.8 \times 10^{-9}$ M, $[Pb^{2+}] = 1.7 \times 10^{-3}$ M
(d) $[Ag^+] = 1.8 \times 10^{-11}$ M, $[Pb^{2+}] = 1.7 \times 10^{-4}$ M
(Mains 2011)

106. H_2S gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because

(a) presence of HCl decreases the sulphide ion concentration
(b) solubility product of group II sulphides is more than that of group IV sulphides
(c) presence of HCl increases the sulphide ion concentration
(d) sulphides of group IV cations are unstable in HCl. *(2005)*

107. The solubility product of a sparingly soluble salt AX_2 is 3.2×10^{-11}. Its solubility (in moles/L) is

(a) 5.6×10^{-6} (b) 3.1×10^{-4}
(c) 2×10^{-4} (d) 4×10^{-4} *(2004)*

108. The solubility product of AgI at 25°C is 1.0×10^{-16} mol^2 L^{-2}. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately (in mol L^{-1})

(a) 1.0×10^{-16} (b) 1.0×10^{-12}
(c) 1.0×10^{-10} (d) 1.0×10^{-8} *(2003)*

109. Solubility of MX_2 type electrolytes is 0.5×10^{-4} mol/lit., then find out K_{sp} of electrolytes.

(a) 5×10^{-12} (b) 25×10^{-10}
(c) 1×10^{-13} (d) 5×10^{-13} *(2002)*

110. Solubility of M_2S salt is 3.5×10^{-6} then find out solubility product.

(a) 1.7×10^{-6} (b) 1.7×10^{-16}
(c) 1.7×10^{-18} (d) 1.7×10^{-12} *(2001)*

111. The solubility of a saturated solution of calcium fluoride is 2×10^{-4} moles per litre. Its solubility product is

(a) 22×10^{-11} (b) 14×10^{-4}
(c) 2×10^{-2} (d) 32×10^{-12} *(1999)*

112. The solubility product of CuS, Ag_2S and HgS are 10^{-31}, 10^{-44} and 10^{-54} respectively. The solubilities of these sulphides are in the order

(a) HgS > Ag_2S > CuS (b) CuS > Ag_2S > HgS
(c) Ag_2S > CuS > HgS (d) Ag_2S > HgS > CuS *(1997)*

113. The solubility of AgCl will be minimum in

(a) 0.01 M $CaCl_2$ (b) pure water
(c) 0.001 M $AgNO_3$ (d) 0.01 M NaCl *(1995)*

114. Which one of the following is most soluble?

(a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-70}$)
(b) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)
(c) CuS ($K_{sp} = 8 \times 10^{-37}$)
(d) MnS ($K_{sp} = 7 \times 10^{-16}$) *(1994)*

ANSWER KEY

1.	(a)	**2.**	(a)	**3.**	(d)	**4.**	(c)	**5.**	(c)	**6.**	(c)	**7.**	(c)	**8.**	(d)	**9.**	(a)	**10.**	(d)
11.	(c)	**12.**	(a)	**13.**	(b)	**14.**	(d)	**15.**	(a)	**16.**	(d)	**17.**	(d)	**18.**	(a)	**19.**	(a)	**20.**	(a)
21.	(b)	**22.**	(c)	**23.**	(a)	**24.**	(a)	**25.**	(c)	**26.**	(a)	**27.**	(d)	**28.**	(a)	**29.**	(a)	**30.**	(d)
31.	(c)	**32.**	(c)	**33.**	(b)	**34.**	(d)	**35.**	(d)	**36.**	(a)	**37.**	(b)	**38.**	(d)	**39.**	(c)	**40.**	(b)
41.	(a)	**42.**	(a)	**43.**	(c)	**44.**	(d)	**45.**	(d)	**46.**	(a)	**47.**	(c)	**48.**	(d)	**49.**	(b)	**50.**	(d)
51.	(b)	**52.**	(a)	**53.**	**(a)**	**54.**	(c)	**55.**	(d)	**56.**	(b)	**57.**	(d)	**58.**	(c)	**59.**	(b)	**60.**	(d)
61.	(a)	**62.**	(d)	**63.**	(d)	**64.**	(d)	**65.**	(d)	**66.**	(a)	**67.**	(a)	**68.**	(c)	**69.**	(d)	**70.**	(b)
71.	(d)	**72.**	(b)	**73.**	(b)	**74.**	(a)	**75.**	(c)	**76.**	(d)	**77.**	(c)	**78.**	(b)	**79.**	(c)	**80.**	(a)
81.	(a)	**82.**	(c)	**83.**	(d)	**84.**	(d)	**85.**	(b)	**86.**	(a)	**87.**	(b)	**88.**	(d)	**89.**	(b)	**90.**	(d)
91.	(b)	**92.**	(b)	**93.**	(d)	**94.**	(b)	**95.**	(c)	**96.**	(a)	**97.**	(c)	**98.**	(b)	**99.**	(d)	**100.**	(b)
101.	(b)	**102.**	(d)	**103.**	(b)	**104.**	(b)	**105.**	(c)	**106.**	(a)	**107.**	(c)	**108.**	(b)	**109.**	(d)	**110.**	(b)
111.	(d)	**112.**	(b)	**113.**	(a)	**114.**	(d)												

Hints & Explanations

1. (a) : Vapour pressure is directly related to temperature. Greater is the temperature, greater will be the vapour pressure. So to keep it constant, temperature should be constant.

2. (a) : From the given equations,

$$2NH_3 \rightleftharpoons N_2 + 3H_2;\ \frac{1}{K_1} \quad \text{...(i)}$$

$$N_2 + O_2 \rightleftharpoons 2NO;\ K_2 \quad \text{...(ii)}$$

$$3H_2 + \frac{3}{2}O_2 \rightleftharpoons 3H_2O;\ K_3^3 \quad \text{...(iii)}$$

By adding equations (i), (ii) and (iii), we get

$$2NH_3 + \frac{5}{2}O_2 \xrightleftharpoons{K} 2NO + 3H_2O,\ K = \frac{K_2K_3^3}{K_1}$$

3. (d) : If the reaction is multiplied by $\frac{1}{2}$, then new equilibrium constant, $K' = K^{1/2}$.

4. (c) : $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, $K = 278$ ...(i)

By reversing the equation (i), we get

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)} \quad \text{...(ii)}$$

Equilibrium constant for this reaction is,

$$K' = \frac{1}{K} = \frac{1}{278}$$

By dividing the equation (ii) by 2, we get desired equation,

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)} \quad \text{...(iii)}$$

Equilibrium constant for this reaction,

$$K'' = \sqrt{K'} = \sqrt{\frac{1}{K}} = \sqrt{\frac{1}{278}} = 0.0599 \approx 0.06 \text{ or } 6 \times 10^{-2}$$

5. (c) : $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$

$$K_c = \frac{[AB]^2}{[A_2][B_2]}$$

$$= \frac{(2.8\times10^{-3})^2}{(3.0\times10^{-3})(4.2\times10^{-3})} = \frac{2.8\times2.8}{3.0\times4.2} = 0.62$$

6. (c) : $N_2 + O_2 \rightleftharpoons 2NO$; K_1

$2NO + O_2 \rightleftharpoons 2NO_2$; K_2

$NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$; K

$$K_1 = \frac{[NO]^2}{[N_2][O_2]};\ K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K=\frac{[N_2]^{1/2}[O_2]}{[NO_2]}=\sqrt{\frac{[N_2][O_2]\times[NO]^2[O_2]}{[NO]^2\times[NO_2]^2}}$$

$$K=\sqrt{\frac{1}{K_1K_2}}$$

7. (c) : Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_1=\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}=1.5\times10^{-5}$$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_2=\frac{[CN^-][H^+]}{[HCN]}=4.5\times10^{-10}$$

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$

$$K=\frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$$

$$K=\frac{K_1}{K_2}=\frac{1.5\times10^{-5}}{4.5\times10^{-10}}\approx0.3\times10^5 \text{ or } K=3\times10^4$$

8. (d) : $HI_{(g)} \rightleftharpoons 1/2H_{2(g)} + 1/2I_{2(g)}$

$$i.e.\quad K=\frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]}=8$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K'=\frac{[HI]^2}{[H_2][I_2]}=\left(\frac{1}{8}\right)^2 \Rightarrow K'=\frac{1}{64}$$

9. (a) : $K_1=\dfrac{p_{NO_2}}{p_{NO}\cdot(p_{O_2})^{1/2}}$ ...(1)

$K_2=\dfrac{(p_{NO})^2\cdot p_{O_2}}{(p_{NO_2})^2}$ ...(2)

Taking square root on both sides in eq. 2,

$$\Rightarrow \sqrt{K_2}=\frac{p_{NO}\cdot(p_{O_2})^{1/2}}{p_{NO_2}} \Rightarrow \sqrt{K_2}=\frac{1}{K_1} \Rightarrow K_2=\frac{1}{K_1^2}$$

10. (d) : Given,

$XeF_6 + H_2O \rightleftharpoons XeOF_4 + 2HF, K_{eq} = K_1$

$XeOF_4 + 2HF \rightleftharpoons XeF_6 + H_2O, K_{eq} = 1/K_1$ ...(1)

and $XeO_4 + XeF_6 \rightleftharpoons XeOF_4 + XeO_3F_2, K_{eq} = K$ ...(2)

The reaction, $XeO_4 + 2HF \rightleftharpoons XeO_3F_2 + H_2O$, can be obtained by adding eq. (1) and eq.(2).

So, the equilibrium constant for the above reaction can be obtained by multiplying the equilibrium constants of eq. (1) and eq. (2).

Hence, the value is $=\dfrac{K_2}{K_1}$

11. (c) : The equilibrium constant for the reverse reaction will be $1/K$.

12. (a) : Reaction (ii) is the reversible reaction of (i) and is half of the reaction (i). Thus, rate constant can be given as :

$$K_2=\sqrt{\frac{1}{K_1}} \text{ or } K_1=\left[\frac{1}{K_2}\right]^2$$

13. (b) :

	$2A_{(g)}$ +	$B_{(g)}$ $\rightleftharpoons$	$3C_{(g)}$ +	$D_{(g)}$
Initial moles :	1	1	0	0
Moles at eq. :	$1-(2\times0.25)$ $=0.5$	$1-0.25$ $=0.75$	3×0.25 $=0.75$	0.25 $=0.25$

Equilibrium constant, $K=\dfrac{[C]^3[D]}{[A]^2[B]}$

$$\therefore\quad K=\frac{(0.75)^3(0.25)}{(0.5)^2(0.75)}$$

14. (d) :

$2AB_{2(g)}$ $\rightleftharpoons$	$2AB_{(g)}$ +	$B_{2(g)}$	
2	0	0	(initially)
$2(1-x)$	$2x$	x	(at equilibrium)

Amount of moles at equilibrium $= 2(1-x) + 2x + x = 2 + x$

$$K_p=\frac{[p_{AB}]^2[p_{B_2}]}{[p_{AB_2}]^2}$$

$$K_p=\frac{\left(\frac{2x}{2+x}\times P\right)^2\times\left(\frac{x}{2+x}\times P\right)}{\left(\frac{2(1-x)}{2+x}\times P\right)^2}=\frac{\frac{4x^3}{2+x}\times P}{4(1-x)^2}$$

$$K_p=\frac{4x^3\times P}{2}\times\frac{1}{4}\quad(\because 1-x\approx1 \text{ and } 2+x\approx2)$$

$$x=\left(\frac{8K_p}{4P}\right)^{1/3} \Rightarrow x=\left(\frac{2K_p}{P}\right)^{1/3}$$

15. (a) : $X \rightleftharpoons Y + Z$ ...(i)

$A \rightleftharpoons 2B$ ...(ii)

	X $\rightleftharpoons$	Y +	Z
Initially	1	0	0
At equilibrium	$1-\alpha$	α	α

Total no. of moles at equilibrium $= 1 - \alpha + 2\alpha = 1+\alpha$

Similarly,

	A $\rightleftharpoons$	$2B$
Initially	1	0
At equilibrium	$1-\alpha$	2α

Total no. of moles at equilibrium $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$\therefore\ K_{p_1}=\frac{p_Y\times p_Z}{p_X}=\frac{\frac{\alpha}{1+\alpha}\times P_1\times\frac{\alpha}{1+\alpha}\times P_1}{\frac{1-\alpha}{1+\alpha}\times P_1}=\frac{\alpha^2P_1}{(1+\alpha)(1-\alpha)}$$

$$K_{p_2}=\frac{(p_B)^2}{p_A}=\frac{\left(\frac{2\alpha}{1+\alpha}\times P_2\right)^2}{\frac{1-\alpha}{1+\alpha}\times P_2}=\frac{(2\alpha)^2P_2}{(1+\alpha)(1-\alpha)}$$

Now $\frac{K_{p_1}}{K_{p_2}} = \frac{P_1}{4P_2} \Rightarrow \frac{K_{P_1}}{K_{P_2}} = \frac{9}{1} = \frac{P_1}{4P_2} \Rightarrow \frac{P_1}{P_2} = \frac{36}{1} = 36:1$

16. (d) : $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}; K_p = 1.6$ atm

$$K_p = \frac{p_{CO_2} \times p_{SrO}}{p_{SrCO_3}} \Rightarrow 1.6 = p_{CO_2} \; (\because p_{SrO} = p_{SrCO_3} = 1)$$

$\therefore$ Maximum pressure of CO_2 = 1.6 atm

Let the maximum volume of the container when pressure of CO_2 is 1.6 atm be V L

During the process, PV = constant

$\therefore \quad 0.4 \times 20 = 1.6 \times V$

$$\Rightarrow V = \frac{0.4 \times 20}{1.6} = 5 \text{ L}$$

17. (d) : K_p and K_c are related by the equation,

$K_p = K_c(RT)^{\Delta n_g}$

where Δn_g = difference in the no. of moles of products and reactants in the gaseous state.

for $\quad 2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

$\Delta n_g = 2 - (1) = 1 \neq 0$

18. (a) : $Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$

$$K = \frac{[Fe^{3+}][OH^-]^3}{[Fe(OH)_3]}$$

$K = [Fe^{3+}]\,[OH^-]^3 \qquad$ ($\because$ activity of solid is taken unity)

Concentration of OH^- ion in the reaction is decreased by 1/4 times then equilibrium concentration of Fe^{3+} will be increased by 64 times in order to keep the value of K constant.

19. (a) : $K_p = p_{CO_2}$

Solids do not exert pressure, so their partial pressure is taken as unity.

20. (a) : The value of K is high which means reaction proceeds almost to completion *i.e.*, the system will contain mostly products.

21. (b) :

$$\begin{array}{ccccc} 3H_2 & + & N_2 & \rightarrow & 2NH_3 \\ 3 & & 1 & & 2 \\ 3/2 & & 1/2 & & 1 \\ 10 \times \frac{3}{2} & & 10 \times \frac{1}{2} & & 10 \times 1 \\ 15 & & 5 & & 10 \end{array}$$

Composition of gaseous mixture under the aforesaid condition in the end will be

H_2 = 30 – 15 = 15 litres

N_2 = 30 – 5 = 25 litres ; NH_3 = 10 litres

22. (c) : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}; \; \Delta n_{(g)} = 2 - 4 = -2$$

Thus, the reaction will go from right to left when $Q > K_c$.

23. (a) : $\Delta G = \Delta G^\circ + RT \ln Q$

At equilibrium, $\Delta G = 0$ and $Q = K_C$

$\therefore \quad 0 = \Delta G^\circ + RT \ln K_C$

$\Rightarrow \quad \Delta G^\circ = -RT \ln K_C$

$= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \ln (2 \times 10^{13})$

24. (a)

25. (c) : When $K_p > Q$, rate of forward reaction > rate of backward reaction.

$\therefore$ Reaction is spontaneous.

When $\Delta G^\circ < RT \ln Q$, ΔG° is positive, reverse reaction is feasible, thus reaction is non spontaneous.

When $K_p = Q$, rate of forward reaction = rate of backward reaction.

$\therefore$ Reaction is in equilibrium.

When $T\Delta S > \Delta H$, ΔG will be negative only when ΔH = +ve.

$\therefore$ Reaction is spontaneous and endothermic.

26. (a) : On increasing the pressure and decreasing the temperature, equilibrium will shift in forward direction.

27. (d) : As the forward reaction is exothermic and leads to lowering of pressure (produces lesser number of gaseous moles) hence, according to Le Chatelier's principle, at high pressure and low temperature, the given reversible reaction will shift in forward direction to form more product.

28. (a) : $\log \frac{K'_p}{K_p} = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

For exothermic reaction, ΔH = –ve *i.e.*, heat is evolved.

The temperature T_2 is higher than T_1.

Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is negative.

so, $\log K'_p - \log K_p$ = –ve or $\log K_p > \log K'_p$

or $\quad K_p > K'_p$

29. (a) : HCl and SO_2 are reducing agents. So, they can reduce MnO_4^-.

CO_2 is neither oxidising nor reducing agent, it will provide only acidic medium. It can shift the reaction in forward direction and the reaction can go to completion.

30. (d) : $X_{2(g)} + 4Y_{2(g)} \rightleftharpoons 2XY_{4(g)}$

Δn_g = –ve and ΔH = –ve

The reaction is favoured in forward direction at low temperature and high pressure.

31. (c) : $CH_{4(g)} + 2O_{2(g)} \rightleftharpoons CO_{2(g)} + 2H_2O_{(l)}$

$$K_p = \frac{p_{CO_2}}{p_{CH_4} \cdot p^2_{O_2}}$$

32. (c) : Pressure of O_2 does not depend on concentration terms of other reactants (because both are in solid state). Since this is an endothermic reaction, if the temperature is raised, dissociation of BaO_2 would occur, more O_2 is produced at equilibrium, pressure of O_2 increases.

33. (b) : For a reaction, $A + B \rightleftharpoons C + D$,

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

Increase in conc. of reactants will proceed the equilibrium in the forward direction giving more products so that the equilibrium constant value remains constant and independent of concentration.

34. (d) : When solid and liquid are in equilibrium, the increase in temperature results in increase in volume of liquid or decrease in the amount of solid.

$$\text{Solid} \rightleftharpoons \text{Liquid}$$

With increase in temperature equilibrium shifts in forward direction.

35. (d) : According to Le Chatelier's principle, if an equilibrium is subjected to a change in concentration, pressure or temperature, etc. equilibrium shift in such a way so as to undo the effect of a change imposed.

36. (a) : HCl is a strong acid and dissociates completely into ions in aqueous solution.

37. (b) : $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

As acetic acid is a weak acid so, it also contains some undissociated CH_3COOH along with CH_3COO^- and H_3O^+ ions.

38. (d) :

Bronsted acid	Conjugate base
H_2O	OH^-
HF	F^-

39. (c) : HCl cannot accept H^+ ion, therefore cannot act as Bronsted Base.

40. (b) : $BF_3 \longrightarrow$ Lewis acid (incomplete octet)

$PF_3 \longrightarrow$ Lewis base (presence of lone pair on P atom)

$CF_4 \longrightarrow$ Complete octet

$SiF_4 \longrightarrow$ Lewis acid (empty *d*-orbital in Si-atom)

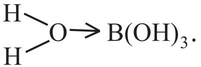
41. (a) : BF_3 is Lewis acid (e^- pair acceptor).

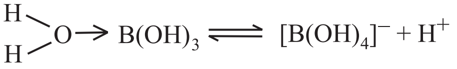
42. (a) : $H\overset{+7}{\underline{Cl}}O_4$ with highest oxidation number and its conjugate base is resonance stabilised, hence it is most acidic. Cl is more electronegative than S.

43. (c) : Compounds that are electron deficient act as Lewis acids. Out of the given hydrides B_2H_6 satisfies this condition and is therefore a Lewis acid.

44. (d) : Lewis acids are electron deficient compounds, since $(CH_3)_3B$ is electron deficient (due to incomplete octet of B), it acts as a Lewis acid.

45. (d) : Due to strong hydrogen-fluorine bond, proton is not given off easily and hence, HF is weakest acid.

46. (a) : $B(OH)_3$ in aqueous medium coordinates a molecule of water to form the hydrated species  $H_2O \rightarrow B(OH)_3$. In this species, B^{3+} ion, because of its small size, has high polarizing power thereby pulling the sigma electron charge of the coordinated O atom towards itself. The coordinated oxygen, in turn, pulls the sigma electron charge of the OH bond of the attached water molecule towards itself. This facilitates the removal of H^+ ion from the O – H bond.



$$H_2O \rightarrow B(OH)_3 \rightleftharpoons [B(OH)_4]^- + H^+$$

Thus, the solution of $B(OH)_3$ in water acts as a weak acid, and it is not a protonic acid.

47. (c) : Proton accepting tendency is known as the strength of basicity.

In $R—\dot{N}H_2$, N has lone pair of electrons which intensify due to electron releasing *R*-group and increase the tendency to donate lone pair of electrons to H^+.

Secondly as the size of the ion increases there is less attraction for H^+ to form bond with H–atom and are less basic. Thus the order of proton accepting tendency :

$RNH_2 > NH_3 > HS^- > I^-$.

48. (d) : $NH_2^- + H^+ \longrightarrow NH_3$ (conjugate acid)

Substance + $H^+ \longrightarrow$ conjugate acid

Substance – $H^+ \longrightarrow$ conjugate base

49. (b) : In BCl_3 the central atom 'B' is sp^2 hybridised and contains only 'six' electrons in its valence shell. Therefore, it is electron deficient.

50. (d) : $\underset{\text{Weak acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Strong conjugate base}}{CH_3COO^-} + H^+$

As CH_3COOH is the weakest acid, so its conjugate base (CH_3COO^-) is the strongest base. H_2SO_4, HCl, HNO_3 are strong acids, so their conjugate bases are weak.

51. (b) : In BF_3 and $FeCl_3$ molecules, the central atoms have incomplete octet and in SiF_4, the central atom has empty *d*-orbitals. Hence, according to Lewis concept, these are Lewis acids.

52. (a) : Ammonium sulphate is a salt of strong acid (H_2SO_4) and weak base (NH_4OH). Therefore, repeated use of ammonium sulphate would increase the concentration of sulphuric acid, while ammonia from NH_4OH is used up by the plant. Hence, the acidity of soil will increase.

53. (a) : $$\underset{s}{Ni(OH)_2} \rightleftharpoons \underset{s}{Ni^{2+}} + \underset{2s}{2OH^-}$$

where s is the solubility of $Ni(OH)_2$.

$$\underset{0.1\,M}{NaOH} \rightleftharpoons \underset{0.1\,M}{Na^+} + \underset{0.1\,M}{OH^-}$$

$[OH^-] = 2s + 0.1 \approx 0.1$ ($\because$ $2s <<< 0.1$)

Ionic product of $Ni(OH)_2 = [Ni^{2+}][OH^-]^2$

$2 \times 10^{-15} = s(0.1)^2$

$$s = \frac{2\times10^{-15}}{0.1\times0.1} = 2\times10^{-13}\ M$$

54. (c) : $$\underset{0.01\ M}{NaOH} \longrightarrow Na^+ + \underset{0.01\ M}{OH^-}$$

$\therefore$ $[OH^-] = 0.01$ M

$\therefore$ $pOH = -\log[OH^-] = -\log(0.01) = 2$

$\therefore$ $pH = 14 - pOH = 14 - 2 = 12$

55. (d) : pH = 1, so $[H^+] = 10^{-1}$

For acid base mixture: $N_1V_1 - N_2V_2 = N_3V_3$

(For NaOH and HCl, Normality = Molarity)

$$A.\ M_1(H^+) = \frac{60\times\frac{1}{10} - 40\times\frac{1}{10}}{100} = 2\times10^{-2}\ M$$

i.e. pH = 1.698 ≈ 1.7

$$B.\ M_2(H^+) = \frac{55\times\frac{1}{10} - 45\times\frac{1}{10}}{100} = \frac{1}{100}$$

$= 10^{-2}$ M *i.e.* pH = 2

$$C.\ M_3(H^+) = \frac{75\times\frac{1}{5} - 25\times\frac{1}{5}}{100} = 10^{-1}\,M\ i.e.\ pH = 1$$

$$D.\ M_4(H^+) = \frac{100\times\frac{1}{10} - 100\times\frac{1}{10}}{200} = 0\ i.e.\ \ pH = 7$$

56. (b): $$\underset{0.10\ M}{C_5H_5N} + H_2O \rightleftharpoons C_5H_5\overset{+}{N}H + OH^-$$

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7\times10^{-9}}{0.10}} = 1.30\times10^{-4}$$

$\therefore$ Percentage of pyridine that forms pyridinium ion $= 1.30 \times 10^{-4} \times 100 = 0.013\%$

57. (d) : One mole of NaOH is completely neutralised by one mole of HCl.

Hence, 0.01 mole of NaOH will be completely neutralised by 0.01 mole of HCl.

$\Rightarrow$ NaOH left unneutralised = 0.1 – 0.01 = 0.09 mol

As equal volumes of two solutions are mixed,

$$[OH]^- = \frac{0.09}{2} = 0.045\ M$$

$\Rightarrow$ $pOH = -\log(0.045) = 1.35$

$\therefore$ $pH = 14 - 1.35 = 12.65$

58. (c) : Na_2CO_3 which is a salt of NaOH (strong base) and H_2CO_3 (weak acid) will produce a basic solution with pH greater than 7.

59. (b) : Degree of dissociation, $\alpha = \frac{3.7}{100} = 0.037$

According to Ostwald's formula,

$K_a = \alpha^2C = (0.037)^2 \times 0.10 = 1.369 \times 10^{-4} \approx 1.4 \times 10^{-4}$

60. (d) : We know that, at 25°C, $K_w = 1 \times 10^{-14}$

At 100°C, $K_w = 55 \times 10^{-14}$ $[\because\ K_w = [H^+][OH^-]$

$\Rightarrow$ $K_w = [H^+]^2$

$$H^+ = \sqrt{K_w}$$

$$H^+ = \sqrt{55\times10^{-14}}$$

$pH = -\log[H^+]$

$$pH = -\log\left[\sqrt{55\times10^{-14}}\right]$$

$$= \frac{1}{2}[-\log(55\times10^{-14})] = \frac{1}{2}[-\log 55 + 14\log 10]$$

$$= \frac{1}{2}[-1.74 + 14] = \frac{1}{2}[12.26] = 6.13$$

61. (a) : $BaCl_2$ is made up of $Ba(OH)_2$ and HCl.

$AlCl_3$ is made up of $Al(OH)_3$ and HCl.

LiCl is made up of LiOH and HCl.

$BeCl_2$ is made up of $Be(OH)_2$ and HCl.

$Ba(OH)_2$ is strongest base among the given options thus have maximum pH.

62. (d) : $$\underset{C-x}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COO^-} + \underset{x}{H^+}$$

$$\underset{0.2\ M}{CH_3COONa} \rightarrow \underset{0.2\ M}{CH_3COO^-} + \underset{0.2\ M}{Na^+}$$

$$\begin{array}{l}[CH_3COOH] = C - x \approx 0.1\ M\\ [CH_3COO^-] = 0.2 + x \approx 0.2\ M\end{array} \left\{\begin{array}{l}\text{acetic acid is a}\\ \text{weak acid so,}\\ \text{dissociation is}\\ \text{minimum } i.e., x\\ \text{can be neglected.}\end{array}\right.$$

$$\therefore\ [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$= \frac{1.8\times10^{-5}\times10^{-1}}{2\times10^{-1}} = 9\times10^{-6}\ M$$

63. (d) : NH_4Cl is a salt of strong acid and weak base, so hydrolysis constant is

$$K_h = \frac{K_w}{K_b}$$

Given, $K_b\ (NH_4OH) = 1.77 \times 10^{-5}$

$K_w = 10^{-14}$

$$\therefore\ K_h = \frac{10^{-14}}{1.77\times10^{-5}} = 0.565\times10^{-9}$$

or $K_h = 5.65 \times 10^{-10}$

64. **(d) :** Millimoles of H^+ produced = 20 × 0.05 = 1
Millimoles of OH^- produced = 30 × 0.1 × 2 = 6
(∵ Each $Ba(OH)_2$ gives $2OH^-$.)
∴ Millimoles of OH^- remaining in solution = 6 – 1 = 5
Total volume of solution = 20 + 30 = 50 mL

$$\therefore\ [OH^-] = \frac{5}{50} = 0.1\,M$$

65. **(d) :** pH = –log[H^+]
or $[H^+] = 10^{-pH}$; $[H^+]$ of soln. 1 = 10^{-3}
$[H^+]$ of soln. 2 = 10^{-4}; $[H^+]$ of soln. 3 = 10^{-5}
Total concentration of $[H^+]$

$$= 10^{-3}(1 + 1 \times 10^{-1} + 1 \times 10^{-2})$$

$$\Rightarrow 10^{-3}\left(\frac{1}{1}+\frac{1}{10}+\frac{1}{100}\right) \Rightarrow 10^{-3}\left(\frac{100+10+1}{100}\right)$$

$$\Rightarrow 10^{-3}\left(\frac{111}{100}\right) = 1.11 \times 10^{-3}$$

So, H^+ ion concentration in mixture of equal volumes of these acid solution $= \dfrac{1.11 \times 10^{-3}}{3} = 3.7 \times 10^{-4}$ M

66. **(a) :** For a weak acid, degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1 \times 10^{-5}}{0.1}} = 10^{-2} \quad \textit{i.e.}\ 1.00\%$$

67. **(a) :** Given, $[H_3O^+] = 1 \times 10^{-10}$ or, pH = 10
Now at 25°C, pH + pOH = pK_w = 14
or, pOH = 14 – pH = 14 – 10 = 4

68. **(c) :** 10^{-8} M HCl = 10^{-8} M H^+
Also from water, $[H^+] = 10^{-7}$
Total $[H^+] = 10^{-7} + 0.10 \times 10^{-7} = 1.1 \times 10^{-7}$ M

69. **(d) :** C = 0.01 M
$K_b = 1 \times 10^{-12}$ at 25°C

$$\begin{array}{llll} & BOH & \rightleftharpoons & B^+ + OH^- \\ \text{Initially} & C & & 0 \quad\ 0 \\ \text{At eq.} & C - C\alpha & & C\alpha \quad C\alpha \end{array}$$

$[OH^-] = C\alpha$

$$[OH^-] = \sqrt{K_b\,C} = \sqrt{1 \times 10^{-12} \times 10^{-2}}$$

$[OH^-] = 10^{-7}$ mol L^{-1}

70. **(b) :** NH_4OH is a weak base but HCl is a strong acid in solution, so pH of NH_4Cl solution is comparatively low.

$NaNO_3$ is a salt of strong base and strong acid, so pH of the solution will be 7.

Hydrolysis of potassium acetate (a salt of a weak acid and a strong alkali) gives a weakly alkaline solution, since the acetate ion acts as a weak base.

$CH_3COOK + H_2O \rightarrow CH_3COOH + K^+ + OH^-$
The pH of this solution ≈ 8.8.

Hydrolysis of sodium carbonate (a salt of strong alkali and a weak acid) gives an alkaline solution.
$Na_2CO_3 + 2H_2O \rightarrow 2(Na^+ + OH^-) + H_2CO_3$
The pH of this solution is > 10.

71. **(d) :** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[CH_3COOH] = \frac{3.4 \times 10^{-4} \times 3.4 \times 10^{-4}}{1.7 \times 10^{-5}} = 6.8 \times 10^{-3}$$

72. **(b) :** (i) $H_2A \overset{K_{a_1}}{\rightleftharpoons} HA^- + H^+$

(ii) $HA^- \overset{K_{a_2}}{\rightleftharpoons} A^{2-} + H^+$

In the 1st step, H^+ ion comes from neutral molecule, while in the 2nd step the H^+ ion comes from negatively charged ions. The presence of –ve charge makes the removal of H^+ ion difficult. Thus, $K_{a_1} > K_{a_2}$.

73. **(b) :** After mixing 1 N solution of CH_3COOH (weak acid) and 1 N NaOH (strong base), the resulting solution will have free OH^- ions. Thus, pH will be higher than 7.

74. **(a) :** $[H^+] = C\,\alpha = 0.1 \times 0.02 = 2 \times 10^{-3}$ M
(As degree of dissociation = 2% = 0.02)

Hence, $[OH^-] = \dfrac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$ M

75. **(c) :** $NaH + H_2O \rightarrow NaOH + H_2$
or, $H^-_{(aq)} + H_2O_{(l)} \rightarrow OH^- + H_2\uparrow$

76. **(d) :** At high temperature, the value of ionic product increases.

77. **(c) :**

$$\begin{array}{llll} & 2HI \rightarrow & H_2 & + \quad I_2 \\ \text{Initially :} & 2 & 0 & 0 \\ \text{After dissociation :} & 2 - 2\alpha & \alpha & \alpha \end{array}$$

Total number of moles = 2(1 – α) + 2α = 2

78. **(b) :** Since NaOH is a strong base, therefore it completely ionises. Thus, the hydroxyl ion concentration is equal to that of the base itself. We know that concentration of OH^- in N/10 NaOH = 0.1 = 10^{-1}.
Therefore value of

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{10^{-1}} = 1 \times 10^{-13}$$

pH = – log $[H_3O^+]$ = – log $[1 \times 10^{-13}]$ = 13

79. **(c) :** Since HCl is a strong acid and it completely ionises, therefore H_3O^+ ions concentration is equal that of the acid itself *i.e.*, $[H_3O^+]$ = [HCl] = 10 M.
Therefore, pH = – log $[H_3O^+]$ = – log [10] = – 1

80. **(a) :** $[H_3O^+] = [OH^-] = 1 \times 10^{-6}$ mole/litre
$K_w = [H_3O^+][OH^-] = [1 \times 10^{-6}] \times [1 \times 10^{-6}] = 1 \times 10^{-12}$

81. (a) : Sodium borate is a salt formed from strong base (NaOH) and weak acid (H_3BO_3). Hence, sodium borate will act as basic solution.

82. (c) : NH_4Cl and $NaHCO_3$ are acidic in nature and NaCl is neutral. Only Na_2CO_3 is basic and thus, have highest pH.

83. (d) : Acid-base titration :

$$\underset{10\text{ mmol}}{HCl} + \underset{20\text{ mmol}}{NH_4OH} \longrightarrow NH_4Cl$$

$\therefore$ HCl is the limiting reagent.

Solution contains NH_4OH (weak base) and NH_4Cl (salt of strong acid and weak base). Therefore, a basic buffer will be formed.

84. (d) : Acidic buffer is a mixture of a weak acid and its salt with a strong base. $HClO_4$ is a strong acid.

85. (b) : $\text{pH} = \text{p}K_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$5 = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \ [\because \text{p}K_a = -\log K_a]$$

$$5 = -\log[1\times10^{-4}] + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$5 = 4 + \log\frac{[\text{Salt}]}{[\text{Acid}]},\ 5-4 = \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$1 = \log\frac{[\text{Salt}]}{[\text{Acid}]},\ \frac{[\text{Salt}]}{[\text{Acid}]} = 10\ \text{i.e. } 10:1$$

86. (a)

87. (b) : $[NH_3] = 0.30$ M, $K_b = 1.8\times10^{-5}$

$[NH_4^+] = 0.20$ M

$pK_b = -\log(1.8\times10^{-5}) = 4.74$

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]} = 4.74 + \log\frac{0.2}{0.3} = 4.56$$

pH = (14 – 4.56) = 9.44

88. (d) : We know, $\text{pOH} = \text{p}K_b + \log\dfrac{[B^-]}{[HB]}$

Since, $[B^-] = [HB]$ (given)

$\therefore$ $\text{pOH} = \text{p}K_b \Rightarrow \text{pOH} = 10$

$\therefore$ pH = 14 – 10 = 4

89. (b) : HNO_2 (weak acid) and $NaNO_2$ (salt of conjugate base) is an example of acidic buffer.

90. (d) : Let us consider the formation of a salt of a weak acid and a strong base.

$$In^- + H_2O \rightleftharpoons HIn + OH^-$$

$$K_h = \frac{[HIn][OH^-]}{[In^-]} \qquad \text{...(i)}$$

Other equations present in the solution are

$$HIn \rightleftharpoons H^+ + In^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \qquad \text{... (ii)}$$

$$K_w = [H^+][OH^-] \qquad \text{... (iii)}$$

From (ii) and (iii),

$$\frac{K_w}{K_{In}} = \frac{[HIn][OH^-]}{[In^-]} = K_h \qquad \text{... (iv)}$$

$$[OH^-] = \frac{K_w}{K_{In}}\frac{[In^-]}{[HIn]}$$

$$\log[OH^-] = \log K_w - \log K_{In} + \log\frac{[In^-]}{[HIn]}$$

$$-\text{pOH} = -\text{p}K_w + \text{p}K_{In} + \log\frac{[In^-]}{[HIn]}$$

$$\text{p}K_w - \text{pOH} = \text{p}K_{In} + \log\frac{[In^-]}{[HIn]}$$

$$\text{or,}\quad \text{pH} = \text{p}K_{In} + \log\frac{[In^-]}{[HIn]}$$

$$\text{i.e. } \log\frac{[In^-]}{[HIn]} = \text{pH} - \text{p}K_{In}$$

91. (b) : Solution of 0.1 N NH_4OH and 0.1 N NH_4Cl is a buffer solution.

According to Henderson equation, the pH of a basic buffer, $\text{pH} = 14 - \text{p}K_b - \log\dfrac{[\text{Salt}]}{[\text{Base}]}$

$$\Rightarrow \quad \text{p}K_b = 14 - \text{pH} - \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$\Rightarrow \quad \text{p}K_b = 14 - 9.25 - \log\frac{0.1}{0.1}$$

$$\Rightarrow \quad \text{p}K_b = 14 - 9.25 = 4.75$$

$\therefore$ $\text{p}K_b$ of NH_4OH = 4.75

92. (b) : pH of an acidic buffer solution is given by Henderson equation :

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

Its buffer capacity = $\text{p}K_a \pm 1$

Since a buffer solution is more effective in pH range $\text{p}K_a \pm 1$ therefore, the weak acid having $\text{p}K_a = 3.58$ together with its sodium salt is chosen. Acetoacetic acid is, therefore, the suitable weak acid.

93. (d) : The pH value of the blood is maintained constant by buffer solution present in the blood itself. Buffer solutions resist the change in pH values.

94. (b) : pH of the saturated solution of $Ca(OH)_2 = 9$

$\therefore$ pOH of the saturated solution of $Ca(OH)_2 = 14 - 9 = 5$

$\Rightarrow$ $[OH^-] = 10^{-5}$ $\qquad (\because$ pH + pOH = 14)

$$Ca(OH)_2 \rightleftharpoons \underset{\substack{s \\ 1/2\times10^{-5}}}{Ca^{2+}} + \underset{\substack{2s \\ 10^{-5}}}{2OH^-}$$

$K_{sp} = [Ca^{2+}]\,[OH^-]^2 = [1/2 \times 10^{-5}]\,[10^{-5}]^2$
$= 0.5 \times 10^{-15}$

95. (c) : $CaF_2 \longrightarrow \underset{s}{Ca^{2+}} + \underset{2s}{2F^-}$

$NaF \longrightarrow \underset{0.1\text{ M}}{Na^+} + \underset{0.1\text{ M}}{F^-}$

$[Ca^{2+}] = s$, $[F^-] = (2s + 0.1) \approx 0.1$ M
$K_{sp} = [Ca^{2+}]\,[F^-]^2$
$5.3 \times 10^{-11} = (s)\,(0.1)^2$

$$s = \frac{5.3\times10^{-11}}{(0.1)^2} = 5.3 \times 10^{-9}\text{ mol L}^{-1}$$

∴ Molar solubility is 5.3×10^{-9} mol L^{-1}

96. (a) : Solubility of $BaSO_4$,

$$s = \frac{2.42\times10^{-3}}{233}\text{ mol L}^{-1} = 1.04 \times 10^{-5}\text{ mol L}^{-1}$$

$BaSO_4$ ionizes completely in the solution as :

$$BaSO_{4(s)} \rightleftharpoons \underset{s}{Ba^{2+}_{(aq)}} + \underset{s}{SO^{2-}_{4(aq)}}$$

$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = s^2$
$= (1.04 \times 10^{-5})^2 = 1.08 \times 10^{-10}$ mol^2 L^{-2}

97. (c) : Let solubility of $Ag_2C_2O_4$ be s mol L^{-1}

$$\underset{s}{Ag_2C_2O_{4(s)}} \rightleftharpoons \underset{2s}{2Ag^+_{(aq)}} + \underset{s}{C_2O^{2-}_{4(aq)}}$$

$K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$
$K_{sp} = (2s)^2(s) = 4s^3$
$K_{sp} = 4 \times (1.1 \times 10^{-4})^3$ $\quad (\because [Ag^+] = 2s = 2.2 \times 10^{-4})$
$K_{sp} = 5.3 \times 10^{-12}$

98. (b) : Let s be the solubility of AgCl in moles per litre.

$$\underset{s}{AgCl_{(aq)}} \rightleftharpoons \underset{s}{Ag^+_{(aq)}} + \underset{(s+0.1)}{Cl^-_{(aq)}}$$

($\because$ 0.1 M NaCl solution also provides 0.1 M Cl$^-$ ion).
$K_{sp} = [Ag^+]\,[Cl^-]$; $1.6 \times 10^{-10} = s(s + 0.1)$
$1.6 \times 10^{-10} = s(0.1)$ $\quad (\because s <<<< 0.1)$

$$s = \frac{1.6\times10^{-10}}{0.1} = 1.6\times10^{-9}\text{ M}$$

99. (d) : For $MY : K_{sp} = s_1^2$

$$\Rightarrow \quad s_1 = \sqrt{K_{sp}} = \sqrt{6.2\times10^{-13}} = 7.87 \times 10^{-7}\text{ mol L}^{-1}$$

For NY_3 : $K_{sp} = (s_2)(3s_2)^3 = 27s_2^4$

$$\Rightarrow \quad s_2 = \sqrt[4]{\frac{6.2\times10^{-13}}{27}} = 3.89 \times 10^{-4}\text{ mol L}^{-1}$$

Hence, molar solubility of MY in water is less than that of NY_3.

100. (b) :

Salt	K_{sp}	**Solubility**
Ag_2CrO_4	$1.1 \times 10^{-12} = 4s^3$	$s = \sqrt[3]{\frac{K_{sp}}{4}} = 0.65\times10^{-4}$
AgCl	$1.8 \times 10^{-10} = s^2$	$s = \sqrt{K_{sp}} = 1.34\times10^{-5}$
AgBr	$5 \times 10^{-13} = s^2$	$s = \sqrt{K_{sp}} = 0.71\times10^{-6}$
AgI	$8.3 \times 10^{-17} = s^2$	$s = \sqrt{K_{sp}} = 0.9\times10^{-8}$

Solubility of Ag_2CrO_4 is highest thus, it will be precipitated at last.

101. (b) : $\Delta G° = -2.303RT\log K_{sp}$
63.3×10^3 J $= -\,2.303 \times 8.314 \times 298 \log K_{sp}$
63.3×10^3 J $= -5705.84 \log K_{sp}$

$$\log K_{sp} = -\frac{63.3\times10^3}{5705.84} = -11.09$$

K_{sp} = antilog $(-11.09) = 8.128 \times 10^{-12}$

102. (d) : $CaCO_3 \rightarrow \underset{x}{Ca^{2+}} + \underset{x}{CO_3^{2-}}$

$CaC_2O_4 \rightarrow \underset{y}{Ca^{2+}} + \underset{y}{C_2O_4^{2-}}$

Now, $[Ca^{2+}] = x + y$
and $x(x + y) = 4.7 \times 10^{-9}$ ...(i)
$y(x + y) = 1.3 \times 10^{-9}$ ...(ii)
Dividing equation (i) and (ii) we get

$$\frac{x}{y} = 3.6$$

∴ $x = 3.6y$
Putting this value in equation (ii), we get
$y(3.6y + y) = 1.3 \times 10^{-9}$
On solving, we get $y = 1.68 \times 10^{-5}$
and $x = 3.6 \times 1.68 \times 10^{-5} = 6.05 \times 10^{-5}$
∴ $[Ca^{2+}] = (x + y) = (1.68 \times 10^{-5}) + (6.05 \times 10^{-5})$
∴ $[Ca^{2+}] = 7.73 \times 10^{-5}$ M

103. (b) : Sodium sulphide is soluble in water. The solubility product (and hence solubility) of ZnS is larger than that of CuS.

104. (b) : pH of solution = 12
$[H^+] = 10^{-12}$

$$[OH^-] = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$$Ba(OH)_2 \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{2s}{2OH^-}$$

$$2s = 10^{-2} \Rightarrow s = \frac{10^{-2}}{2}$$

$K_{sp} = (s)\,(2s)^2 = 4s^3$

$$= 4 \times \left(\frac{10^{-2}}{2}\right)^3 = \frac{4}{8} \times 10^{-6} = 5 \times 10^{-7}$$

105. (c) : $K_{sp}[AgCl] = [Ag^+][Cl^-]$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{10^{-1}} = 1.8 \times 10^{-9}\ M$$

$K_{sp}[PbCl_2] = [Pb^{2+}][Cl^-]^2$

$$[Pb^{2+}] = \frac{1.7 \times 10^{-5}}{10^{-1} \times 10^{-1}} = 1.7 \times 10^{-3}\ M$$

106. (a) : The cations of group II are precipitated as their sulphides.

Solubility product of sulphide of group II radicals are very low. Therefore, even with low conc. of S^{2-} ions, the ionic product exceeds the value of their solubility product and the radicals of group II gets precipitated. The low conc. of S^{2-} ions is obtained by passing H_2S gas through the solution of the salt in the presence of dil. HCl which suppresses degree of ionisation of H_2S by common ion effect.

$$H_2S \rightleftharpoons \boxed{\begin{array}{c} 2H^+ \\ H^+ \end{array}} \begin{array}{l} + S^{2-} \\ + Cl^- \end{array}$$

common ion

Note that solubility product of group IV radicals are quite high. It is necessary to suppress the conc. of S^{2-} ions, otherwise radical of group IV will also get precipitated along with group II radicals.

107. (c) : $K_{sp} = 3.2 \times 10^{-11}$

$$AX_2 \rightleftharpoons \underset{s}{A^{2+}} + \underset{2s}{2X^-}$$

$K_{sp} = s \times (2s)^2 = 4s^3$; *i.e.*, $3.2 \times 10^{-11} = 4s^3$

or, $s^3 = 0.8 \times 10^{-11} = 8 \times 10^{-12}$

$\therefore\ s = 2 \times 10^{-4}$

108. (b) : $AgI \rightleftharpoons Ag^+ + I^-$

$$KI \rightleftharpoons \underset{10^{-4}\,M}{K^+} + \underset{10^{-4}\,M}{I^-}$$

[For KI, 1 N = 1 M]

$[I^-] = s + 10^{-4}$

$K_{sp} = [Ag^+][I^-]$

$1 \times 10^{-16} = s(s + 10^{-4})$

$1 \times 10^{-16} = s^2 + 10^{-4}\,s$

$1 \times 10^{-16} = 10^{-4}\,s$ $[\because s^2 <<< 10^{-4}\,s]$

$$\Rightarrow \quad s = \frac{1 \times 10^{-16}}{10^{-4}} = 1 \times 10^{-12}\ \text{mol L}^{-1}$$

109. (d) : Let s be the solubility of the electrolyte MX_2.

$[M^{2+}] = s$, $[X^-] = 2s$

Solubility product, $K_{sp} = s \times (2s)^2 = 4s^3$;

$s = 0.5 \times 10^{-4}$ mol/litre

$\therefore\ K_{sp} = 4 \times (0.5 \times 10^{-4})^3$; $K_{sp} = 5 \times 10^{-13}$

110. (b) : For reaction, $M_2S \rightleftharpoons \underset{2s}{2M^+} + \underset{s}{S^{2-}}$

Solubility $= 3.5 \times 10^{-6}$

Solubility product, $K_{sp} = [M^+]^2\,[S^{2-}]$

$= (2s)^2\,s = 4s^3 = 4 \times (3.5 \times 10^{-6})^3 = 1.7 \times 10^{-16}$

111. (d) : For CaF_2, decomposition is as follows :

$$CaF_2 \rightarrow \underset{s}{Ca^{2+}} + \underset{2s}{2F^-}$$

$\Rightarrow\ K_{sp} = [Ca^{2+}]\,[F^-]^2 = s \times (2s)^2$

or $K_{sp} = 4s^3 \Rightarrow K_{sp} = 4 \times (2 \times 10^{-4})^3$

$\Rightarrow\ K_{sp} = 32 \times 10^{-12}$

112. (b) : The greater the solubility product, the greater is the solubility.

113. (a) : There are greater number of Cl^- ions in $CaCl_2$ compared to others. Hence, solubility of AgCl will be minimum in 0.01M $CaCl_2$ due to common ion effect.

114. (d) : Higher the value of solubility product, greater is the solubility.

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CHAPTER
8

Redox Reactions

8.1 Classical Idea of Redox Reactions - Oxidation and Reduction Reactions

1. Which of the following is redox reaction?
   (a) Evaporation of H_2O
   (b) Both oxidation and reduction
   (c) H_2SO_4 with NaOH
   (d) In atmosphere O_3 from O_2 by lightning *(1997)*

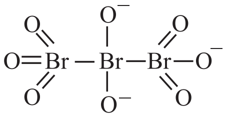
8.2 Redox Reactions in Terms of Electron Transfer Reactions

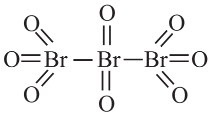
2. Without losing its concentration, $ZnCl_2$ solution cannot be kept in contact with
   (a) Pb (b) Al
   (c) Au (d) Ag *(1998)*

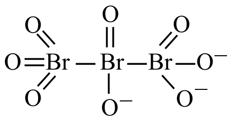
8.3 Oxidation Number

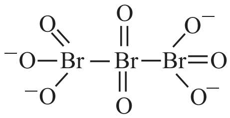
3. What is the change in oxidation number of carbon in the following reaction?
   $CH_{4(g)} + 4Cl_{2(g)} \rightarrow CCl_{4(l)} + 4HCl_{(g)}$
   (a) + 4 to + 4 (b) 0 to + 4
   (c) – 4 to + 4 (d) 0 to – 4 *(NEET 2020)*

4. The correct structure of tribromooctaoxide is

(a)


(b)


(c)


(d)


(NEET 2019)

5. Which of the following reactions are disproportionation reactions?
   (i) $2Cu^+ \longrightarrow Cu^{2+} + Cu^0$
   (ii) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$
   (iii) $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$
   (iv) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$
   Select the correct option from the following.
   (a) (i) and (iv) only (b) (i) and (ii) only
   (c) (i), (ii) and (iii) (d) (i), (iii) and (iv)
   (NEET 2019)

6. The oxidation state of Cr in CrO_5 is
   (a) −6 (b) +12
   (c) +6 (d) +4
   (Odisha NEET 2019, 2014)

7. The correct order of N-compounds in its decreasing order of oxidation states is
   (a) HNO_3, NO, N_2, NH_4Cl
   (b) HNO_3, NO, NH_4Cl, N_2
   (c) HNO_3, NH_4Cl, NO, N_2
   (d) NH_4Cl, N_2, NO, HNO_3 *(NEET 2018)*

8. For the redox reaction,
   $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$
   The correct coefficients of the reactants for the balanced equation are

	MnO_4^-	**$C_2O_4^{2-}$**	**H^+**
(a)	16	5	2
(b)	2	5	16
(c)	2	16	5
(d)	5	16	2

(NEET 2018)

9. Hot concentrated sulphuric acid is a moderately strong oxidizing agent. Which of the following reactions does not show oxidizing behaviour?
   (a) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
   (b) $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
   (c) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
   (d) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$ *(NEET-II 2016)*

10. (I) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
(II) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$
Role of hydrogen peroxide in the above reactions is respectively
(a) oxidizing in (I) and reducing in (II)
(b) reducing in (I) and oxidizing in (II)
(c) reducing in (I) and (II)
(d) oxidizing in (I) and (II) *(2014)*

11. The pair of compounds that can exist together is
(a) $FeCl_3$, $SnCl_2$ (b) $HgCl_2$, $SnCl_2$
(c) $FeCl_2$, $SnCl_2$ (d) $FeCl_3$, KI *(2014)*

12. A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. During the reaction which element undergoes maximum change in the oxidation number?
(a) S (b) H
(c) Cl (d) C *(2012)*

13. Oxidation numbers of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively
(a) +3, +6 and +5
(b) +5, +3 and +6
(c) –3, +6 and +6
(d) +5, +6 and +6 *(2009)*

14. Number of moles of MnO_4^- required to oxidize one mole of ferrous oxalate completely in acidic medium will be
(a) 7.5 moles (b) 0.2 moles
(c) 0.6 moles (d) 0.4 moles. *(2008)*

15. Which is the best description of the behaviour of bromine in the reaction given below?
$H_2O + Br_2 \rightarrow HOBr + HBr$
(a) Proton acceptor only
(b) Both oxidised and reduced
(c) Oxidised only
(d) Reduced only *(2004)*

16. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order
(a) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
(b) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$
(c) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$
(d) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$ *(2003)*

17. Oxidation state of Fe in Fe_3O_4 is
(a) $\frac{5}{4}$ (b) $\frac{4}{5}$
(c) $\frac{3}{2}$ (d) $\frac{8}{3}$ *(1999)*

18. Reaction of sodium thiosulphate with iodine gives
(a) tetrathionate ion (b) sulphide ion
(c) sulphate ion (d) sulphite ion. *(1996)*

19. The oxide, which cannot act as a reducing agent is
(a) CO_2 (b) ClO_2
(c) NO_2 (d) SO_2 *(1995)*

20. Which substance is serving as a reducing agent in the following reaction?
$14H^+ + Cr_2O_7^{2-} + 3Ni \rightarrow 7H_2O + 2Cr^{3+} + 3Ni^{2+}$
(a) H^+ (b) $Cr_2O_7^{2-}$
(c) H_2O (d) Ni *(1994)*

21. The oxidation state of I in $H_4IO_6^-$ is
(a) + 1 (b) – 1
(c) + 7 (d) + 5 *(1994)*

8.4 Redox Reactions and Electrode Processes

22. Consider the change in oxidation state of bromine corresponding to different emf values as shown in the given diagram :

$$\begin{tikzcd} BrO_4^- \arrow[r, "1.82\text{ V}"] & BrO_3^- \arrow[r, "1.5\text{ V}"] & HBrO \arrow[dl, dash, "1.595\text{ V}"] \\ Br^- & Br_2 \arrow[l, "1.0652\text{ V}"'] & \end{tikzcd}$$

Then the species undergoing disproportionation is
(a) BrO_3^- (b) BrO_4^-
(c) Br_2 (d) HBrO *(NEET 2018)*

ANSWER KEY

1. (b) **2.** (b) **3.** (c) **4.** (b) **5.** (b) **6.** (c) **7.** (a) **8.** (b) **9.** (d) **10.** (c)
11. (c) **12.** (c) **13.** (d) **14.** (d) **15.** (b) **16.** (a) **17.** (d) **18.** (a) **19.** (a) **20.** (d)
21. (c) **22.** (d)

Hints & Explanations

1. (b) : Redox reactions are those chemical reactions which involve both oxidation and reduction simultaneously.

2. (b) : Only 'Al' lies above 'Zn' in electrochemical series, which can displace Zn from $ZnCl_2$ solution. Therefore, conc. of $ZnCl_2$ will decrease when kept in 'Al' container.

$2Al + 3ZnCl_2 \rightarrow 2AlCl_3 + 3Zn$

3. (c) : In CH_4, oxidation number of carbon is −4 while in CCl_4, oxidation number of carbon is +4. Thus, the change in oxidation number of carbon in the given reaction is from −4 to +4.

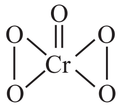
4. (b)

5. (b) : Disproportionation reactions are those in which the same element/compound gets oxidised and reduced simultaneously.

$2Cu^+ \rightarrow Cu^{2+} + Cu^0$

$3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow 2\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + 2H_2O$

6. (c) : CrO_5 has butterfly structure having two peroxo bonds.



Peroxo oxygen has −1 oxidation state.

Let oxidation state of Cr be 'x'

$CrO_5 : x + 4(-1) + 1\,(-2) = 0 \Rightarrow x = +6$

7. (a) : $H\overset{+5}{N}O_3,\ \overset{+2}{N}O,\ \overset{0}{N_2},\ \overset{-3}{N}H_4Cl$

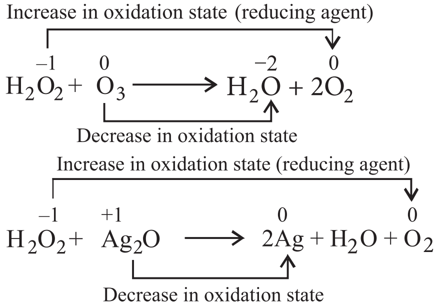
8. (b) : The correct balanced equation is

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

9. (d) : $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

Here, the oxidation state of every atom remains the same so, it is not a redox reaction.

10. (c) :



$H_2\overset{-1}{O_2} + \overset{0}{O_3} \longrightarrow H_2\overset{-2}{O} + 2\overset{0}{O_2}$

$H_2\overset{-1}{O_2} + \overset{+1}{Ag_2}O \longrightarrow 2\overset{0}{Ag} + H_2O + \overset{0}{O_2}$

H_2O_2 acts as reducing agent in both the reactions in which O_2 is evolved.

11. (c) : Both $FeCl_2$ and $SnCl_2$ are reducing agents with low oxidation numbers.

12. (c) : $\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3} + (COOH)_2 + H_2\overset{+6}{S}O_4 \longrightarrow K_2\overset{+6}{S}O_4 + K\overset{-1}{Cl} + CO_2 + H_2O$

Maximum change in oxidation number occurs in case of chlorine, *i.e.*, from +5 to −1.

13. (d) : Let oxidation number of P in PO_4^{3-} be x.

$\therefore\ x + 4(-2) = -3 \Rightarrow x = +5$

Let oxidation number of S in SO_4^{2-} be y.

$\therefore\ y + 4(-2) = -2 \Rightarrow y = +6$

Let oxidation number of Cr in $Cr_2O_7^{2-}$ be z.

$\therefore\ 2z + 7(-2) = -2 \Rightarrow z = +6$

14. (d) : $[5e^- + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \text{ ..(i)}] \times 2$

$[C_2O_4^{2-} \rightarrow 2e^- + 2CO_2 \text{ ....(ii)}] \times 5$

On addition, we get

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

2 moles of MnO_4^- required to oxidise 5 moles of oxalate.

$\therefore$ Number of moles of MnO_4^- required to oxidise 1 mole of oxalate = 2/5 = 0.4

15. (b) : $H_2O + \overset{0}{Br_2} \rightarrow HO\overset{+1}{Br} + H\overset{-1}{Br}$

In the above reaction, the oxidation number of Br_2 increases from zero (in Br_2) to +1 (in HOBr) and decreases from zero (in Br_2) to −1 (in HBr). Thus, Br_2 is oxidised as well as reduced and hence, it is a redox reaction.

16. (a) : $SO_3^{2-} : x + (-2)3 = -2$ or $x - 6 = -2$ or $x = +4$

$S_2O_4^{2-} : 2x + (-2)4 = -2$

or $2x - 8 = -2$ or $2x = +6 \therefore x = +3$

$S_2O_6^{2-} : 2x + (-2)6 = -2$

or $2x - 12 = -2$ or $2x = +10 \therefore x = +5$

Oxidation states follow the order : $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

17. (d) : $Fe_3O_4 : 3x + 4(-2) = 0 \Rightarrow x = +\frac{8}{3}$

18. (a) : $2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{(Sodium tetrathionate)}}{Na_2S_4O_6} + 2\,NaI$

19. (a) : Since carbon is in its maximum oxidation state of +4, therefore, carbon dioxide (CO_2) cannot act as a reducing agent.

20. (d) : Since the oxidation number of Ni increases from 0 to 2, therefore it acts as a reducing agent.

21. (c) : Let x = Oxidation state of I. Since oxidation state of H = + 1 and oxidation state of O = − 2, therefore for $H_4IO_6^-$, we get

$(4 \times 1) + x + (6 \times -2) = -1$ or $x = +7$

22. (d) : For a reaction to be spontaneous, E°_{cell} should be positive as $\Delta G^\circ = -nFE^\circ_{cell}$

$HBrO \longrightarrow Br_2 ; E^\circ = 1.595$ V, SRP (cathode)

$HBrO \longrightarrow BrO_3^- ; E^\circ = -1.5$ V, SOP (anode)

$2HBrO \longrightarrow Br_2 + BrO_3^-$

E°_{cell} = SRP (cathode) − SRP (anode)

= 1.595 − 1.5 = 0.095 V

$E^\circ_{cell} > 0 \Rightarrow \Delta G^\circ < 0$ (spontaneous)

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CHAPTER
9

Hydrogen

9.1 Position of Hydrogen in the Periodic Table

1. One would expect proton to have very large
(a) charge
(b) ionization potential
(c) hydration energy
(d) radius. *(1993)*

2. The ionization of hydrogen atom would give rise to
(a) hydride ion
(b) hydronium ion
(c) proton
(d) hydroxyl ion. *(1990)*

9.3 Preparation of Dihydrogen, H_2

3. Which one of the following pairs of substances on reaction will not evolve H_2 gas?
(a) Copper and HCl (aqueous)
(b) Iron and steam
(c) Iron and H_2SO_4 (aqueous)
(d) Sodium and ethyl alcohol *(1998)*

4. Water gas is produced by
(a) passing steam through a red hot coke
(b) saturating hydrogen with moisture
(c) mixing oxygen and hydrogen in the ratio of 1 : 2
(d) heating a mixture of CO_2 and CH_4 in petroleum refineries. *(1992)*

5. Which of the following metal evolves hydrogen on reacting with cold dilute HNO_3?
(a) Mg (b) Al
(c) Fe (d) Cu *(1989)*

9.4 Properties of Dihydrogen

6. Which of the following statements about hydrogen is incorrect?
(a) Hydronium ion, H_3O^+ exists freely in solution.
(b) Dihydrogen does not act as a reducing agent.
(c) Hydrogen has three isotopes of which tritium is the most common.
(d) Hydrogen never acts as cation in ionic salts. *(NEET-I 2016)*

9.5 Hydrides

7. Which of the following is electron-deficient?
(a) $(BH_3)_2$ (b) PH_3
(c) $(CH_3)_2$ (d) $(SiH_3)_2$ *(NEET 2013)*

9.6 Water

8. The method used to remove temporary hardness of water is
(a) synthetic resins method
(b) Calgon's method
(c) Clark's method
(d) ion-exchange method. *(NEET 2019)*

9. The number of hydrogen bonded water molecule(s) associated with $CuSO_4 . 5H_2O$ is
(a) 3 (b) 1
(c) 2 (d) 5
(Odisha NEET 2019)

10. Which of the following groups of ions makes the water hard?
(a) Sodium and bicarbonate
(b) Magnesium and chloride
(c) Potassium and sulphate
(d) Ammonium and chloride *(1994)*

11. At its melting point, ice is lighter than water because
(a) H_2O molecules are more closely packed in solid state
(b) ice crystals have hollow hexagonal arrangement of H_2O molecules
(c) on melting of ice the H_2O molecules shrinks in size
(d) ice forms mostly heavy water on first melting.
(1992)

9.7 Hydrogen Peroxide (H_2O_2)

12. Match the following and identify the correct option.

(A) $CO_{(g)} + H_{2(g)}$	(i) $Mg(HCO_3)_2 + Ca(HCO_3)_2$
(B) Temporary hardness of water	(ii) An electron deficient hydride
(C) B_2H_6	(iii) Synthesis gas
(D) H_2O_2	(iv) Non-planar structure

	(A)	(B)	(C)	(D)
(a)	(iii)	(i)	(ii)	(iv)
(b)	(iii)	(ii)	(i)	(iv)
(c)	(iii)	(iv)	(ii)	(i)
(d)	(i)	(iii)	(ii)	(iv)

(NEET 2020)

13. The structure of H_2O_2 is
(a) spherical (b) non-planar
(c) planar (d) linear. *(2003)*

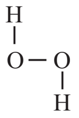
14. The volume strength of 1.5 N H_2O_2 solution is
(a) 8.8 (b) 8.4
(c) 4.8 (d) 5.2 *(1997,1996)*

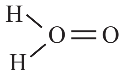
15. The O – O – H bond angle in H_2O_2 is
(a) 106° (b) 109°28′
(c) 120° (d) 97° *(1994)*

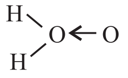
16. Hydrogen peroxide molecules are
(a) monoatomic and form X_2^{2-} ions
(b) diatomic and form X^- ions
(c) diatomic and form X_2^- ions
(d) monoatomic and form X^- ions. *(1991)*

17. Which of the following is the true structure of H_2O_2?

(a) H—O—O—H

(b) 

(c) 

(d) 

(1989)

18. The reaction of H_2O_2 with H_2S is an example of .... reaction.
(a) addition (b) oxidation
(c) reduction (d) acidic *(1988)*

9.8 Heavy Water, D_2O

19. Some statements about heavy water are given below.
(i) Heavy water is used as a moderator in nuclear reactors.
(ii) Heavy water is more associated than ordinary water.
(iii) Heavy water is more effective solvent than ordinary water.
Which of the above statements are correct?
(a) (i) and (ii) (b) (i), (ii) and (iii)
(c) (ii) and (iii) (d) (i) and (iii)
(Mains 2010)

ANSWER KEY

1.	(c)	**2.**	(c)	**3.**	(a)	**4.**	(a)	**5.**	(a)	**6.**	(b,c)	**7.**	(a)	**8.**	(c)	**9.**	(b)	**10.**	(b)
11.	(b)	**12.**	(a)	**13.**	(b)	**14.**	(b)	**15.**	(d)	**16.**	(b)	**17.**	(b)	**18.**	(b)	**19.**	(a)		

Hints & Explanations

1. (c) : Proton (H^+) ion being very small in size would have very large hydration energy.

2. (c) : It gives rise to proton.

$$H_{(g)} \rightarrow \underset{\text{Proton}}{H^+_{(aq)}} + e^-$$

3. (a) : Copper is a noble metal, as it lies below hydrogen in the electrochemical series. Therefore, it cannot displace hydrogen from dilute HCl. While iron and sodium lie above hydrogen in the electrochemical series, so they can liberate H_2 either from steam or H_2SO_4 solution.

$C_2H_5 - OH + Na \rightarrow C_2H_5 - ONa + 1/2H_2$

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$

4. (a) : $\underset{\text{Steam}}{H_2O} + \underset{\text{Red hot}}{C} \rightarrow \underbrace{H_2 + CO}_{\text{Water gas}}$

5. (a) : Mg reacts with nitric acid to give $Mg(NO_3)_2$ and evolves H_2 gas.

$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$

6. (b, c) : Dihydrogen acts as a powerful reducing agent and reduces metal oxides such as CuO, ZnO, PbO and Fe_3O_4 to their respective metals.

$CuO + H_2 \rightarrow Cu + H_2O$

$ZnO + H_2 \rightarrow Zn + H_2O$

$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$

Hydrogen has three isotopes of which protium is the most common and tritium is radioactive.

7. (a) : Boron hydrides are electron-deficient compounds.

8. (c) : Clark's process is used to remove temporary hardness of water. In this method quick lime is added. The bicarbonates present in temporary hard water react with lime water to form insoluble calcium and magnesium carbonates which can be easily filtered off.

$$\underset{\text{Quick lime}}{CaO} + H_2O \longrightarrow \underset{\text{Lime water}}{Ca(OH)_2}$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$$

9. (b) : The ionic formulation of $CuSO_4.5H_2O$ is $[Cu(H_2O)_4]H_2O{\cdot}SO_4$, in which four H_2O molecules are coordinated to a central Cu^{2+} ion while the fifth H_2O molecule is hydrogen bonded to sulphate group.

10. (b) : Hardness of water is due to the presence of bicarbonates, chlorides and sulphates of Ca and Mg. Hence, hard water will consist of Mg^{2+} and Cl^- ions.

11. (b) : In ice crystals, water molecules are linked through H-bonds in hollow hexagonal arrangement so, volume is large and density is less. In liquid state this hollow arrangement breaks into more closer arrangement of molecules. Consequently the density is increased in liquid state.

12. (a)

13. (b) : Hydrogen peroxide has a non-planar structure.

14. (b) : Normality (*N*) = 1.5

We know that equivalent weight of H_2O_2 is 17 and strength of H_2O_2 = Normality × Equivalent weight

$= 1.5 \times 17 = 25.5$

$$\underset{(2 \times 34 = 68\ g)}{2H_2O_2} \rightarrow 2H_2O + \underset{(22.4\ L)}{O_2}$$

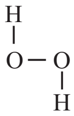
Since 68 grams of H_2O_2 produces 22.4 litres oxygen at NTP, therefore, 25.5 grams of H_2O_2 will produce

$$= \frac{22.4}{68} \times 25.5 = 8.4 \text{ litre of oxygen.}$$

Thus, volume strength of given H_2O_2 solution is 8.4.

15. (d) : Bond angle of O – O – H in H_2O_2 is 97°.

16. (b) : H_2O_2 is diatomic and forms $H^+ + HO_2^-$ (X^-) (hydroperoxide ion).

17. (b) : 

$$\overset{\displaystyle H}{\overset{|}{O}}-\underset{\displaystyle H}{\underset{|}{O}}$$

is the true structure of H_2O_2.

18. (b) : It is an example of oxidation reaction.

$H_2S + H_2O_2 \rightarrow 2H_2O + S$

H_2O_2 oxidises H_2S into S.

19. (a) : Heavy water is used for slowing down the speed of neutrons in nuclear reactors, hence used as moderator. Boiling point of heavy water is greater (374.42 K) than that of ordinary water (373 K), hence heavy water is more associated. Dielectric constant of ordinary water is greater than that of heavy water, hence ordinary water is a better solvent.

❖❖❖

CHAPTER

10

The *s*-Block Elements

10.1 Group 1 Elements : Alkali Metals

1. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field?

(a) K (b) Rb
(c) Li (d) Na *(NEET 2017)*

2. Which one of the alkali metals, forms only, the normal oxide, M_2O on heating in air?

(a) Rb (b) K
(c) Li (d) Na *(2012)*

3. The ease of adsorption of the hydrated alkali metal ions on an ion-exchange resins follows the order

(a) $Li^+ < K^+ < Na^+ < Rb^+$
(b) $Rb^+ < K^+ < Na^+ < Li^+$
(c) $K^+ < Na^+ < Rb^+ < Li^+$
(d) $Na^+ < Li^+ < K^+ < Rb^+$ *(2012)*

4. The sequence of ionic mobility in aqueous solution is

(a) $Rb^+ > K^+ > Cs^+ > Na^+$
(b) $Na^+ > K^+ > Rb^+ > Cs^+$
(c) $K^+ > Na^+ > Rb^+ > Cs^+$
(d) $Cs^+ > Rb^+ > K^+ > Na^+$ *(2008)*

5. When a substance (*A*) reacts with water it produces a combustible gas (*B*) and a solution of substance (*C*) in water. When another substance (*D*) reacts with this solution of (*C*), it also produces the same gas (*B*) on warming but (*D*) can produce gas (*B*) on reaction with dilute sulphuric acid at room temperature. Substance (*A*) imparts a deep golden yellow colour to a smokeless flame of Bunsen burner. Then (*A*), (*B*), (*C*) and (*D*) respectively are

(a) Ca, H_2, $Ca(OH)_2$, Sn
(b) K, H_2, KOH, Al
(c) Na, H_2, NaOH, Zn
(d) CaC_2, C_2H_2, $Ca(OH)_2$, Fe *(1998)*

6. Which one of the following properties of alkali metals increases in magnitude as the atomic number rises?

(a) Ionic radius (b) Melting point
(c) Electronegativity
(d) First ionization energy *(1989)*

10.2 General Characteristics of the Compounds of the Alkali Metals

7. In the case of alkali metals, the covalent character decreases in the order

(a) $MF > MCl > MBr > MI$
(b) $MF > MCl > MI > MBr$
(c) $MI > MBr > MCl > MF$
(d) $MCl > MI > MBr > MF$ *(2009)*

8. The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders?

(a) NaH > LiH > KH > RbH > CsH
(b) LiH > NaH > KH > RbH > CsH
(c) CsH > RbH > KH > NaH > LiH
(d) KH > NaH > LiH > CsH > RbH *(2008)*

9. Which compound will show the highest lattice energy?

(a) RbF (b) CsF
(c) NaF (d) KF *(1993)*

10.3 Anomalous Properties of Lithium

10. Which of the alkali metal chloride (*M*Cl) forms its dihyrate salt ($MCl.2H_2O$) easily ?

(a) LiCl (b) CsCl
(c) RbCl (d) KCl
(Odisha NEET 2019)

10.4 Some Important Compounds of Sodium

11. Crude sodium chloride obtained by crystallisation of brine solution does not contain

(a) $MgSO_4$ (b) Na_2SO_4
(c) $MgCl_2$ (d) $CaSO_4$
(Odisha NEET 2019)

12. In Castner-Kellner cell for production of sodium hydroxide
(a) brine is electrolyzed using graphite electrodes
(b) molten sodium chloride is electrolysed
(c) sodium amalgam is formed at mercury cathode
(d) brine is electrolyzed with Pt electrodes.
(Karnataka NEET 2013)

13. Which of the following statements is incorrect?
(a) Pure sodium metal dissolves in liquid ammonia to give blue solution.
(b) NaOH reacts with glass to give sodium silicate.
(c) Aluminium reacts with excess NaOH to give $Al(OH)_3$.
(d) $NaHCO_3$ on heating gives Na_2CO_3.
(Mains 2011)

14. In which of the following processes, fused sodium hydroxide is electrolysed at a 330 °C temperature for extraction of sodium?
(a) Castner's process (b) Down's process
(c) Cyanide process (d) Both (b) and (c).
(2000)

15. Which of the following is known as fusion mixture?
(a) Mixture of $Na_2CO_3 + NaHCO_3$
(b) $Na_2CO_3.10H_2O$
(c) Mixture of $K_2CO_3 + Na_2CO_3$
(d) $NaHCO_3$ *(1994)*

16. Washing soda has formula
(a) $Na_2CO_3.7H_2O$ (b) $Na_2CO_3.10H_2O$
(c) $Na_2CO_3.3H_2O$ (d) Na_2CO_3 *(1990)*

10.5 Biological Importance of Sodium and Potassium

17. The following metal ion activates many enzymes, participates in the oxidation of glucose to produce ATP and with Na, is responsible for the transmission of nerve signals.
(a) Iron (b) Copper
(c) Calcium (d) Potassium
(NEET 2020)

18. The function of "Sodium pump" is a biological process operating in each and every cell of all animals. Which of the following biologically important ions is also a constituent of this pump?
(a) K^+ (b) Fe^{2+}
(c) Ca^{2+} (d) Mg^{2+} *(2015, Cancelled)*

10.6 Group 2 Elements : Alkaline Earth Metals

19. Magnesium reacts with an element (X) to form an ionic compound. If the ground state electronic configuration of (X) is $1s^2\ 2s^2\ 2p^3$, the simplest formula for this compound is
(a) Mg_2X_3 (b) MgX_2
(c) Mg_2X (d) Mg_3X_2 *(NEET 2018)*

20. Electronic configuration of calcium atom may be written as
(a) $[Ne]\ 4p^2$ (b) $[Ar]\ 4s^2$
(c) $[Ne]\ 4s^2$ (d) $[Ar]\ 4p^2$ *(1992)*

21. Compared with the alkaline earth metals, the alkali metals exhibit
(a) smaller ionic radii
(b) highest boiling points
(c) greater hardness
(d) lower ionization energies. *(1990)*

22. Which of the following atoms will have the smallest size?
(a) Mg (b) Na
(c) Be (d) Li *(1989)*

10.7 General Characteristics of Compounds of Alkaline Earth Metals

23. HCl was passed through a solution of $CaCl_2$, $MgCl_2$ and NaCl. Which of the following compound(s) crystallise(s)?
(a) Both $MgCl_2$ and $CaCl_2$
(b) Only NaCl
(c) Only $MgCl_2$
(d) NaCl, $MgCl_2$ and $CaCl_2$ *(NEET 2020)*

24. Which of the following is an amphoteric hydroxide?
(a) $Be(OH)_2$ (b) $Sr(OH)_2$
(c) $Ca(OH)_2$ (d) $Mg(OH)_2$
(NEET 2019)

25. Among CaH_2, BeH_2, BaH_2, the order of ionic character is
(a) $BeH_2 < CaH_2 < BaH_2$
(b) $CaH_2 < BeH_2 < BaH_2$
(c) $BeH_2 < BaH_2 < CaH_2$
(d) $BaH_2 < BeH_2 < CaH_2$ *(NEET 2018)*

26. On heating which of the following releases CO_2 most easily?
(a) Na_2CO_3 (b) $MgCO_3$
(c) $CaCO_3$ (d) K_2CO_3 *(2015)*

27. Solubility of the alkaline earth metal sulphates in water decreases in the sequence
(a) Sr > Ca > Mg > Ba (b) Ba > Mg > Sr > Ca
(c) Mg > Ca > Sr > Ba (d) Ca > Sr > Ba > Mg
(2015, Cancelled)

28. Which of the following compounds has the lowest melting point?
(a) $CaCl_2$ (b) $CaBr_2$
(c) CaI_2 (d) CaF_2 *(2011)*

29. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy?
(a) $CaSO_4$ (b) $BeSO_4$
(c) $BaSO_4$ (d) $SrSO_4$ *(2010)*

30. Which one of the following compounds is a peroxide?
(a) KO_2 (b) BaO_2
(c) MnO_2 (d) NO_2 *(2010)*

31. Property of the alkaline earth metals that increases with their atomic number
(a) solubility of their hydroxides in water
(b) solubility of their sulphates in water
(c) ionization energy
(d) electronegativity *(2010)*

32. Which of the following oxides is not expected to react with sodium hydroxide?
(a) CaO (b) SiO_2
(c) BeO (d) B_2O_3 *(2009)*

33. The correct order of increasing thermal stability of K_2CO_3, $MgCO_3$, $CaCO_3$ and $BeCO_3$ is
(a) $BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$
(b) $MgCO_3 < BeCO_3 < CaCO_3 < K_2CO_3$
(c) $K_2CO_3 < MgCO_3 < CaCO_3 < BeCO_3$
(d) $BeCO_3 < MgCO_3 < K_2CO_3 < CaCO_3$ *(2007)*

34. In which of the following the hydration energy is higher than the lattice energy?
(a) $MgSO_4$ (b) $RaSO_4$
(c) $SrSO_4$ (d) $BaSO_4$ *(2007)*

35. The solubility in water of sulphate down the Be group is Be > Mg > Ca > Sr > Ba. This is due to
(a) decreasing lattice energy
(b) high heat of solvation for smaller ions like Be^{2+}
(c) increase in melting points
(d) increasing molecular weight. *(1995)*

36. All the following substances react with water. The pair that gives the same gaseous product is
(a) K and KO_2 (b) Na and Na_2O_2
(c) Ca and CaH_2 (d) Ba and BaO_2. *(1994)*

37. Which of the following statement is false?
(a) Strontium decomposes water readily than beryllium.
(b) Barium carbonate melts at a higher temperature than calcium carbonate.
(c) Barium hydroxide is more soluble in water than magnesium hydroxide.
(d) Beryllium hydroxide is more basic than barium hydroxide. *(1994)*

10.8 Anomalous Behaviour of Beryllium

38. In context with beryllium, which one of the following statements is incorrect?
(a) It is rendered passive by nitric acid.
(b) It forms Be_2C.
(c) Its salts rarely hydrolyse.
(d) Its hydride is electron-deficient and polymeric. *(NEET-II 2016)*

10.9 Some Important Compounds of Calcium

39. The suspension of slaked lime in water is known as
(a) lime water (b) quick lime
(c) milk of lime
(d) aqueous solution of slaked lime. *(NEET-II 2016)*

40. The product obtained as a result of a reaction of nitrogen with CaC_2 is
(a) $CaCN_3$ (b) Ca_2CN
(c) $Ca(CN)_2$ (d) CaCN *(NEET-I 2016)*

41. Which one of the following is present as an active ingredient in bleaching powder for bleaching action?
(a) $CaOCl_2$ (b) $Ca(OCl)_2$
(c) CaO_2Cl (d) $CaCl_2$ *(2011)*

42. Match List-I with List-II for the compositions of substances and select the correct answer using the code given :

List-I (Substances)	**List-II (Composition)**
(A) Plaster of Paris	(i) $CaSO_4 \cdot 2H_2O$
(B) Epsomite	(ii) $CaSO_4 \cdot 1/2\ H_2O$
(C) Kieserite	(iii) $MgSO_4 \cdot 7H_2O$
(D) Gypsum	(iv) $MgSO_4 \cdot H_2O$
	(v) $CaSO_4$

(a) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)
(b) (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i)
(c) (A)-(i), (B)-(ii), (C)-(iii), (D)-(v)
(d) (A)-(iv), (B)-(iii), (C)-(ii), (D)-(i) *(Mains 2011)*

43. The compound *A* on heating gives a colourless gas and a residue that is dissolved in water to obtain *B*. Excess of CO_2 is bubbled through aqueous solution of *B*, *C* is formed which is recovered in the solid form. Solid *C* on gentle heating gives back *A*. The compound is
(a) $CaCO_3$ (b) Na_2CO_3
(c) K_2CO_3 (d) $CaSO_4 \cdot 2H_2O$
(Mains 2010)

44. Which of the following represents calcium chlorite?
(a) $Ca(ClO_3)_2$ (b) $Ca(ClO_2)_2$
(c) $CaClO_2$ (d) $Ca(ClO_4)_2$ *(1996)*

45. Identify the correct statement.
(a) Plaster of Paris can be obtained by hydration of gypsum.
(b) Plaster of Paris is obtained by partial oxidation of gypsum.
(c) Gypsum contains a lower percentage of calcium than Plaster of Paris.
(d) Gypsum is obtained by heating Plaster of Paris. *(1995)*

46. Bleaching powder is obtained by the action of chlorine gas and
(a) dilute solution of $Ca(OH)_2$
(b) concentrated solution of $Ca(OH)_2$
(c) dry CaO
(d) dry slaked lime. *(1988)*

10.10 Biological Importance of Magnesium and Calcium

47. Enzymes that utilize ATP in phosphate transfer require an alkaline earth metal (M) as the cofactor. M is
(a) Sr (b) Be
(c) Mg (d) Ca *(NEET 2019)*

48. Which of the following statements is false?
(a) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
(b) Mg^{2+} ions are important in the green parts of the plants.
(c) Mg^{2+} ions form a complex with ATP.
(d) Ca^{2+} ions are important in blood clotting. *(NEET-I 2016)*

49. Which of the following metal ions play an important role in muscle contraction?
(a) K^+ (b) Na^+
(c) Mg^{2+} (d) Ca^{2+} *(1994)*

ANSWER KEY

1.	(c)	**2.**	(c)	**3.**	(b)	**4.**	(d)	**5.**	(c)	**6.**	(a)	**7.**	(c)	**8.**	(b)	**9.**	(c)	**10.**	(a)
11.	(a)	**12.**	(c)	**13.**	(c)	**14.**	(a)	**15.**	(c)	**16.**	(b)	**17.**	(d)	**18.**	(a)	**19.**	(d)	**20.**	(b)
21.	(d)	**22.**	(c)	**23.**	(b)	**24.**	(a)	**25.**	(a)	**26.**	(b)	**27.**	(c)	**28.**	(c)	**29.**	(b)	**30.**	(b)
31.	(a)	**32.**	(a)	**33.**	(a)	**34.**	(a)	**35.**	(b)	**36.**	(c)	**37.**	(d)	**38.**	(c)	**39.**	(c)	**40.**	(c)
41.	(b)	**42.**	(b)	**43.**	(a)	**44.**	(b)	**45.**	(c)	**46.**	(d)	**47.**	(c)	**48.**	(a)	**49.**	(d)		

Hints & Explanations

1. (c) : The hydration enthalpy of alkali metal ions decreases with increase in ionic sizes *i.e.*,
$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
Hence, lithium having maximum degree of hydration will be least mobile.
The order of ionic mobility is
$[Li_{(aq)}]^+ < [Na_{(aq)})]^+ < [K_{(aq)}]^+ < [Rb_{(aq)}]^+$

2. (c) : When alkali metals heated in atmosphere of oxygen, the alkali metals ignite and form oxides. On combustion Li forms Li_2O; sodium gives the peroxide Na_2O_2 and potassium and rubidium give superoxide (MO_2).

3. (b) : The order of decreasing hydration enthalpy of alkali metal ions is : $Li^+ > Na^+ > K^+ > Rb^+$
Thus, ease of adsorption of hydrated ions is in the order :
$Rb^+ < K^+ < Na^+ < Li^+$.

4. (d) : Smaller the size of cation, higher will be the hydration and its effective size will increase and hence mobility in aqueous solution will decrease. Hence, the correct sequence of ionic mobility in aqueous solution of the given cations is $Cs^+ > Rb^+ > K^+ > Na^+$.

5. (c) : Only 'Na' imparts golden colour to Bunsen flame, therefore, A = Na, B = H_2, C = NaOH, D = Zn.

$$\underset{(A)}{2Na} + 2H_2O \rightarrow \underset{(C)}{2NaOH} + \underset{(B)}{H_2}$$

$$\underset{(D)}{Zn} + \underset{(C)}{2NaOH} \rightarrow Na_2ZnO_2 + \underset{(B)}{H_2}$$

$$\underset{(D)}{Zn} + H_2SO_4(\text{dil.}) \rightarrow ZnSO_4 + \underset{(B)}{H_2}$$

6. (a) : In a group, ionic radius increases with increase in atomic number whereas the m.pt. decreases down in a group due to weakening of metallic bonds. Similarly, electronegativity and ionization energy also decrease down the group.

7. (c) : Alkali metals are highly electropositive and halogens are electronegative. Thus, for the halides of a given alkali metal, the covalent character decreases with increase in electronegativity of halogens.

∴ Order of covalent character of halides is
$MI > MBr > MCl > MF$.

8. (b) : The ionic character of the bonds in hydrides increases from LiH to CsH due to weakening of M—H bond so, thermal stability of these hydrides decreases in the order of LiH > NaH > KH > RbH > CsH.

9. (c) : With the same anion, smaller the size of the cation, higher is the lattice energy. Therefore, NaF will show the highest lattice energy among the given compounds.

10. (a) : LiCl is deliquescent and crystallises from aqueous solution as hydrates, $LiCl.2H_2O$.

11. (a) : Crude sodium chloride, generally obtained by crystallisation of brine solution contains sodium sulphate (Na_2SO_4), calcium sulphate ($CaSO_4$), calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) as impurities. Crude sodium chloride does not contain $MgSO_4$.

12. (c) : In Castner-Kellner cell, sodium amalgam is formed at mercury cathode.
A brine solution is electrolysed using a mercury cathode and a carbon anode.

13. (c) : Al reacts with NaOH to give sodium aluminate.

14. (a) : In Castner's process, for production of sodium metal, sodium hydroxide (NaOH) is electrolysed at temperature 330 °C.

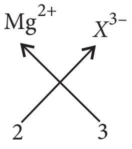
15. (c) : K_2CO_3 and Na_2CO_3 mixture is called as fusion mixture.

16. (b) : $Na_2CO_3.10H_2O$ is washing soda.

17. (d) : Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

18. (a)

19. (d) : Electronic configuration of X is $1s^2, 2s^2\,2p^3$.
So, valency of X will be 3.
Magnesium ion = Mg^{2+}



Formula : Mg_3X_2

20. (b) : $_{20}Ca \longrightarrow 1s^2, 2s^22p^6, 3s^23p^6, 4s^2$
$_{18}Ar \longrightarrow 1s^2, 2s^22p^6, 3s^23p^6$
Hence, $_{20}Ca \longrightarrow [Ar]4s^2$

21. (d) : The alkali metals are larger in size and have smaller nuclear charge thus they have lower ionization energy in comparison to alkaline earth metals.

22. (c) : The atomic size decreases within a period from left to right, therefore Li > Be and Na > Mg. The size increases in a group from top to bottom. Hence, the size of Na is greater than Li. Overall order Na > Mg > Li > Be. Thus, Be has smallest size.

23. (b) : $CaCl_2$ and $MgCl_2$ are more soluble than NaCl. Thus, when HCl was passed through a solution containing $CaCl_2$, $MgCl_2$ and NaCl, only NaCl got crystallised.

24. (a) : $Be(OH)_2$ is amphoteric in nature as it reacts with acid and alkali both.
$Be(OH)_2 + 2OH^- \rightarrow [Be(OH)_4]^{2-}$
$Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$

25. (a) : $BeH_2 < CaH_2 < BaH_2$
On moving down the group, metallic character of metals increases. So, ionic character of metal hydrides increases. Hence, BeH_2 will be least ionic.

26. (b) : Stability of carbonates increases down the group with increase in the size of metal ion. Also the alkali metal carbonates are more stable than alkaline earth metal carbonates.
Hence, $MgCO_3$ is least stable and it releases CO_2 most easily.

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

27. (c) : Solubility of alkaline earth metal sulphates decreases down the group because hydration energy decreases.

28. (c) : As the covalent character in compound increases and ionic character decreases, melting point of the compound decreases. So, CaI_2 has the highest covalent character and lowest melting point.

29. (b) : The hydration enthalpy of $BeSO_4$ is higher than its lattice energy. Within group 2, the hydration energy decreases down the group while lattice energy is almost the same.

30. (b) : BaO_2 has peroxide linkage.

31. (a) : The solubility of an ionic compound depends on two factors :
(a) lattice energy, and (b) hydration energy
In case of alkaline earth metal hydroxides, the lattice energy decreases as we move down the group. This decrease is more than the decrease in the hydration energy down the group.

32. (a) : CaO being a basic oxide does not react with NaOH, however SiO_2 (acidic oxide), BeO (amphoteric oxide) and B_2O_3 (acidic oxide) react with NaOH.

33. (a) : In all cases, for a particular set of group 1 or group 2 compounds, the thermal stability increases down the group as the ionic radius of the cation increases, and its polarising power decreases.

Group 1 compounds tend to be more thermally stable than group 2 compounds because group 1 cation has a smaller charge and a larger ionic radius, and so, a lower polarising power, particularly when adjacent metals on the same period are compared.

Hence, the order of increasing thermal stability of K_2CO_3, $MgCO_3$, $CaCO_3$ and $BeCO_3$ is

$BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$.

34. (a) : When hydration energy exceeds lattice energy, the compound becomes soluble in water. The solubility of alkaline earth metal sulphates decreases in the order :

$$\underset{\text{very high}}{BeSO_4} > \underset{\text{high}}{MgSO_4} > \underset{\text{sparingly soluble}}{CaSO_4} > \underbrace{SrSO_4 > BaSO_4 > RaSO_4}_{\text{almost insoluble}}$$

The solubilities of $BeSO_4$ and $MgSO_4$ are due to high energy of solvation of smaller Be^{2+} and Mg^{2+} ions.

35. (b) : As we move down the group from $BeSO_4$ to $BaSO_4$, the enthalpy of hydration of the positive ion becomes smaller due to increase in ionic size. Salts of heavier metal ions are less soluble than those of lighter ions.

36. (c) : The pair which gives the same gaseous product is Ca and CaH_2.

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

Whereas, K gives H_2 while KO_2 gives O_2 and H_2O_2.

$2K + 2H_2O \rightarrow 2KOH + H_2$

$2KO_2 + 2H_2O \rightarrow 2KOH + O_2 + H_2O_2$

Similarly, Na gives H_2, while Na_2O_2 gives H_2O_2.

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$

Likewise Ba gives H_2 while BaO_2 gives H_2O_2.

$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$

$BaO_2 + 2H_2O \rightarrow Ba(OH)_2 + H_2O_2$

37. (d) : Beryllium hydroxide although amphoteric, is however less basic than barium hydroxide.

38. (c) : Due to very small size of Be^{2+}, beryllium salts are readily hydrolysed because of high hydration energy.

$BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$

39. (c) : $\underset{\text{Quick lime}}{CaO} + H_2O \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2} + \text{Heat}$

This process is known as slaking of lime.

The paste of lime in water (*i.e.*, suspension) is called milk of lime while the filtered and clear solution is known as lime water.

40. (c) : Read $Ca(CN)_2$ as $CaCN_2$.

$CaC_2 + N_2 \longrightarrow \underset{\text{Nitrolim}}{CaCN_2} + C$

41. (b) : Active ingredient in bleaching powder for bleaching action is $Ca(OCl)_2$.

42. (b) : Plaster of Paris - $CaSO_4 \cdot \frac{1}{2} H_2O$

Epsomite - $MgSO_4 \cdot 7H_2O$

Kieserite - $MgSO_4 \cdot H_2O$

Gypsum - $CaSO_4 \cdot 2H_2O$

43. (a) : The reactions can be summarised as follows :

$A \xrightarrow{\Delta}$ colourless gas + residue

$\text{Residue} + H_2O \rightarrow B \xrightarrow{\text{excess } CO_2} C \xrightarrow{\Delta} A$

This is possible only when *A* is $CaCO_3$. The reactions are as follows :

$$\underset{(A)}{CaCO_3} \xrightarrow{\Delta} \underset{\text{(colourless gas)}}{CO_2} + \underset{\text{(residue)}}{CaO}$$

$$CaO + H_2O \longrightarrow \underset{(B)}{Ca(OH)_2} \xrightarrow[\text{(excess)}]{CO_2}$$

$$\underset{(C)}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{(A)}{CaCO_3}$$

44. (b) : Since the valency of calcium is 2 and a chlorite ion is ClO_2^-, therefore calcium chlorite is $Ca(ClO_2)_2$.

45. (c) : Gypsum is $CaSO_4 \cdot 2H_2O$ and Plaster of Paris is $(CaSO_4)_2 \cdot H_2O$. Therefore, gypsum contains a lower percentage of calcium than Plaster of Paris.

46. (d) : Cl_2 gas reacts with dry slaked lime, $Ca(OH)_2$ to give bleaching powder.

$Ca(OH)_2 + Cl_2 \xrightarrow{\Delta} CaOCl_2 + H_2O$

47. (c) : All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor.

48. (a) : Ca^{2+} ions are required to trigger the contraction of muscles and to maintain the regular beating of the heart.

49. (d) : Calcium is an essential element for the contraction of muscles.

* * *

CHAPTER

11

The *p*-Block Elements

11.1 Group 13 Elements : The Boron Family

1. The correct order of atomic radii in group 13 elements is
(a) B < Al < In < Ga < Tl
(b) B < Al < Ga < In < Tl
(c) B < Ga < Al < Tl < In
(d) B < Ga < Al < In < Tl *(NEET 2018)*

2. AlF_3 is soluble in HF only in presence of KF. It is due to the formation of
(a) $K_3[AlF_3H_3]$ (b) $K_3[AlF_6]$
(c) AlH_3 (d) $K[AlF_3H]$
(NEET-II 2016)

3. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence
(a) Al < Ga < In < Tl (b) Tl < In < Ga < Al
(c) In < Tl < Ga < Al (d) Ga < In < Al < Tl
(2015, 2009)

4. Aluminium(III) chloride forms a dimer because aluminium
(a) belongs to 3rd group
(b) can have higher coordination number
(c) cannot form a trimer
(d) has high ionization energy. *(1995)*

11.2 Important Trends and Anomalous Properties of Boron

5. Which one of the following elements is unable to form MF_6^{3-} ion?
(a) Ga (b) Al
(c) B (d) In *(NEET 2018)*

6. The tendency of BF_3, BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence
(a) $BCl_3 > BF_3 > BBr_3$
(b) $BBr_3 > BCl_3 > BF_3$
(c) $BBr_3 > BF_3 > BCl_3$
(d) $BF_3 > BCl_3 > BBr_3$ *(2010)*

7. Boron compounds behave as Lewis acids, because of their
(a) ionisation property
(b) electron deficient nature
(c) acidic nature
(d) covalent nature. *(1996)*

11.3 Some Important Compounds of Boron

8. Boric acid is an acid because its molecule
(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water, molecule.
(NEET-II 2016)

9. Which of the following structure is similar to graphite?
(a) B_4C (b) B_2H_6
(c) BN (d) B *(NEET 2013)*

10. The type of hybridisation of boron in diborane is
(a) sp^3-hybridisation (b) sp^2-hybridisation
(c) sp-hybridisation (d) sp^3d^2-hybridisation.
(1999)

11. Which of the following statements about H_3BO_3 is not correct?
(a) It has a layer structure in which planar BO_3 units are joined by hydrogen bonds.
(b) It does not act as proton donor but acts as a Lewis acid by accepting hydroxyl ion.
(c) It is a strong tribasic acid.
(d) It is prepared by acidifying an aqueous solution of borax. *(1994)*

11.5 Group 14 Elements : The Carbon Family

12. Which of the following is incorrect statement?
(a) SnF_4 is ionic in nature.
(b) PbF_4 is covalent in nature.
(c) $SiCl_4$ is easily hydrolysed.
(d) GeX_4 (X = F, Cl, Br, I) is more stable than GeX_2.
(NEET 2019)

13. Which of the following species is not stable?

(a) $[SiCl_6]^{2-}$ (b) $[SiF_6]^{2-}$

(c) $[GeCl_6]^{2-}$ (d) $[Sn(OH)_6]^{2-}$

(NEET 2019)

14. It is because of inability of *ns*^{2} electrons of the valence shell to participate in bonding that

(a) Sn^{2+} is oxidising while Pb^{4+} is reducing

(b) Sn^{2+} and Pb^{2+} are both oxidising and reducing

(c) Sn^{4+} is reducing while Pb^{4+} is oxidising

(d) Sn^{2+} is reducing while Pb^{4+} is oxidising.

(NEET 2017)

15. Which of the following oxidation states are the most characteristic for lead and tin respectively?

(a) +2, +4 (b) +4, +4

(c) +2, +2 (d) +4, +2 *(2007)*

16. Carbon and silicon belong to (IV) group. The maximum coordination number of carbon in commonly occurring compounds is 4, whereas that of silicon is 6. This is due to

(a) availability of low lying *d*-orbitals in silicon

(b) large size of silicon

(c) more electropositive nature of silicon

(d) both (b) and (c). *(1994)*

11.7 Allotropes of Carbon

17. Which of the following does not show electrical conduction?

(a) Diamond (b) Graphite

(c) Potassium (d) Sodium *(1999)*

18. Percentage of lead in lead pencil is

(a) 80 (b) 20

(c) zero (d) 70 *(1999)*

19. In graphite, electrons are

(a) localised on each C-atom

(b) localised on every third C-atom

(c) spread out between the structure

(d) present in antibonding orbital. *(1997, 1993)*

20. Which of the following types of forces bind together the carbon atoms in diamond?

(a) Ionic (b) Covalent

(c) Dipolar (d) van der Waals *(1992)*

21. Which of the following is an insulator?

(a) Graphite (b) Aluminium

(c) Diamond (d) Silicon *(1992)*

11.8 Some Important Compounds of Carbon and Silicon

22. Identify the correct statements from the following :

(A) $CO_{2(g)}$ is used as refrigerant for ice-cream and frozen food.

(B) The structure of C_{60} contains twelve six carbon rings and twenty five carbon rings.

(C) ZSM-5, a type of zeolite, is used to convert alcohols into gasoline.

(D) CO is colourless and odourless gas.

(a) (A), (B) and (C) only

(b) (A) and (C) only

(c) (B) and (C) only

(d) (C) and (D) only *(NEET 2020)*

23. Which of the following compounds is used in cosmetic surgery?

(a) Silica (b) Silicates

(c) Silicones (d) Zeolites

(Odisha NEET 2019)

24. Which of these is not a monomer for a high molecular mass silicone polymer?

(a) Me_3SiCl (b) $PhSiCl_3$

(c) $MeSiCl_3$ (d) Me_2SiCl_2

(NEET 2013)

25. The basic structural unit of silicates is

(a) SiO_3^{2-} (b) SiO_4^{2-}

(c) SiO^- (d) SiO_4^{4-} *(NEET 2013)*

26. Which statement is wrong?

(a) Beryl is an example of cyclic silicate.

(b) Mg_2SiO_4 is orthosilicate.

(c) Basic structural unit in silicates is the SiO_4 tetrahedron.

(d) Feldspars are not aluminosilicates.

(Karnataka NEET 2013)

27. Name the two types of the structure of silicate in which one oxygen atom of $[SiO_4]^{4-}$ is shared?

(a) Linear chain silicate (b) Sheet silicate

(c) Pyrosilicate (d) Three dimensional

(2011)

28. The straight chain polymer is formed by

(a) hydrolysis of CH_3SiCl_3 followed by condensation polymerisation

(b) hydrolysis of $(CH_3)_4Si$ by addition polymerisation

(c) hydrolysis of $(CH_3)_2SiCl_2$ followed by condensation polymerisation

(d) hydrolysis of $(CH_3)_3SiCl$ followed by condensation polymerisation. *(2009)*

29. Which of the following anions is present in the chain structure of silicates?

(a) $(Si_2O_5^{2-})_n$ (b) $(SiO_3^{2-})_n$

(c) SiO_4^{4-} (d) $Si_2O_7^{6-}$ *(2007)*

30. Which one of the following statements about the zeolite is false?

(a) They are used as cation exchangers.

(b) They have open structure which enables them to take up small molecules.

(c) Zeolites are aluminosilicates having three dimensional network.

(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites. *(2004)*

31. The substance used as a smoke screen in warfare is

(a) $SiCl_4$ (b) PH_3

(c) PCl_5 (d) acetylene. *(1989)*

ANSWER KEY

1.	(d)	**2.**	(b)	**3.**	(a)	**4.**	(b)	**5.**	(c)	**6.**	(b)	**7.**	(b)	**8.**	(c)	**9.**	(c)	**10.**	(a)
11.	(c)	**12.**	(b)	**13.**	(a)	**14.**	(d)	**15.**	(a)	**16.**	(a)	**17.**	(a)	**18.**	(c)	**19.**	(c)	**20.**	(b)
21.	(c)	**22.**	(d)	**23.**	(c)	**24.**	(a)	**25.**	(d)	**26.**	(d)	**27.**	(c)	**28.**	(c)	**29.**	(b)	**30.**	(d)
31.	(a)																		

Hints & Explanations

1. (d)

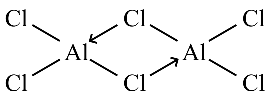
2. (b) : AlF_3 is insoluble in anhydrous HF because the F^- ions are not available in hydrogen bonded HF molecules but, it becomes soluble in presence of little amount of KF due to formation of complex, $K_3[AlF_6]$.

$AlF_3 + 3KF \rightarrow K_3[AlF_6]$

3. (a) : In group 13 elements, stability of +3 oxidation state decreases down the group while that of +1 oxidation state increases due to inert pair effect. Hence, stability of +1 oxidation state increases in the sequence :

Al < Ga < In < Tl.

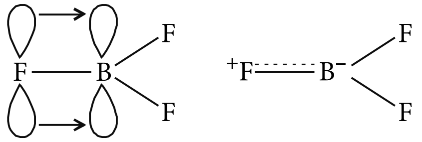
4. (b) : $AlCl_3$ forms a dimer, as Al due to the presence of 3*d*-orbitals can expand its covalency from four to six. Also dimerisation enables Al atoms to complete their octets.



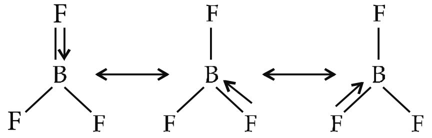
5. (c) : Boron does not have vacant *d*-orbitals in its valence shell, so it cannot expand its covalency beyond 4 *i.e.*, 'B' cannot form the ions like MF_6^{3-}.

6. (b) : The relative Lewis acid character of boron trihalides is found to follow the following order, $BBr_3 > BCl_3 > BF_3$, but the expected order on the basis of electronegativity of the halogens (electronegativity of halogens decreases from F to I) should be, $BF_3 > BCl_3 > BBr_3$.

This anomaly is explained on the basis of the relative tendency of the halogen atom to back donate its unutilised electrons to vacant *p*-orbital of boron atom. In BF_3, boron has a vacant 2*p*-orbital and each fluorine has fully filled unutilised 2*p*-orbitals. Fluorine transfers two electrons to vacant 2*p*-orbital of boron, thus forming *p*π-*p*π bond.



This type of bond has some double bond character and is known as dative or back bonding. All the three bond lengths are same. It is possible when double bond is delocalized. The delocalization may be represented as :



The tendency to back donate decreases from F to I as energy level difference between B and halogen atom increases from F to I. So, the order of Lewis acid strength is $BF_3 < BCl_3 < BBr_3$.

7. (b) : Lewis acids are those substances which can accept a pair of electrons and boron compounds usually are deficient in electrons.

8. (c) : Boric acid behaves as a Lewis acid, by accepting a pair of electrons from OH^- ion of water thereby releasing a proton.

9. (c) : BN is known as inorganic graphite and has structure similar to graphite.

10. (a) : Each 'B' atom in diborane (B_2H_6) is sp^3-hybridised. Of the 4-hybrid orbitals, three have one electron each, while the 4th is empty. Two orbitals of each form σ bonds with two 'H'-atoms, while one of the remaining hybrid orbital (either filled or empty), 1*s* orbital of 'H' atom and one of the hybrid orbitals of other 'B' atom overlap to form three centered two electron bond. So there exists two such type of three centered bonds.

11. (c) : H_3BO_3 is a weak monobasic acid.

$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

12. (b) : Generally halides of group-14 elements are covalent in nature. PbF_4 and SnF_4 are exceptions which are ionic in nature.

13. (a) : $[SiCl_6]^{2-}$ is not stable due to steric hindrance by large sized Cl atoms.

14. (d) : The inertness of *s*-subshell electrons towards bond formation is known as inert pair effect. This effect increases down the group thus, for Sn, +4 oxidation state is more stable, whereas, for Pb, +2 oxidation state is more stable, *i.e.*, Sn^{2+} is reducing while Pb^{4+} is oxidising.

15. (a) : When ns^2 electrons of outermost shell do not participate in bonding then these ns^2 electrons are called inert pair and the effect is called inert pair effect. Due to this inert pair effect Ge, Sn and Pb of group 14 have a tendency to form both +4 and +2 ions. Now the inert pair effect increases down the group, hence the stability of M^{2+} ions increases and M^{4+} ions decreases down the group. For this reason, Pb^{2+} is more stable than Pb^{4+} and Sn^{4+} is more stable than Sn^{2+}.

16. (a) : Carbon has no *d*-orbitals, while silicon contains *d*-orbitals in its valence shell which can be used for bonding purposes.

17. (a) : Except diamond other three conduct electricity. Potassium and sodium are metallic conductors, while graphite is a non-metallic conductor.

18. (c) : Lead pencil contains graphite and clay. It does not contain lead.

19. (c) : In graphite each carbon atom undergoes sp^2-hybridisation and is covalently bonded to three other carbon atoms by single bonds. The fourth electron forms π-bond. The electrons are delocalised over the whole sheet *i.e.* electrons are spread out between the structure.

20. (b) : In diamond, each carbon atom is sp^3 hybridized and thus, forms covalent bonds with four other carbon atoms lying at the corners of a regular tetrahedron.

21. (c) : All the above are conductors except diamond. Diamond is an insulator.

22. (d) : (A) Solid CO_2 (dry ice) is used as refrigerant for ice-cream and frozen food.

(B) The structure of C_{60} contains twenty six-membered rings and twelve five-membered rings.

(C) and (D) are correct statements.

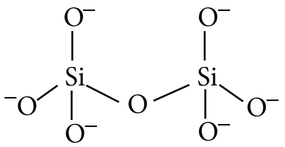
23. (c) : Silicones being biocompatible are used in surgical and cosmetic plants.

24. (a) : It can form only dimer.

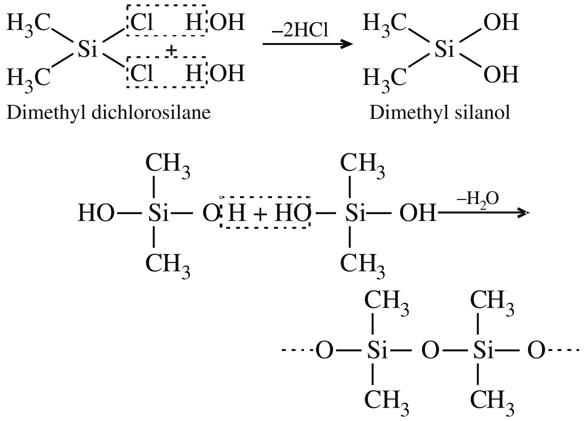
25. (d) : SiO_4^{4-} orthosilicate is basic unit of silicates.

26. (d) : Feldspars are three dimensional alumino-silicates.

27. (c) : Pyrosilicate contains two units of SiO_4^{4-} joined along a corner containing oxygen atom.



28. (c) : Hydrolysis of substituted chlorosilanes yields corresponding silanols which undergo polymerisation. Out of the given chlorosilanes, only $(CH_3)_2SiCl_2$ will give linear polymer on hydrolysis followed by polymerisation.



Dimethyl dichlorosilane

Dimethyl silanol

29. (b) : Chain silicates are formed by sharing two oxygen atoms by each tetrahedra. Anions of chain silicate have two general formula :

(i) $(SiO_3)_n^{2n-}$ (ii) $(Si_4O_{11})_n^{6n-}$

30. (d) : In zeolites, some of the Si^{4+} ions may be replaced by Al^{3+} ions. This results in unbalanced anionic charge. To maintain electrical neutrality, positive ions must be introduced.

31. (a) : $SiCl_4$ gets hydrolysed in moist air and gives white fumes which are used as a smoke screen in warfare.

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CHAPTER

12

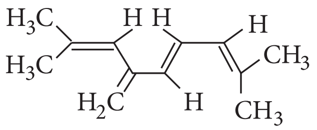
Organic Chemistry - Some Basic Principles and Techniques

12.2 Tetravalence of Carbon : Shapes of Organic Compounds

1. The number of sigma (σ) and pi (π) bonds in pent-2-en-4-yne is
(a) 13 σ bonds and no π bond
(b) 10 σ bonds and 3 π bonds
(c) 8 σ bonds and 5 π bonds
(d) 11 σ bonds and 2 π bonds. *(NEET 2019)*

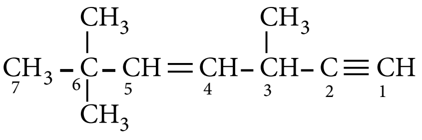
2. Which of the following molecules represents the order of hybridisation sp^2, sp^2, sp, sp from left to right atoms?
(a) $HC\equiv C-C\equiv CH$
(b) $CH_2=CH-C\equiv CH$
(c) $CH_2=CH-CH=CH_2$
(d) $CH_3-CH=CH-CH_3$ *(NEET 2018)*

3. The total number of π-bond electrons in the following structure is



(a) 12 (b) 16 (c) 4 (d) 8
(2015, Cancelled)

4. The state of hybridisation of C_2, C_3, C_5 and C_6 of the hydrocarbon,



$$\underset{7}{CH_3}-\underset{6}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{2}{C}\equiv\underset{1}{CH}$$

is in the following sequence
(a) sp^3, sp^2, sp^2 and sp (b) sp, sp^2, sp^2 and sp^3
(c) sp, sp^2, sp^3 and sp^2 (d) sp, sp^3, sp^2 and sp^3
(2009)

5. In the hydrocarbon,
$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{C}\equiv\underset{1}{CH}$
the state of hybridisation of carbons 1, 3 and 5 are in the following sequence
(a) sp, sp^2, sp^3 (b) sp^3, sp^2, sp
(c) sp^2, sp, sp^3 (d) sp, sp^3, sp^2 *(2008)*

6. In which of the following compounds there is more than one kind of hybridisation (sp, sp^2, sp^3) for carbon?
(a) $CH_2=CH-CH=CH_2$
(b) $H-C\equiv C-H$
(c) $CH_3CH_2CH_2CH_3$
(d) $CH_3-CH=CH-CH_3$ *(1995)*

7. A straight chain hydrocarbon has the molecular formula C_8H_{10}. The hybridisation of the carbon atoms from one end of the chain to the other are respectively sp^3, sp^2, sp^2, sp^3, sp^2, sp^2, sp and sp. The structural formula of the hydrocarbon would be
(a) $CH_3C\equiv CCH_2-CH=CHCH=CH_2$
(b) $CH_3CH_2-CH=CHCH=CHC\equiv CH$
(c) $CH_3CH=CHCH_2-C\equiv CCH=CH_2$
(d) $CH_3CH=CHCH_2-CH=CHC\equiv CH$ *(1991)*

8. Which of the following possesses a sp-carbon in its structure?
(a) $CH_2=CCl-CH=CH_2$
(b) $CCl_2=CCl_2$ (c) $CH_2=C=CH_2$
(d) $CH_2=CH-CH=CH_2$ *(1989)*

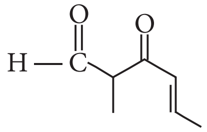
9. The Cl–C–Cl angle in 1, 1, 2, 2-tetrachloro-ethene and tetrachloromethane respectively will be about
(a) 120° and 109.5° (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°
(1988)

12.4 Classification of Organic Compounds

10. An organic compound X(molecular formula $C_6H_7O_2N$) has six carbon atoms in a ring system, two double bonds and a nitro group as substituent, X is
(a) homocyclic but not aromatic
(b) aromatic but not homocyclic
(c) homocyclic and aromatic
(d) heterocyclic and aromatic. *(1990)*

12.5 Nomenclature of Organic Compounds

11. The IUPAC name of the compound

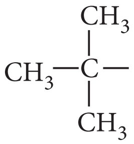


is ________.

(a) 5-formylhex-2-en-3-one
(b) 5-methyl-4-oxohex-2-en-5-al
(c) 3-keto-2-methylhex-5-enal
(d) 3-keto-2-methylhex-4-enal *(NEET 2017)*

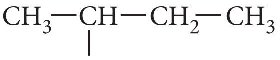
12. The structure of isobutyl group in an organic compound is

(a) $CH_3-CH_2-CH_2-CH_2-$

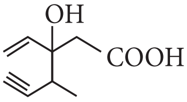
(b)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-$

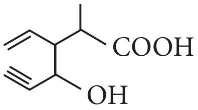
(c)

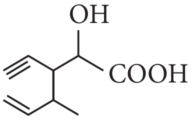
$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH-CH_2-$

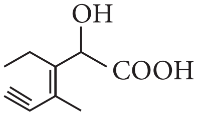
(d)

$CH_3-\underset{|}{CH}-CH_2-CH_3$ *(NEET 2013)*

13. Structure of the compound whose IUPAC name is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is

(a)


(b)


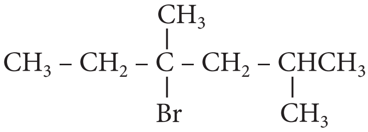
(c)


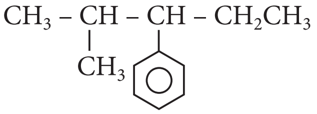
(d)


(NEET 2013)

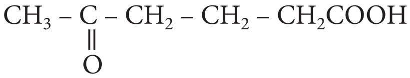
14. Which nomenclature is not according to IUPAC system?

(a) $Br-CH_2-CH{=}CH_2$
1-Bromoprop-2-ene

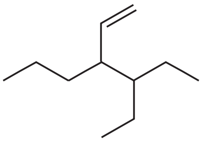
(b)

$CH_3-CH_2-\overset{CH_3}{\underset{Br}{C}}-CH_2-\underset{CH_3}{CHCH_3}$
4-Bromo-2,4-dimethylhexane

(c)


2-Methyl-3-phenylpentane

(d)

$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_2-CH_2COOH$
5-Oxohexanoic acid *(2012)*

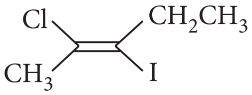
15. The correct IUPAC name for the compound



is

(a) 4-ethyl-3-propylhex-1-ene
(b) 3-ethyl-4-ethenylheptane
(c) 3-ethyl-4-propylhex-5-ene
(d) 3-(1-ethylpropyl)hex-1-ene. *(2011)*

16. The IUPAC name of the following compound is

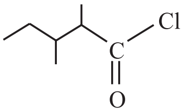


(a) *trans*-2-chloro-3-iodo-2-pentene
(b) *cis*-3-iodo-4-chloro-3-pentane
(c) *trans*-3-iodo-4-chloro-3-pentene
(d) *cis*-2-chloro-3-iodo-2-pentene.
(Mains 2011, 1998)

17. The IUPAC name of the compound $CH_3CH{=}CHC{\equiv}CH$ is
(a) pent-4-yn-2-ene (b) pent-3-en-1-yne
(c) pent-2-en-4-yne (d) pent-1-yn-3-ene.
(Mains 2010)

18. The IUPAC name of the compound having the formula $CH{\equiv}C{-}CH{=}CH_2$ is
(a) 1-butyne-3-ene (b) but-1-yne-3-ene
(c) 1-butene-3-yne (d) 3-butene-1-yne.
(2009)

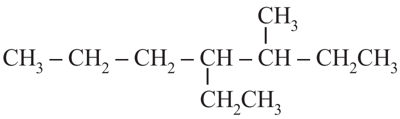
19. The IUPAC name of

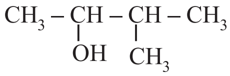


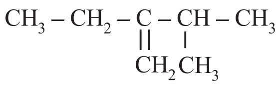
is

(a) 1-chloro-1-oxo-2,3-dimethylpentane
(b) 2-ethyl-3-methylbutanoyl chloride
(c) 2,3-dimethylpentanoyl chloride
(d) 3,4-dimethylpentanoyl chloride. *(2006)*

20. Names of some compounds are given. Which one is not in IUPAC system?

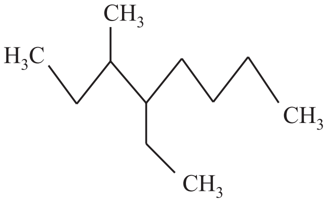
(a)

$CH_3-CH_2-CH_2-\underset{CH_2CH_3}{CH}-\overset{CH_3}{CH}-CH_2CH_3$
3-Methyl-4-ethylheptane

(b)

$CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3$
3-Methyl-2-butanol

(c)

$CH_3-CH_2-\underset{CH_2}{\underset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$
2-Ethyl-3-methylbut-1-ene

(d) $CH_3-C{\equiv}C-CH(CH_3)_2$ *(2005)*
4-Methyl-2-pentyne

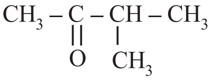
21. Name of the compound given below is

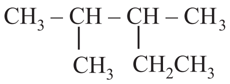


(a) 4-ethyl-3-methyloctane
(b) 3-methyl-4-ethyloctane
(c) 2,3-diethylheptane
(d) 5-ethyl-6-methyloctane. *(2003)*

22. IUPAC name of the following is
$CH_2=CH-CH_2-CH_2-C\equiv CH$
(a) 1,5-hexenyne (b) 1-hexene-5-yne
(c) 1-hexyne-5-ene (d) 1,5-hexynene. *(2002)*

23. The incorrect IUPAC name is

(a) 
$CH_3-\underset{\underset{O}{||}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ - 2-methyl-3-butanone

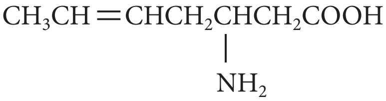
(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_3$ -2,3-dimethylpentane

(c) $CH_3-C\equiv CCH(CH_3)_2$ -4-methyl-2-pentyne

(d) 
$CH_3\underset{\underset{Cl}{|}}{CH}\underset{\underset{Br}{|}}{CH}CH_3$ -3-bromo-2-chlorobutane. *(2001)*

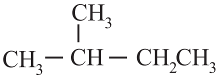
24. The IUPAC name of $(CH_3)_2CH-CH_2-CH_2Br$ is
(a) 1-bromo-3-methylbutane
(b) 2-methyl-3-bromopropane
(c) 1-bromopentane
(d) 2-methyl-4-bromobutane. *(1996)*

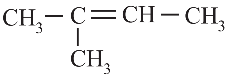
25. The IUPAC name for

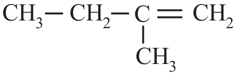

$CH_3CH=CHCH_2\underset{\underset{NH_2}{|}}{CH}CH_2COOH$ is

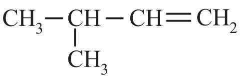
(a) 3-amino-5-heptenoic acid
(b) β-amino-δ-heptenoic acid
(c) 5-amino-2-heptenoic acid
(d) 5-amino-hex-2-enecarboxylic acid. *(1995)*

26. 2-Methyl-2-butene will be represented as

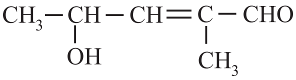
(a) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$

(b) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$

(c) 
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$

(d) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$ *(1992)*

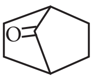
27. The IUPAC name of

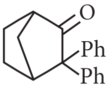

$CH_3-\underset{\underset{OH}{|}}{CH}-CH=\underset{\underset{CH_3}{|}}{C}-CHO$ is

(a) 4-hydroxy-1-methylpentanal
(b) 4-hydroxy-2-methylpent-2-en-1-al
(c) 2-hydroxy-4-methylpent-3-en-5-al
(d) 2-hydroxy-3-methylpent-2-en-5-al. *(1992)*

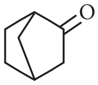
12.6 Isomerism

28. Which among the given molecules can exhibit tautomerism?


I

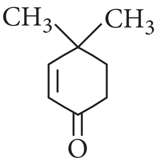


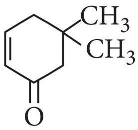
II

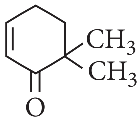

III

(a) III only (b) Both I and III
(c) Both I and II (d) Both II and III
(NEET-II 2016)

29. Given :

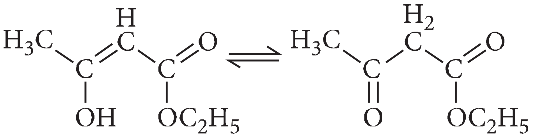

(I)


(II)


(III)

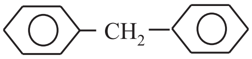
Which of the given compounds can exhibit tautomerism?
(a) II and III (b) I, II and III
(c) I and II (d) I and III
(2015, Cancelled)

30. The enolic form of ethyl acetoacetate as shown below has



(a) 9 sigma bonds and 2 pi-bonds
(b) 9 sigma bonds and 1 pi-bond
(c) 18 sigma bonds and 2 pi-bonds
(d) 16 sigma bonds and 1 pi-bond. *(2015, Cancelled)*

31. Which one of the following pairs represents stereoisomerism?
(a) Structural isomerism and geometrical isomerism
(b) Optical isomerism and geometrical isomerism
(c) Chain isomerism and rotational isomerism
(d) Linkage isomerism and geometrical isomerism
(2005)

32. The molecular formula of diphenylmethane,  is $C_{13}H_{12}$.

How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom?
(a) 6 (b) 4 (c) 8 (d) 7 *(2004)*

33. Tautomerism is exhibited by
(a) R_3CNO_2 (b) RCH_2NO_2
(c) $(CH_3)_3CNO$ (d) $(CH_3)_2NH$ *(1997)*

34. The number of isomers in $C_4H_{10}O$ will be
(a) 7 (b) 8 (c) 5 (d) 6 *(1996)*

35. Isomers of a substance must have the same
(a) structural formula (b) physical properties
(c) chemical properties (d) molecular formula. *(1991)*

36. How many chain isomers could be obtained from the alkane C_6H_{14}?
(a) Four (b) Five
(c) Six (d) Seven *(1988)*

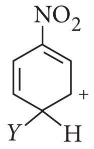
12.7 Fundamental Concepts in Organic Reaction Mechanism

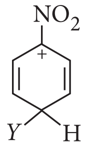
37. A tertiary butyl carbocation is more stable than a secondary butyl carbocation because of which of the following?
(a) $-I$ effect of $-CH_3$ groups
(b) $+R$ effect of $-CH_3$ groups
(c) $-R$ effect of $-CH_3$ groups
(d) Hyperconjugation *(NEET 2020)*

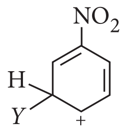
38. The most stable carbocation, among the following is
(a) $(CH_3)_3C—\overset{+}{C}H—CH_3$
(b) $CH_3—CH_2—\overset{+}{C}H—CH_2—CH_3$
(c) $CH_3—\overset{+}{C}H—CH_2—CH_2—CH_3$
(d) $CH_3—CH_2—\overset{+}{C}H_2$ *(Odisha NEET 2019)*

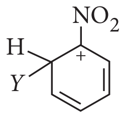
39. Which of the following is correct with respect to $-I$ effect of the substituents? (R = alkyl)
(a) $-NH_2 < -OR < -F$ (b) $-NR_2 < -OR < -F$
(c) $-NH_2 > -OR > -F$ (d) $-NR_2 > -OR > -F$ *(NEET 2018, 1998)*

40. Which of the following carbocations is expected to be most stable?

(a) 

(b) 

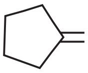
(c) 

(d) 

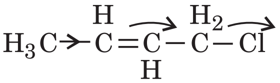
(NEET 2018)

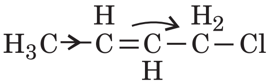
41. The correct statement regarding electrophile is
(a) electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
(b) electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
(c) electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile
(d) electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile. *(NEET 2017)*

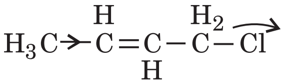
42. Which of the following statements is not correct for a nucleophile?
(a) Ammonia is a nucleophile.
(b) Nucleophiles attack low e^- density sites.
(c) Nucleophiles are not electron seeking.
(d) Nucleophile is a Lewis acid. *(2015)*

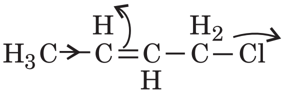
43. Treatment of cyclopentanone  with methyl lithium gives which of the following species?
(a) Cyclopentanonyl radical
(b) Cyclopentanonyl biradical
(c) Cyclopentanonyl anion
(d) Cyclopentanonyl cation *(2015, Cancelled)*

44. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place?

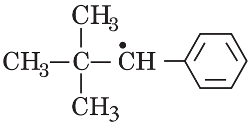
(a) 

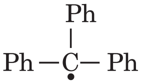
(b) 

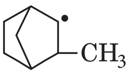
(c) 

(d)  *(2015, Cancelled)*

45. Consider the following compounds :

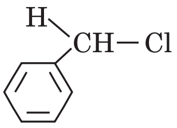

(I)

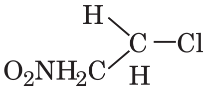

(II)

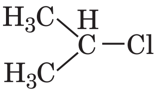

(III)

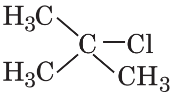
Hyperconjugation occurs in
(a) III only (b) I and III
(c) I only (d) II only. *(2015, Cancelled)*

46. In which of the following compounds, the C—Cl bond ionisation shall give most stable carbonium ion?

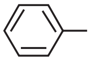
(a) 

(b) 

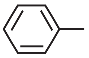
(c) 

(d) 

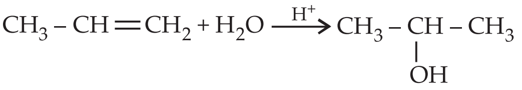
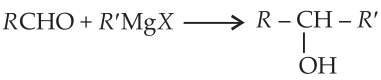
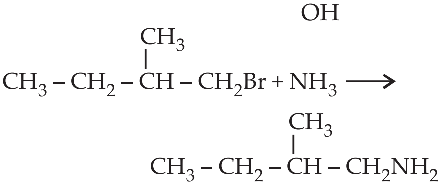
(2015, Cancelled)

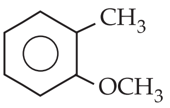
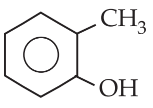
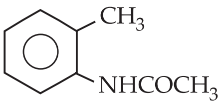
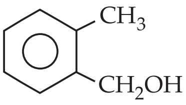
47. The radical,  $\dot{C}H_2$ is aromatic because it has
(a) 7 *p*-orbitals and 7 unpaired electrons
(b) 6 *p*-orbitals and 7 unpaired electrons
(c) 6 *p*-orbitals and 6 unpaired electrons
(d) 7 *p*-orbitals and 6 unpaired electrons.
(NEET 2013)

48. Arrange the following in increasing order of stability.
1. $(CH_3)_2-\overset{+}{C}-CH_2-CH_3$
2. $(CH_3)_3-\overset{+}{C}$
3. $(CH_3)_2-\overset{+}{C}H$ 4. $CH_3-\overset{+}{C}H_2$
5. $\overset{+}{C}H_3$
(a) $5 < 4 < 3 < 1 < 2$ (b) $4 < 5 < 3 < 1 < 2$
(c) $1 < 5 < 4 < 3 < 2$ (d) $5 < 4 < 3 < 2 < 1$
(Karnataka NEET 2013)

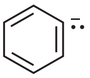
49. What is the hybridisation state of benzyl carbonium ion  $\overset{+}{C}H_2$?
(a) sp^2 (b) spd^2 (c) sp^2d (d) sp^3
(Karnataka NEET 2013)

50. Homolytic fission of the following alkanes forms free radicals CH_3-CH_3, $CH_3-CH_2-CH_3$, $(CH_3)_2CH-CH_3$, $CH_3-CH_2-CH(CH_3)_2$. Increasing order of stability of the radicals is
(a) $(CH_3)_2\dot{C}-CH_2-CH_3 < CH_3-\dot{C}H-CH_3 < CH_3-\dot{C}H_2 < (CH_3)_3\dot{C}$
(b) $CH_3-\dot{C}H_2 < CH_3-\dot{C}H-CH_3 < (CH_3)_2\dot{C}-CH_2-CH_3 < (CH_3)_3\dot{C}$
(c) $CH_3-\dot{C}H_2 < CH_3-\dot{C}H-CH_3 < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}-CH_2-CH_3$
(d) $(CH_3)_3\dot{C} < (CH_3)_2\dot{C}-CH_2-CH_3 < CH_3-\dot{C}H-CH_3 < CH_3-\dot{C}H_2$
(Karnataka NEET 2013)

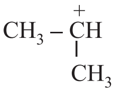
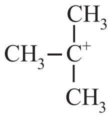
51. Which one is a nucleophilic substitution reaction among the following?
(a) 
$CH_3-CH=CH_2+H_2O \xrightarrow{H^+} CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_3$
(b) 
$RCHO+R'MgX \longrightarrow R-\underset{\displaystyle OH}{\underset{|}{C}H}-R'$
(c) 
$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2Br+NH_3 \longrightarrow CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2NH_2$
(d) $CH_3CHO+HCN \longrightarrow CH_3CH(OH)CN$ *(2011)*

52. Which one of the following is most reactive towards electrophilic reagent?
(a) 
(b) 
(c) 
(d) 
(2011, 2010)

53. Which of the following species is not electrophilic in nature?
(a) $\overset{+}{Cl}$ (b) BH_3
(c) H_3O^+ (d) $\overset{+}{N}O_2$ *(Mains 2010)*

54. The stability of carbanions in the following:
(i) $RC\equiv\bar{C}$ (ii) 
(iii) $R_2C=\bar{C}H$ (iv) $R_3C-\bar{C}H_2$
is in the order of
(a) (iv) > (ii) > (iii) > (i) (b) (i) > (iii) > (ii) > (iv)
(c) (i) > (ii) > (iii) > (iv) (d) (ii) > (iii) > (iv) > (i)
(2008)

55. For (i) I^-, (ii) Cl^-, (iii) Br^-, the increasing order of nucleophilicity would be
(a) $Cl^- < Br^- < I^-$ (b) $I^- < Cl^- < Br^-$
(c) $Br^- < Cl^- < I^-$ (d) $I^- < Br^- < Cl^-$ *(2007)*

56. Which amongst the following is the most stable carbocation?
(a) $\overset{+}{C}H_3$ (b) $CH_3\overset{+}{C}H_2$
(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}H}}$
(d) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C^+}}}}$
(2005)

57. Which of the following is the most stable carbocation (carbonium ion)?
(a) $CH_3\overset{+}{C}H_2$ (b) $(CH_3)_2\overset{+}{C}H$
(c) $(CH_3)_3\overset{+}{C}$ (d) $C_6H_5\overset{+}{C}H_2$ *(1991)*

58. Cyclic hydrocarbon '*A*' has all the carbon and hydrogen atoms in a single plane. All the carbon–carbon bonds have the same length, less than 1.54 Å, but more than 1.34 Å. The bond angle will be
(a) 109°28′ (b) 100°
(c) 180° (d) 120° *(1989)*

12.8 Methods of Purification of Organic Compounds

59. Paper chromatography is an example of
(a) adsorption chromatography
(b) partition chromatography
(c) thin layer chromatography
(d) column chromatography. *(NEET 2020)*

60. The most suitable method of separation of 1 : 1 mixture of *ortho* and *para*-nitrophenols is
(a) chromatography (b) crystallisation
(c) steam distillation (d) sublimation.
(NEET 2017, 1999, 1993)

61. The best method for the separation of naphthalene and benzoic acid from their mixture is
(a) distillation (b) sublimation
(c) chromatography (d) crystallisation. *(2005)*

62. In steam distillation of toluene, the pressure of toluene in vapour is
(a) equal to pressure of barometer
(b) less than pressure of barometer
(c) equal to vapour pressure of toluene in simple distillation
(d) more than vapour pressure of toluene in simple distillation. *(2001)*

63. Which of the following technique is most suitable for purification of cyclohexanone from a mixture containing benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone?
(a) Sublimation (b) Evaporation
(c) Crystallisation (d) IR spectroscopy
(1997)

12.9 Qualitative Analysis of Organic Compounds

64. Nitrogen detection in an organic compound is carried out by Lassaigne's test. The blue colour formed corresponds to which of the following formulae?
(a) $Fe_3[Fe(CN)_6]_2$ (b) $Fe_4[Fe(CN)_6]_3$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$
(Karnataka NEET 2013)

65. The Lassaigne's extract is boiled with conc. HNO_3 while testing for halogens. By doing so it
(a) decomposes Na_2S and NaCN, formed
(b) helps in the precipitation of AgCl
(c) increases the solubility product of AgCl
(d) increases the concentration of NO_3^- ions.
(2011)

66. In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into
(a) sodamide (b) sodium cyanide
(c) sodium nitrite (d) sodium nitrate.
(1991)

67. Lassaigne's test is used in qualitative analysis to detect
(a) nitrogen (b) sulphur
(c) chlorine (d) all of these. *(1989)*

68. A blue colouration is not obtained when
(a) ammonium hydroxide dissolves in copper sulphate
(b) copper sulphate solution reacts with $K_4[Fe(CN)_6]$
(c) ferric chloride reacts with sod. ferrocyanide
(d) anhydrous $CuSO_4$ is dissolved in water. *(1989)*

12.10 Quantitative Analysis

69. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is
(a) 16.76 (b) 15.76 (c) 17.36 (d) 18.20
(2015, Cancelled)

70. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is
(a) 37.33 (b) 45.33
(c) 35.33 (d) 43.33 *(2014)*

71. In Dumas' method of estimation of nitrogen 0.35 g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be (aqueous tension at 300 K = 15 mm)
(a) 15.45 (b) 16.45
(c) 17.45 (d) 14.45 *(2011)*

72. Kjeldahl's method is used in the estimation of
(a) nitrogen (b) halogens
(c) sulphur (d) oxygen. *(1990)*

ANSWER KEY

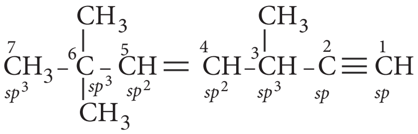
1.	(b)	**2.**	(b)	**3.**	(d)	**4.**	(d)	**5.**	(d)	**6.**	(d)	**7.**	(d)	**8.**	(c)	**9.**	(a)	**10.**	(a)
11.	(d)	**12.**	(c)	**13.**	(d)	**14.**	(a)	**15.**	(a)	**16.**	(a)	**17.**	(b)	**18.**	(c)	**19.**	(c)	**20.**	(a)
21.	(a)	**22.**	(b)	**23.**	(a)	**24.**	(a)	**25.**	(a)	**26.**	(b)	**27.**	(b)	**28.**	(a)	**29.**	(b)	**30.**	(c)
31.	(b)	**32.**	(b)	**33.**	(b)	**34.**	(a)	**35.**	(d)	**36.**	(b)	**37.**	(d)	**38.**	(c)	**39.**	(a,b)	**40.**	(c)
41.	(c)	**42.**	(d)	**43.**	(c)	**44.**	(a)	**45.**	(a)	**46.**	(d)	**47.**	(c)	**48.**	(a)	**49.**	(a)	**50.**	(b)
51.	(c)	**52.**	(b)	**53.**	(c)	**54.**	(c)	**55.**	(a)	**56.**	(d)	**57.**	(c)	**58.**	(d)	**59.**	(b)	**60.**	(c)
61.	(b)	**62.**	(b)	**63.**	(d)	**64.**	(b)	**65.**	(a)	**66.**	(b)	**67.**	(d)	**68.**	(b)	**69.**	(a)	**70.**	(a)
71.	(b)	**72.**	(a)																

Hints & Explanations

1. (b) : $\overset{5}{\mathrm{HC}}\equiv\overset{4}{\mathrm{C}}-\overset{3}{\mathrm{CH}}=\overset{2}{\mathrm{CH}}-\overset{1}{\mathrm{CH_3}}$
Pent-2-en-4-yne
(10 σ-bonds and 3π-bonds)

2. (b) : $\overset{sp^2}{\mathrm{CH_2}}=\overset{sp^2}{\mathrm{CH}}-\overset{sp}{\mathrm{C}}\equiv\overset{sp}{\mathrm{CH}}$

3. (d) : There are four double bonds. Hence, no. of π-electrons = 2 × 4 = 8.

4. (d) : 

$$\underset{sp^3}{\overset{7}{\mathrm{CH_3}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\overset{6}{\underset{sp^3}{\mathrm{C}}}}}-\underset{sp^2}{\overset{5}{\mathrm{CH}}}=\underset{sp^2}{\overset{4}{\mathrm{CH}}}-\overset{\mathrm{CH_3}}{\underset{sp^3}{\overset{3}{\mathrm{CH}}}}-\underset{sp}{\overset{2}{\mathrm{C}}}\equiv\underset{sp}{\overset{1}{\mathrm{CH}}}$$

∴ C_2 - sp, C_3 - sp^3, C_5 - sp^2 and C_6 - sp^3

5. (d) : $\underset{6}{\overset{sp^3}{\mathrm{CH_3}}}-\underset{5}{\overset{sp^2}{\mathrm{CH}}}=\underset{4}{\overset{sp^2}{\mathrm{CH}}}-\underset{3}{\overset{sp^3}{\mathrm{CH_2}}}-\underset{2}{\overset{sp}{\mathrm{C}}}\equiv\underset{1}{\overset{sp}{\mathrm{CH}}}$

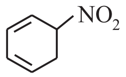
The state of hybridisation of carbon in 1, 3 and 5 position are sp, sp^3 and sp^2.

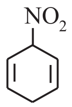
6. (d) : $\underset{\underset{sp^3}{\downarrow}}{\mathrm{CH_3}}-\underset{\underset{sp^2}{\downarrow}}{\mathrm{CH}}=\underset{\underset{sp^2}{\downarrow}}{\mathrm{CH}}-\underset{\underset{sp^3}{\downarrow}}{\mathrm{CH_3}}$

7. (d) : $\overset{sp^3}{\mathrm{CH_3}}\overset{sp^2}{\mathrm{CH}}=\overset{sp^2}{\mathrm{CH}}-\overset{sp^3}{\mathrm{CH_2}}-\overset{sp^2}{\mathrm{CH}}=\overset{sp^2}{\mathrm{CH}}-\overset{sp}{\mathrm{C}}\equiv\overset{sp}{\mathrm{CH}}$

8. (c) : $\overset{sp^2}{\mathrm{CH_2}}=\overset{sp}{\mathrm{C}}=\overset{sp^2}{\mathrm{CH_2}}$

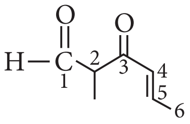
9. (a) : Tetrachloroethene being an alkene has sp^2-hybridised C-atoms and hence the angle Cl – C – Cl is 120° while in tetrachloromethane, carbon is sp^3 hybridised, therefore the angle Cl – C – Cl is 109°28′.

10. (a) : 

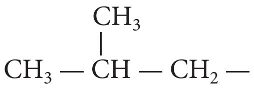
or


($C_6H_7O_2N$)

Hence, it is homocyclic (as the ring system is made of one type of atoms, *i.e.*, carbon) but not aromatic.

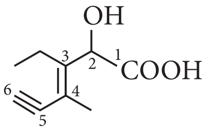
11. (d) : 

3-Keto-2-methylhex-4-enal

12. (c) : 

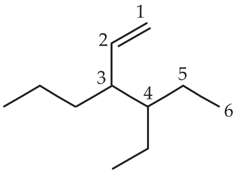
$$\mathrm{CH_3}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-$$

(*iso*-butyl group)

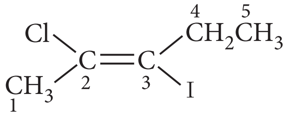
13. (d) : 

IUPAC name of the compound is
3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid.

14. (a) : Br – $\overset{3}{\mathrm{CH_2}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}$
3-Bromopropene

15. (a) : 

4-Ethyl-3-propylhex-1-ene

16. (a) : 

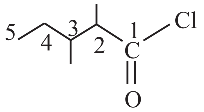
trans-2-Chloro-3-iodo-2-pentene

17. (b) : $\overset{5}{\mathrm{CH_3}}\overset{4}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}\overset{2}{\mathrm{C}}\equiv\overset{1}{\mathrm{CH}}$
Pent-3-en-1-yne

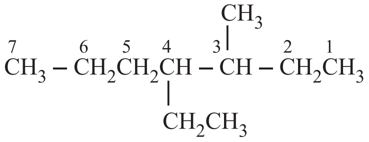
If a molecule contains both carbon-carbon double or triple bonds, the two are treated as per in seeking the lowest number combination. However, if the sum of numbers turns out to be the same starting from either of the carbon chain, then lowest number is given to the $\mathrm{C{=}C}$ double bond.

18. (c) : $\overset{4}{\mathrm{CH}}\equiv\overset{3}{\mathrm{C}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}$
1-Butene-3-yne

Since the sum of numbers starting from either side of the carbon chain turns out to be the same, so lowest number is given to the $\mathrm{C{=}C}$ end.

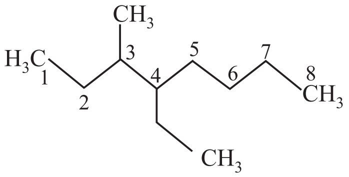
19. (c) : 

It is 2,3-dimethylpentanoyl chloride.

20. (a) : 

$$\overset{7}{\mathrm{CH_3}}-\overset{6}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2}}\underset{\underset{\mathrm{CH_2CH_3}}{|}}{\overset{4}{\mathrm{CH}}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_3}}$$

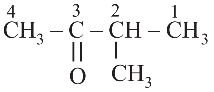
4-Ethyl-3-methylheptane

21. (a) : 

4-Ethyl-3-methyloctane

22. (b) : $\overset{1}{\mathrm{CH_2}}=\overset{2}{\mathrm{CH}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{C}}\equiv\overset{6}{\mathrm{CH}}$

The double bond gets priority over triple bond. Therefore, correct IUPAC name is 1-hexene-5-yne.

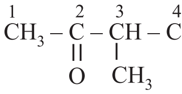
23. (a) : 

$$\overset{4}{\mathrm{CH_3}}-\underset{\underset{\mathrm{O}}{\|}}{\overset{3}{\mathrm{C}}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{1}{\mathrm{CH_3}}$$

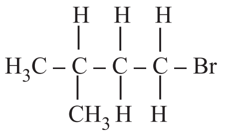
(wrong numbering)

The $-\overset{\overset{O}{\|}}{C}-$ group should get priority over methyl group.

∴ Correct IUPAC name is

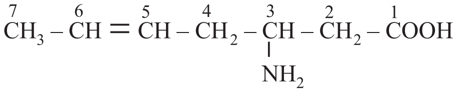

$\overset{1}{C}H_3-\underset{\underset{O}{\|}}{\overset{2}{C}}-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{4}{C}H_3$: 3-Methyl-2-butanone

24. (a) :


$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-Br$

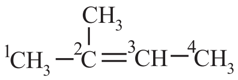
1-Bromo-3-methylbutane

25. (a) :


$\overset{7}{C}H_3-\overset{6}{C}H=\overset{5}{C}H-\overset{4}{C}H_2-\underset{\underset{NH_2}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}OOH$

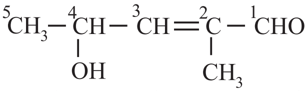
As —COOH group is highest priority group, it is numbered one. So, the IUPAC name is 3-amino-5-heptenoic acid.

26. (b) :


$^1CH_3-\overset{\overset{CH_3}{|}}{^2C}=^3CH-^4CH_3$

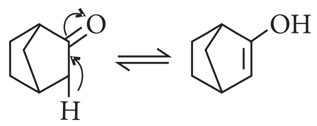
2-Methyl-2-butene

27. (b) :


$^5CH_3-\underset{\underset{OH}{|}}{^4CH}-^3CH=\underset{\underset{CH_3}{|}}{^2C}-^1CHO$

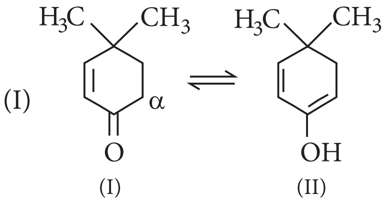
4-Hydroxy-2-methylpent-2-en-1-al

28. (a) : α-Hydrogen at bridge carbon never participate in tautomerism. Thus, only (III) exhibits tautomerism.

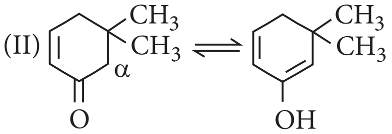


keto-form (III) enol-form

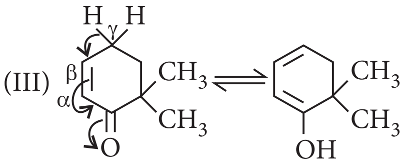
29. (b) : In keto-enol tautomerism,



here, α-H participates.



here, α-H participates.

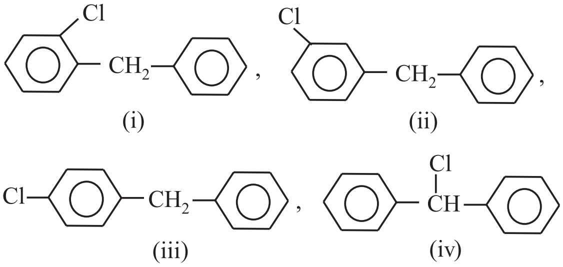


here, γ-H participates (*p*-tautomerism).

30. (c) : Enolic form of ethyl acetoacetate has 18 σ-bonds and 2 π-bonds.

31. (b)

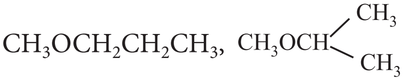
32. (b) : Only four structural isomers are possible for monochlorinated diphenylmethane.



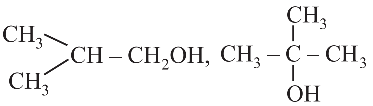
33. (b) : It is a special type of functional isomerism, in which both the isomers are represented by one and the same substance and are always present in equilibrium. It is exhibited by nitroalkane (RCH_2NO_2) and isonitroalkane.

34. (a) : There are 7 isomers in $C_4H_{10}O$. Out of these, 4 are alcohols and 3 are ethers.

$CH_3CH_2-O-CH_2CH_3$,


$CH_3OCH_2CH_2CH_3$, $CH_3OCH(CH_3)_2$

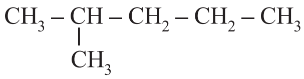

$CH_3CH_2CH_2CH_2OH$, $CH_3CH_2\underset{\underset{OH}{|}}{C}H-CH_3$

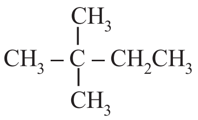

$(CH_3)_2CH-CH_2OH$, $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

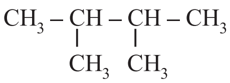
35. (d) : Isomers must have same molecular formula but different structural formula.

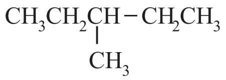
36. (b) : 5-chain isomers are obtained from alkane C_6H_{14}.

(i) $CH_3CH_2CH_2CH_2CH_2CH_3$

(ii)

$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_2-CH_3$

(iii)

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$

(iv)

$CH_3-\underset{\underset{CH_3}{|}}{C}H-\underset{\underset{CH_3}{|}}{C}H-CH_3$

(v)

$CH_3CH_2\underset{\underset{CH_3}{|}}{C}H-CH_2CH_3$

37. (d) : *tert*-Butyl carbocation, $(CH_3)_3\overset{+}{C}$ is more stable than *sec*-butyl carbocation $(CH_3)_2\overset{+}{C}H$ due to hyperconjugation.

$(CH_3)_3\overset{+}{C}$ has nine C — H bonds while $(CH_3)_2\overset{+}{C}H$ has six C — H bonds. Thus, there is more hyperconjugative structures in *tert*-butyl carbocation.

38. (c) : Among the given carbocations, $CH_3-\overset{+}{C}H-CH_2-CH_2-CH_3$ is most stable carbocation. As is consists of maximum number of α-hydrogens and stablised by hyperconjugation.

39. (a, b) : $-I$ effect increases on increasing the electronegativity of atom.

∴ $-NH_2 < -OR < -F$ ($-I$ effect)

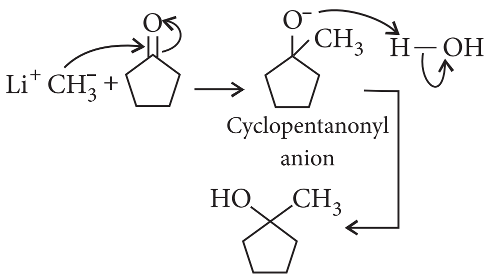
Also, $-NR_2 < -OR < -F$ ($-I$ effect)

40. (c) : $-NO_2$ group is *meta*-directing, thus will stabilize a electrophile at *m*-position.

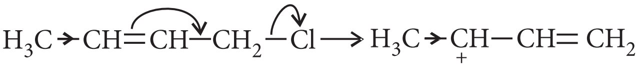
41. (c)

42. (d) : Nucleophiles are electron rich species hence, they are Lewis bases.

43. (c) :



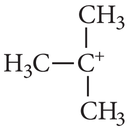
44. (a) : Nucleophile will attack a stable carbocation (S_N1 reaction).


$H_3C \rightarrow CH{=}CH{-}CH_2{-}Cl \longrightarrow H_3C \rightarrow \underset{+}{CH}{-}CH{=}CH_2$

(Stable due to $+I$ effect of $-CH_3$ group)

45. (a) : Hyperconjugation can occur only in compound III as it has α-hydrogen atom.

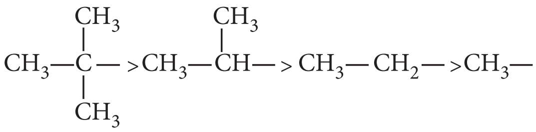
46. (d) :


$H_3C-\overset{CH_3}{\underset{CH_3}{C^+}}$

is most stable due to hyperconjugation.

47. (c)

48. (a) : Greater the number of electron donating alkyl groups ($+I$ effect), greater is the stability of carbocations. $+I$ effect is in the order :


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}- > CH_3-\overset{CH_3}{CH}- > CH_3-CH_2- > CH_3-$

More the number of hyperconjugative structures of carbocations, more is the stability.

Hence, the order of stability of carbocations is

$5 < 4 < 3 < 1 < 2.$

49. (a)

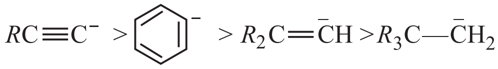
50. (b) : More the number of hyperconjugative structures, the greater is the stability.

51. (c) : Nucleophilic substitution reaction involves the displacement of a nucleophile by another.

52. (b) : $+R$ effect of —OH group is greater than that of $-OCH_3$ group.

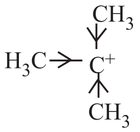
53. (c)

54. (c) : Higher the no. of electron releasing groups lower will be stability of carbanion, and vice-versa. So, the order of stability of carbanions is



55. (a) : In case of different nucleophiles, but present in the same group in the periodic table, then larger is the atomic mass, higher is the nucleophilicity. Hence, the increasing order of nucleophilicity of the halide ions is $F^- < Cl^- < Br^- < I^-$.

56. (d) :


$H_3C \rightarrow \overset{CH_3}{\underset{CH_3}{C^+}}$

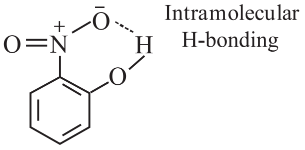
3° carbon is more stable due to the stabilization of the charge by three methyl groups (or $+I^-$ effect). It can also be explained on the basis of hyperconjugation. Greater the number of hyperconjugative α-H atoms, more will be the hyperconjugative structures and more will be the stability.

57. (c) : 3° > 2° > 1° more the delocalisation of positive charge, more is its stability.

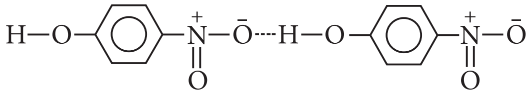
58. (d) : All the properties mentioned in the question suggest that it is a benzene molecule. Since in benzene all carbons are sp^2-hybridised, therefore, C – C – C angle is 120°.

59. (b) : Paper chromatography is a type of partition chromatography.

60. (c) : The *o*- and *p*-nitrophenols are separated by steam distillation since *o*-isomer is steam volatile due to intramolecular H-bonding while *p*-isomer is not steam volatile due to association of molecules by intermolecular H-bonding.



(*o*-Nitrophenol)



Intermolecular H-bonding (*p*-Nitrophenol)

61. (b) : Sublimation method is used for those organic substances which pass directly from solid to vapour state on heating and vice-versa on cooling *e.g.* benzoic acid, naphthalene, camphor, anthracene, etc. Naphthalene is volatile and benzoic acid is non-volatile due to the formation of the dimer.

62. (b) : In steam distillation of toluene, the pressure of toluene in vapour is less than pressure of barometer, because it is carried out when a solid or liquid is insoluble in water and is volatile with steam but the impurities are non-volatile.

63. (d) : In the IR spectroscopy, each functional group appears at a certain peak (in cm^{-1}). So, cyclohexanone can be identified by carbonyl peak.

64. (b) : $$\underset{\text{Sodium ferrocyanide}}{3Na_4[Fe(CN)_6]} + 2Fe_2(SO_4)_3 \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\\text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$$

65. (a) : In case of Lassaigne's test of halogens, it is necessary to remove sodium cyanide and sodium sulphide from the sodium extract if nitrogen and sulphur are present. This is done by boiling the sodium extract with conc. HNO_3.

$$NaCN + HNO_3 \rightarrow NaNO_3 + HCN\uparrow$$
$$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S\uparrow$$

66. (b) : Sodium cyanide ($Na + C + N \rightarrow NaCN$).

67. (d)

68. (b) : $$2CuSO_4 + K_4[Fe(CN)_6] \rightarrow \underset{\text{chocolate ppt.}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

69. (a) : Mass of organic compound = 0.25 g

Experimental values, At STP

$V_1 = 40$ mL, $V_2 = ?$

$T_1 = 300$ K, $T_2 = 273$ K

$P_1 = 725 - 25 = 700$ mm, $P_2 = 760$ mm

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{700 \times 40 \times 273}{300 \times 760} = 33.52 \text{ mL}$$

22400 mL of N_2 at STP weighs = 28 g

$$\therefore 33.52 \text{ mL of } N_2 \text{ at STP weighs} = \frac{28 \times 33.52}{22400} = 0.0419 \text{ g}$$

$$\% \text{ of N} = \frac{\text{Mass of nitrogen at STP}}{\text{Mass of organic compound taken}} \times 100$$

$$= \frac{0.0419}{0.25} \times 100 = 16.76\%$$

70. (a) : $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$

10 mL of 1 M H_2SO_4 = 10 mmol

$[\because M \times V_{(\text{mL})} = \text{mmol}]$

Acid used for the absorption of ammonia

= 10 mL of 2 N (or 1 M) H_2SO_4

$$\% \text{ of N} = \frac{1.4 \times N \times V}{W} = \frac{1.4 \times 2 \times 10}{0.75} = 37.33\%$$

71. (b) : Given : $V_1 = 55$ mL, $V_2 = ?$

$P_1 = 715 - 15 = 700$ mm, $P_2 = 760$ mm

$T_1 = 300$ K, $T_2 = 273$ K

General gas equation, $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

Volume of nitrogen at STP,

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{700 \times 55 \times 273}{760 \times 300} = 46.099 \text{ mL}$$

% of nitrogen = $\dfrac{V_2}{8W}$, where W = the mass of organic compound.

$$\% \text{ of N} = \frac{46.099}{8 \times 0.35} = 16.46$$

72. (a)

❖❖❖

CHAPTER
13

Hydrocarbons

13.2 Alkanes

1. Which of the following alkane cannot be made in good yield by Wurtz reaction?
(a) *n*-Hexane (b) 2, 3-Dimethylbutane
(c) *n*-Heptane (d) *n*-Butane
(NEET 2020)

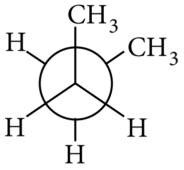
2. The alkane that gives only one monochloro product on chlorination with Cl_2 in presence of diffused sunlight is
(a) 2,2-dimethylbutane (b) neopentane
(c) *n*-pentane (d) isopentane.
(Odisha NEET 2019)

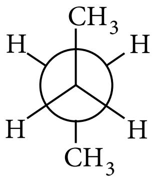
3. Hydrocarbon (*A*) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. (*A*) is
(a) $CH \equiv CH$ (b) $CH_2 = CH_2$
(c) $CH_3 - CH_3$ (d) CH_4 *(NEET 2018)*

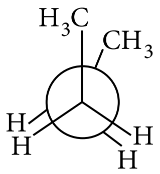
4. With respect to the conformers of ethane, which of the following statements is true?
(a) Bond angle changes but bond length remains same.
(b) Both bond angle and bond length change.
(c) Both bond angle and bond length remain same.
(d) Bond angle remains same but bond length changes. *(NEET 2017)*

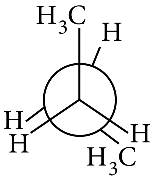
5. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is
(a) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
(b) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
(c) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
(d) the eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain.
(NEET-I 2016)

6. In the following the most stable conformation of *n*-butane is

(a)


(b)


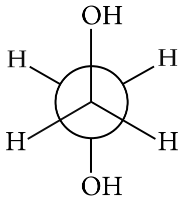
(c)


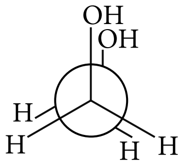
(d)


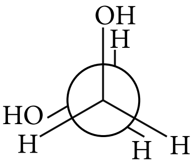
(2010)

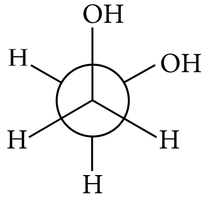
7. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by
(a) oxidation
(b) cracking
(c) distillation under reduced pressure
(d) hydrolysis. *(2010)*

8. Which of the following conformers for ethylene glycol is most stable?

(a)


(b)


(c)


(d)


(Mains 2010)

9. Dihedral angle in staggered form of ethane is
(a) 0° (b) 120°
(c) 60° (d) 180° *(2000)*

10. Which of the following reaction is expected to readily give a hydrocarbon product in good yields?
(a) $CH_3CH_3 \xrightarrow[h\nu]{Cl_2}$ (b) $(CH_3)_2CHCl \xrightarrow{C_2H_5OH}$
(c) $RCOOK \xrightarrow[\text{Oxidation}]{\text{Electrolysis}}$ (d) $RCOOAg \xrightarrow{I_2}$
(1997)

11. In the commercial gasolines, the type of hydrocarbons which are more desirable is
(a) linear unsaturated hydrocarbon
(b) toluene
(c) branched hydrocarbon
(d) straight-chain hydrocarbon. *(1997)*

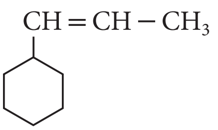
12. The most stable conformation of *n*-butane is
(a) gauche (b) staggered
(c) skew boat (d) eclipsed. *(1997)*

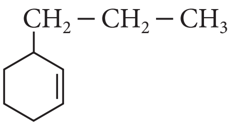
13. Which of the following is used as an antiknocking material?
(a) Glyoxal (b) Freon
(c) T.E.L. (d) Ethyl alcohol *(1996)*

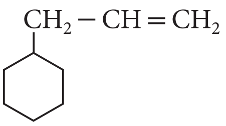
14. Reactivity of hydrogen atoms attached to different carbon atoms in alkanes has the order
(a) tertiary > primary > secondary
(b) primary > secondary > tertiary
(c) both (a) and (b)
(d) tertiary > secondary > primary. *(1993)*

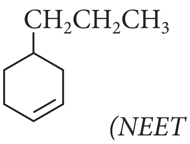
13.3 Alkenes

15. An alkene on ozonolysis gives methanal as one of the product. Its structure is

(a)


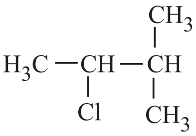
(b)


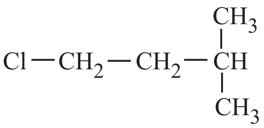
(c)


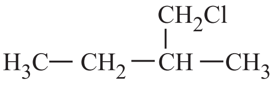
(d)


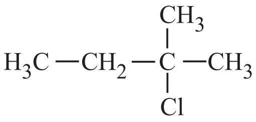
(NEET 2020)

16. An alkene *A* on reaction with O_3 and Zn—H_2O gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene *A* gives *B* as the major product. The structure of product *B* is

(a)

$H_3C-\underset{Cl}{CH}-\underset{CH_3}{\overset{CH_3}{CH}}$

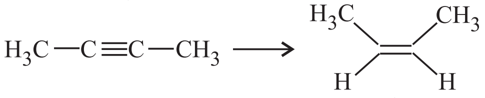
(b)

$Cl-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{CH}}$

(c)

$H_3C-CH_2-\overset{CH_2Cl}{CH}-CH_3$

(d)

$H_3C-CH_2-\underset{Cl}{\overset{CH_3}{C}}-CH_3$

(NEET 2019)

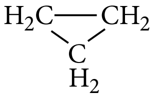
17. The most suitable reagent for the following conversion, is

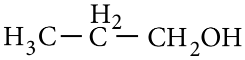


cis-2-butene

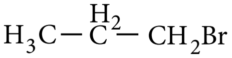
(a) $Hg^{2+}/H^+, H_2O$ (b) Na/liquid NH_3
(c) H_2, Pd/C, quinoline (d) Zn/HCl *(NEET 2019)*

18. Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction?

(a)


(b)

$H_3C-\overset{H_2}{C}-CH_2OH$

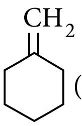
(c) $H_2C=C=O$

(d)

$H_3C-\overset{H_2}{C}-CH_2Br$

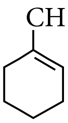
(NEET-II 2016)

19. The compound that will react most readily with gaseous bromine has the formula
(a) C_3H_6 (b) C_2H_2
(c) C_4H_{10} (d) C_2H_4 *(NEET-II 2016)*

20. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule to give a product 1-chloro-1-methyl-cyclohexane. The possible alkene is

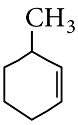
(a)


(*A*)

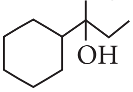
(b)


(*B*)

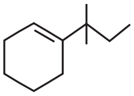
(c) (*A*) and (*B*)

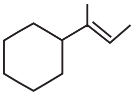
(d)


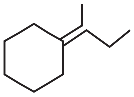
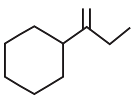
(2015)

21. Which of the following is not the product of dehydration of


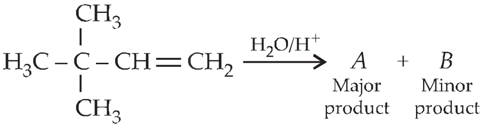
?

(a)


(b)


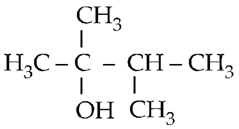
(c)  (d)  *(2015)*

22. In the following reaction

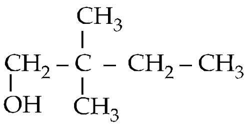


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{H_2O/H^+} \underset{\text{Major product}}{A} + \underset{\text{Minor product}}{B}$$

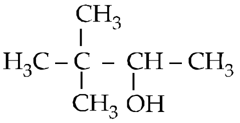
The major product is

(a) 

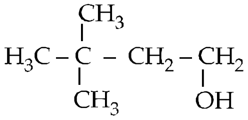
$$H_3C-\overset{CH_3}{\underset{OH}{C}}-\underset{CH_3}{CH}-CH_3$$

(b) 

$$\underset{OH}{CH_2}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

(c) 

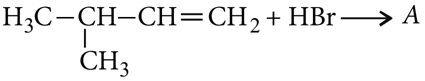
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-CH_3$$

(d)  *(2012)*

$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{OH}{CH_2}$$

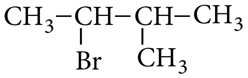
23. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism?

(a) Butanol (b) 2-Butyne
(c) 2-Butenol (d) 2-Butene *(2009)*

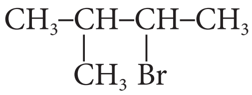
24. 

$$H_3C-\underset{CH_3}{CH}-CH=CH_2 + HBr \longrightarrow A$$

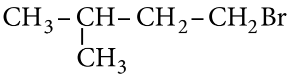
A (predominantly) is

(a) 

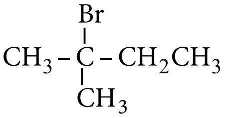
$$CH_3-\underset{Br}{CH}-\underset{CH_3}{CH}-CH_3$$

(b) 

$$CH_3-\underset{CH_3}{CH}-\underset{Br}{CH}-CH_3$$

(c) 

$$CH_3-\underset{CH_3}{CH}-CH_2-CH_2Br$$

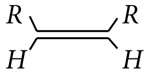
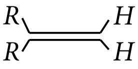
(d)  *(2008)*

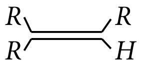
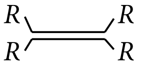
$$CH_3-\overset{Br}{\underset{CH_3}{C}}-CH_2CH_3$$

25. Which of the compound with molecular formula C_5H_{10} yields acetone on ozonolysis?

(a) 3-Methyl-1-butene (b) Cyclopentane
(c) 2-Methyl-1-butene (d) 2-Methyl-2-butene
(2007)

26. Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation conditions?

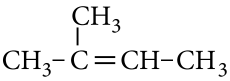
(a)  (b) 

(c)  (d) 

(R = alkyl substituent)
(2005)

27. Reaction of HBr with propene in the presence of peroxide gives

(a) isopropyl bromide (b) 3-bromopropane
(c) allyl bromide (d) *n*-propyl bromide.
(2004)

28. The compound,  $CH_3-\overset{CH_3}{C}=CH-CH_3$ on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

(a) CH_3COCH_3
(b) $CH_3COCH_3 + CH_3COOH$
(c) $CH_3COCH_3 + CH_3CHO$
(d) $CH_3CHO + CO_2$ *(2003)*

29. Geometrical isomers differ in

(a) position of functional group
(b) position of atoms
(c) spatial arrangement of atoms
(d) length of carbon chain. *(2002)*

30. In preparation of alkene from alcohol using Al_2O_3 which is the effective factor?

(a) Porosity of Al_2O_3
(b) Temperature
(c) Concentration
(d) Surface area of Al_2O_3 *(2001)*

31. Which reagent converts propene to 1-propanol?

(a) H_2O, H_2SO_4
(b) B_2H_6, H_2O_2, OH^-
(c) $Hg(OAc)_2$, $NaBH_4/H_2O$
(d) Aq. KOH *(2000)*

32. Which is maximum stable?

(a) 1-Butene
(b) *cis*-2-Butene
(c) *trans*-2-Butene
(d) All have same stability. *(2000)*

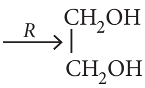
33. 2-Butene shows geometrical isomerism due to

(a) restricted rotation about double bond
(b) free rotation about double bond
(c) free rotation about single bond
(d) chiral carbon. *(2000)*

34. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is

(a) *trans*-2-pentene (b) 1-pentene
(c) 2-ethoxy pentane (d) 2-*cis*-pentene.
(1998)

35. In a reaction, $CH_2{=}CH_2 \xrightarrow[\text{acid}]{\text{Hypochlorous}} M \xrightarrow{R}$



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

where, M = Molecule and R = Reagent. M and R are
(a) CH_3CH_2OH and HCl
(b) $CH_2{=}CH_2$ and heat
(c) CH_3CH_2Cl and NaOH
(d) $CH_2Cl - CH_2OH$ and aq. $NaHCO_3$. *(1997)*

36. The reaction,
$CH_2{=}CH - CH_3 + HBr \longrightarrow CH_3CHBr - CH_3$ is
(a) electrophilic substitution
(b) free radical addition
(c) nucleophilic addition
(d) electrophilic addition. *(1996)*

37. Which of the following has zero dipole moment?
(a) 1-Butene (b) 2-Methyl-1-propene
(c) *cis*-2-Butene (d) *trans*-2-Butene *(1996)*

38. One of the following which does not observe the anti-Markownikoff's addition of HBr, is
(a) pent-2-ene (b) propene
(c) but-2-ene (d) but-1-ene. *(1994)*

39. Reduction of 2-butyne with sodium in liquid ammonia gives predominantly
(a) *cis*-2-butene (b) no reaction
(c) *trans*-2-butene (d) *n*-butane. *(1993)*

40. The restricted rotation about carbon carbon double bond in 2-butene is due to
(a) overlap of one *s* and sp^2-hybridized orbitals
(b) overlap of two sp^2-hybridized orbitals
(c) overlap of one *p* and one sp^2-hybridized orbitals
(d) sideways overlap of two *p*-orbitals. *(1993)*

41. Which one of the following can exhibit *cis-trans* isomerism?
(a) $CH_3 - CHCl - COOH$
(b) $H - C{\equiv}C - Cl$
(c) $ClCH{=}CHCl$
(d) $ClCH_2 - CH_2Cl$ *(1989)*

13.4 Alkynes

42. In the following reaction,

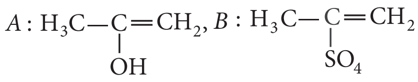
$$H_3C - C{\equiv}CH \xrightarrow[873\text{ K}]{\text{red hot iron tube}} A,$$

the number of sigma(σ) bonds present in the product A, is
(a) 21 (b) 9
(c) 24 (d) 18
(Odisha NEET 2019)

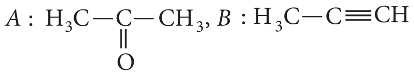
43. Which one is the correct order of acidity?
(a) $CH{\equiv}CH > CH_3{-}C{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$
(b) $CH{\equiv}CH > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH > CH_3{-}CH_3$
(c) $CH_3{-}CH_3 > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH > CH{\equiv}CH$
(d) $CH_2{=}CH_2 > CH_3{-}CH{=}CH_2 > CH_3{-}C{\equiv}CH > CH{\equiv}CH$
(NEET 2017)

44. Predict the correct intermediate and product in the following reaction :

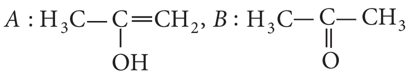
$$H_3C - C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{(A)}{\text{Intermediate}} \rightarrow \underset{(B)}{\text{Product}}$$

(a)


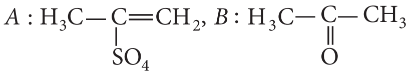
$A: H_3C{-}\underset{\underset{OH}{|}}{C}{=}CH_2,\ B: H_3C{-}\underset{\underset{SO_4}{|}}{C}{=}CH_2$

(b)


$A: H_3C{-}\underset{\underset{O}{\|}}{C}{-}CH_3,\ B: H_3C{-}C{\equiv}CH$

(c)


$A: H_3C{-}\underset{\underset{OH}{|}}{C}{=}CH_2,\ B: H_3C{-}\underset{\underset{O}{\|}}{C}{-}CH_3$

(d)


$A: H_3C{-}\underset{\underset{SO_4}{|}}{C}{=}CH_2,\ B: H_3C{-}\underset{\underset{O}{\|}}{C}{-}CH_3$

(NEET 2017)

45. The pair of electrons in the given carbanion, $CH_3C{\equiv}C^-$, is present in which of the following orbitals?
(a) sp^2 (b) sp
(c) $2p$ (d) sp^3 *(NEET-I 2016)*

46. In the reaction

$$H{-}C{\equiv}CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq. } NH_3} X \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq. } NH_3} Y,$$

X and Y are
(a) X = 2-butyne, Y = 2-hexyne
(b) X = 1-butyne, Y = 2-hexyne
(c) X = 1-butyne, Y = 3-hexyne
(d) X = 2-butyne, Y = 3-hexyne. *(NEET-I 2016)*

47. Which of the following organic compounds has same hybridization as its combustion product (CO_2)?
(a) Ethane (b) Ethyne
(c) Ethene (d) Ethanol *(2014)*

48. In the following reaction :

$$HC{\equiv}CH \xrightarrow[Hg^{2+}]{H_2SO_4} \text{'}P\text{'}$$

Product '*P*' will not give
(a) Tollens' reagent test
(b) Brady's reagent test
(c) Victor Meyer test
(d) Iodoform test. *(Karnataka NEET 2013)*

49. Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne?

(a) $NaNH_2$ (b) HCl
(c) O_2 (d) Br_2 *(Mains 2012)*

50. Considering the state of hybridization of carbon atoms, find out the molecule among the following which is linear?

(a) $CH_3-CH=CH-CH_3$
(b) $CH_3-C\equiv C-CH_3$
(c) $CH_2=CH-CH_2-C\equiv CH$
(d) $CH_3-CH_2-CH_2-CH_3$ *(2011)*

51. Base strength of

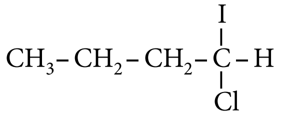
$\underset{(i)}{H_3C\bar{C}H_2}$, $\underset{(ii)}{H_2C=\bar{C}H}$ and $\underset{(iii)}{H-C\equiv\bar{C}}$

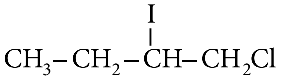
is in the order of

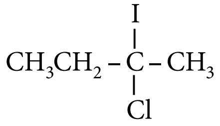
(a) (i) > (iii) > (ii) (b) (i) > (ii) > (iii)
(c) (ii) > (i) > (iii) (d) (iii) > (ii) > (i) *(2008)*

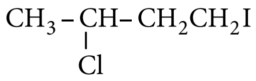
52. Predict the product *C* obtained in the following reaction of 1-butyne.

$$CH_3CH_2-C\equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$$

(a) 
$CH_3-CH_2-CH_2-\overset{I}{\underset{Cl}{C}}-H$

(b) 
$CH_3-CH_2-\overset{I}{C}H-CH_2Cl$

(c) 
$CH_3CH_2-\overset{I}{\underset{Cl}{C}}-CH_3$

(d) 
$CH_3-\underset{Cl}{C}H-CH_2CH_2I$ *(2007)*

53. Products of the following reaction :

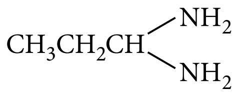
$$CH_3C\equiv CCH_2CH_3 \xrightarrow[\text{(ii) hydrolysis}]{\text{(i) } O_3}$$

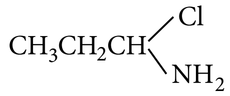
are

(a) $CH_3COOH + CO_2$
(b) $CH_3COOH + HOOCCH_2CH_3$
(c) $CH_3CHO + CH_3CH_2CHO$
(d) $CH_3COOH + CH_3COCH_3$ *(2005)*

54. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

(a) $CH_3-CH=CH_2$ (b) $CH_3-C\equiv CH$

(c) 

(d)  *(2002)*

55. When acetylene is passed through dil. H_2SO_4 in the presence of $HgSO_4$, the compound formed is

(a) acetic acid (b) ketone
(c) ether (d) acetaldehyde. *(1999)*

56. The cylindrical shape of an alkyne is due to

(a) two sigma C – C and one π C – C bonds
(b) one sigma C – C and two π C – C bonds
(c) three sigma C – C bonds
(d) three π C – C bonds. *(1997)*

57. $R-CH_2-CCl_2-R \xrightarrow{\text{Reagent}} R-C\equiv C-R$

The reagent is

(a) Na (b) HCl in H_2O
(c) KOH in C_2H_5OH (d) Zn in alcohol. *(1993)*

58. A compound is treated with $NaNH_2$ to give sodium salt. Identify the compound.

(a) C_2H_2 (b) C_6H_6
(c) C_2H_6 (d) C_2H_4 *(1993)*

59. The shortest C–C bond distance is found in

(a) diamond (b) ethane
(c) benzene (d) acetylene. *(1991)*

60. Acetylenic hydrogens are acidic because

(a) sigma electron density of C – H bond in acetylene is nearer to carbon, which has 50% *s*-character
(b) acetylene has only open hydrogen in each carbon
(c) acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons
(d) acetylene belongs to the class of alkynes with molecular formula, C_nH_{2n-2}. *(1989)*

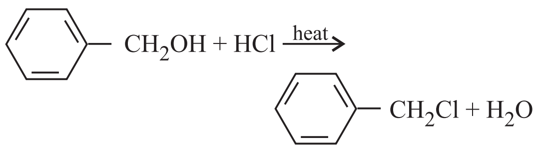
61. Which is the most suitable reagent among the following to distinguish compound (3) from rest of the compounds?

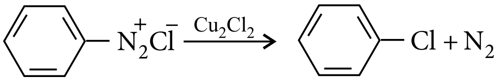
(1) $CH_3-C\equiv C-CH_3$
(2) $CH_3-CH_2-CH_2-CH_3$
(3) $CH_3-CH_2C\equiv CH$
(4) $CH_3-CH=CH_2$

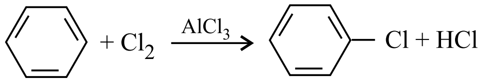
(a) Bromine in carbon tetrachloride
(b) Bromine in acetic acid
(c) Alk. $KMnO_4$
(d) Ammoniacal silver nitrate *(1989)*

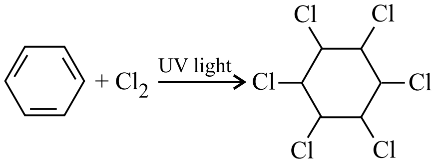
13.5 Aromatic hydrocarbons

62. Among the following the reaction that proceeds through an electrophilic substitution is

(a) 

(b) 

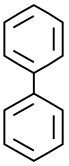
(c) 

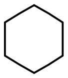
(d) 

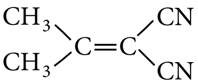
(NEET 2019)

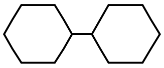
63. Which of the following can be used as the halide component for Friedel–Crafts reaction?
(a) Chlorobenzene (b) Bromobenzene
(c) Chloroethene (d) Isopropyl chloride
(NEET-II 2016)

64. In which of the following molecules, all atoms are coplanar?

(a) 

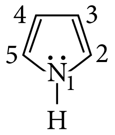
(b) 

(c) 
$(CH_3)_2C=C(CN)_2$

(d) 

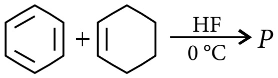
(NEET-II 2016)

65. In pyrrole the electron density is maximum on

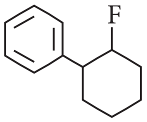


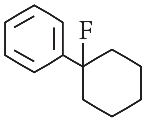
(a) 2 and 3 (b) 3 and 4
(c) 2 and 4 (d) 2 and 5
(NEET-II 2016)

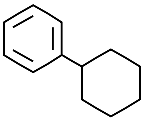
66. In the given reaction,

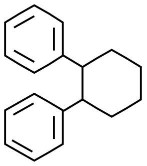


the product *P* is

(a) 

(b) 

(c) 

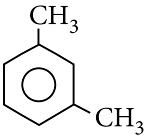
(d) 

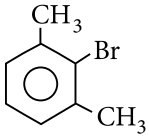
(NEET-II 2016)

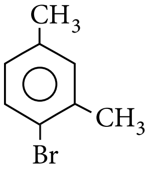
67. Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3. If a large amount of $KHSO_4$ is added to the mixture, the rate of nitration will be
(a) unchanged (b) doubled
(c) faster (d) slower.
(NEET-I 2016)

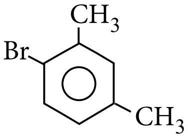
68. The oxidation of benzene by V_2O_5 in the presence of air produces
(a) maleic anhydride
(b) benzoic acid
(c) benzaldehyde
(d) benzoic anhydride. *(2015)*

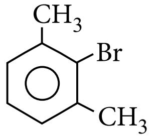
69. What products are formed when the following compound is treated with Br_2 in the presence of $FeBr_3$?

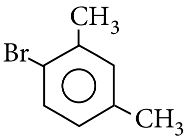


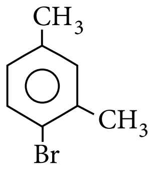
(a) 

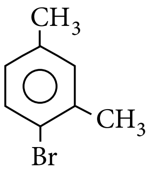
and 

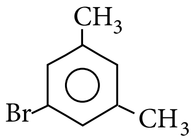
(b) 

and 

(c) 

and 

(d) 

and 

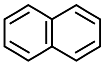
(2014)

70. Some *meta*-directing substituents in aromatic substitution are given. Which one is most deactivating?
(a) — COOH (b) — NO_2
(c) — $C\equiv N$ (d) — SO_3H
(NEET 2013)

71. Which of the following compounds will not undergo Friedel-Crafts reaction easily?
(a) Nitrobenzene (b) Toluene
(c) Cumene (d) Xylene *(NEET 2013)*

72. Which of the following chemical system is non aromatic?

(a) 

(b) 

(c) 

(d) 

(Karnataka NEET 2013)

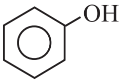
73. Among the following compounds the one that is most reactive towards electrophilic nitration is
(a) benzoic acid (b) nitrobenzene
(c) toluene (d) benzene.
(2012, 1992)

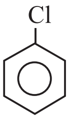
74. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives X and reaction in presence of light gives Y. Thus, X and Y are
(a) X = benzal chloride,
Y = *o*-chlorotoluene
(b) X = *m*-chlorotoluene,
Y = *p*-chlorotoluene
(c) X = *o*- and *p*-chlorotoluene,
Y = trichloromethyl benzene
(d) X = benzyl chloride,
Y = *m*-chlorotoluene. *(2010)*

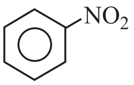
75. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form
(a) chlorobenzene (b) benzyl chloride
(c) xylene (d) toluene. *(2009)*

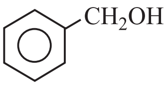
76. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the mixture, nitric acid acts as a/an
(a) acid (b) base
(c) catalyst (d) reducing agent.
(2009)

77. Which one of the following is most reactive towards electrophilic attack?

(a) 

(b) 

(c) 

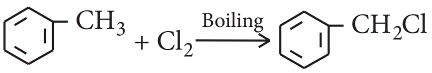
(d) 

(2008)

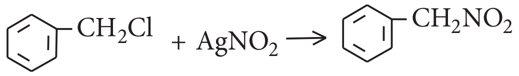
78. The order of decreasing reactivity towards an electrophilic reagent, for the following would be
(i) benzene (ii) toluene
(iii) chlorobenzene (iv) phenol
(a) (ii) > (iv) > (i) > (iii)
(b) (iv) > (iii) > (ii) > (i)
(c) (iv) > (ii) > (i) > (iii)
(d) (i) > (ii) > (iii) > (iv) *(2007)*

79. Using anhydrous $AlCl_3$ as catalyst, which one of the following reactions produces ethylbenzene (PhEt)?
(a) $H_3C - CH_2OH + C_6H_6$
(b) $CH_3 - CH{=}CH_2 + C_6H_6$
(c) $H_2C{=}CH_2 + C_6H_6$
(d) $H_3C - CH_3 + C_6H_6$ *(2004)*

80. Which one of the following is a free-radical substitution reaction?

(a) 

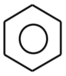
(b) 

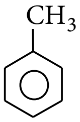
(c) 

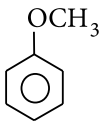
(d) $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$ *(2003)*

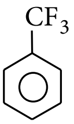
81. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is
(a) III > II > I (b) II > III > I
(c) I < II > III (d) I > II > III *(2003)*

82. Increasing order of electrophilic substitution for following compounds

(I) 

(II) 

(III) 

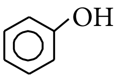
(IV) 

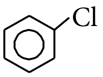
(a) IV < I < II < III (b) III < II < I < IV
(c) I < IV < III < II (d) II < III < I < IV
(2000)

83. In Friedel-Crafts reaction, toluene can be prepared by
(a) $C_6H_6 + CH_3Cl$ (b) $C_6H_5Cl + CH_4$
(c) $C_6H_6 + CH_2Cl_2$
(d) $C_6H_6 + CH_3COCl$ *(2000)*

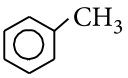
84. In Friedel-Crafts alkylation, besides $AlCl_3$ the other reactants are
(a) $C_6H_6 + CH_3Cl$ (b) $C_6H_6 + CH_4$
(c) $C_6H_6 + NH_3$ (d) $C_6H_6 + CH_3COCl$
(1999)

85. Which of the following compounds will be most easily attacked by an electrophile?

(a) 

(b) 

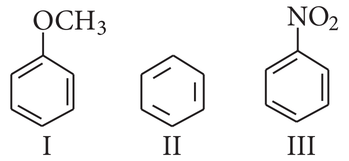
(c) 

(d) 

(1999, 1998)

86. Which one of these is not compatible with arenes?
(a) Electrophilic additions
(b) Delocalisation of π-electrons
(c) Greater stability
(d) Resonance *(1998)*

87. Among the following compounds (I-III) the correct order of reaction with electrophile is



(a) I > II > III (b) I = II > III
(c) II > III > I (d) III < I < II *(1997)*

88. Electrophile in the case of chlorination of benzene in the presence of $FeCl_3$ is
(a) Cl (b) $FeCl_3$
(c) Cl^+ (d) Cl^- *(1996)*

89. The reactive species in the nitration of benzene is
(a) NO_3 (b) HNO_3
(c) NO_2^+ (d) NO_2^- *(1994)*

90. Which is the correct symbol relating the two Kekule structures of benzene?
(a) $\rightleftharpoons$ (b) $\longrightarrow$
(c) $\equiv$ (d) $\longleftrightarrow$ *(1993)*

91. Select the true statement about benzene amongst the following
(a) because of unsaturation benzene easily undergoes addition
(b) there are two types of C – C bonds in benzene molecule
(c) there is cyclic delocalisation of π-electrons in benzene
(d) monosubstitution of benzene gives three isomeric products. *(1992)*

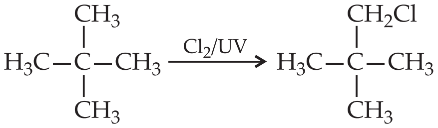
ANSWER KEY

1.	(c)	**2.**	(b)	**3.**	(d)	**4.**	(c)	**5.**	(b)	**6.**	(b)	**7.**	(b)	**8.**	(d)	**9.**	(c)	**10.**	(c)
11.	(c)	**12.**	(b)	**13.**	(c)	**14.**	(d)	**15.**	(c)	**16.**	(d)	**17.**	(c)	**18.**	(c)	**19.**	(a)	**20.**	(c)
21.	(a)	**22.**	(a)	**23.**	(d)	**24.**	(d)	**25.**	(d)	**26.**	(a)	**27.**	(d)	**28.**	(b)	**29.**	(c)	**30.**	(b)
31.	(b)	**32.**	(c)	**33.**	(a)	**34.**	(a)	**35.**	(d)	**36.**	(d)	**37.**	(d)	**38.**	(c)	**39.**	(c)	**40.**	(d)
41.	(c)	**42.**	(a)	**43.**	(a)	**44.**	(c)	**45.**	(b)	**46.**	(c)	**47.**	(b)	**48.**	(c)	**49.**	(a)	**50.**	(b)
51.	(b)	**52.**	(c)	**53.**	(b)	**54.**	(b)	**55.**	(d)	**56.**	(b)	**57.**	(c)	**58.**	(a)	**59.**	(d)	**60.**	(a)
61.	(d)	**62.**	(c)	**63.**	(d)	**64.**	(a)	**65.**	(d)	**66.**	(c)	**67.**	(d)	**68.**	(a)	**69.**	(c)	**70.**	(b)
71.	(a)	**72.**	(d)	**73.**	(c)	**74.**	(c)	**75.**	(d)	**76.**	(b)	**77.**	(a)	**78.**	(c)	**79.**	(c)	**80.**	(a)
81.	(d)	**82.**	(a)	**83.**	(a)	**84.**	(a)	**85.**	(a)	**86.**	(a)	**87.**	(a)	**88.**	(c)	**89.**	(c)	**90.**	(d)
91.	(c)																		

Hints & Explanations

1. (c) : Wurtz reaction is used for the preparation of higher alkanes containing even number of C-atoms. Thus this reaction cannot be used for the preparation of *n*-heptane.

2. (b) : In chlorination of alkanes, hydrogen is replaced by chlorine. In *neo*-pentane, only one type of hydrogen is present, hence replacement of any hydrogen atom will give the same product.



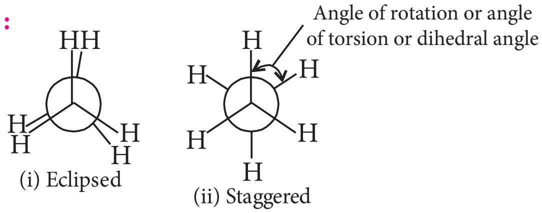
$$\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{H_3C-C-CH_3}} \xrightarrow{Cl_2/UV} \underset{\substack{|\\CH_3}}{\overset{\substack{CH_2Cl\\|}}{H_3C-C-CH_3}}$$

neo-pentane

3. (d) : $\underset{(A)}{CH_4} \xrightarrow{Br_2/h\nu} CH_3Br \xrightarrow{\substack{\text{Na/dry ether}\\ \text{Wurtz reaction}}} \underset{\substack{\text{(Less than 4}\\ \text{caron atoms)}}}{CH_3-CH_3}$

4. (c) : Conformers of ethane have different dihedral angles but same bond angle and bond lengths.

5. (b) :



(i) Eclipsed (ii) Staggered

Newman's projections of ethane

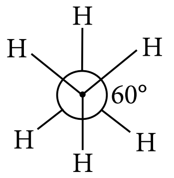
Magnitude of torsional strain depends upon the angle of rotation about C—C bond. Staggered form has the least torsional strain and the eclipsed form has the maximum torsional strain. So, the staggered conformation of ethane is more stable than the eclipsed conformation.

6. (b) : The anti-conformation is the most stable conformation of *n*-butane as in this, the bulky methyl groups are as far apart as possible thereby keeping steric repulsion at a minimum.

7. (b) : The process of cracking converts higher alkanes into smaller alkanes and alkenes. This process can be used for production of natural gas.

8. (d) : The conformation (d) is most stable because of intermolecular H-bonding.

9. (c) : The staggered form of ethane has the following structure and the dihedral angle is 60°, which means 'H' atoms are at an angle of 60° to each other.



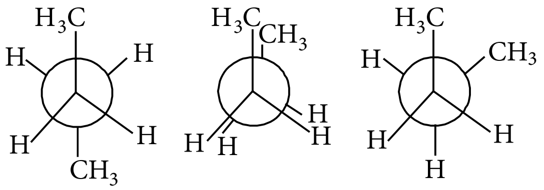
10. (c) : When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, hydrocarbon is evolved at anode.

$$2RCOOK \xrightarrow[\text{Oxidation}]{\text{Electrolysis}} \underset{\text{Anode}}{2RCOO^-} + \underset{\text{Cathode}}{2K^+}$$

At anode : $2RCOO^- - 2e^- \rightarrow \underset{\text{Alkane}}{R-R} + 2CO_2$

11. (c) : The branching of chain increases the octane number of a fuel. High octane number means better fuel.

12. (b) : Newman projections for *n*-butane are



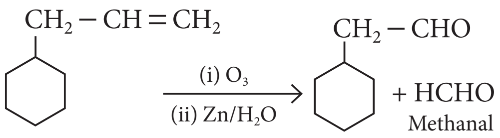
staggered eclipsed skew or gauche

The staggered conformation has minimum repulsion between the hydrogen atoms attached tetrahedrally to the two carbon atoms. Thus, it is the most stable conformation.

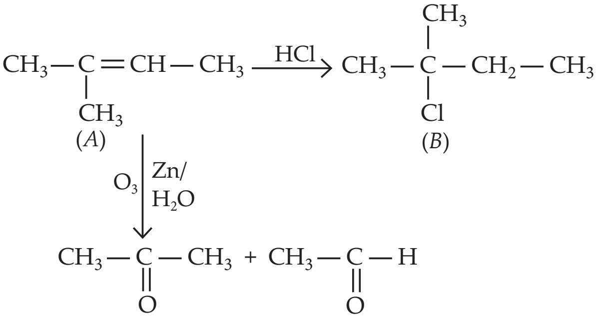
13. (c) : Tetraethyl lead $(C_2H_5)_4Pb$, is used as an antiknocking agent in gasoline used for running automobiles.

14. (d) : The reactivity of H-atom depends upon the stability of free radicals, therefore reactivity of H-atom follows the order : 3° > 2° > 1°.

15. (c) :



16. (d) :

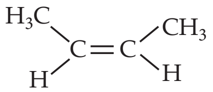


$$\underset{(A)}{CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_3} \xrightarrow{HCl} \underset{(B)}{CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2-CH_3}$$

$$\xrightarrow[O_3]{Zn/H_2O} CH_3-\underset{O}{\underset{||}{C}}-CH_3 + CH_3-\underset{O}{\underset{||}{C}}-H$$

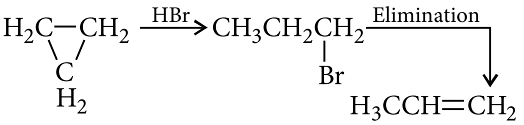
Addition of HCl to an alkene (*A*) will take place according to Markownikoff's rule.

17. (c) : $CH_3C\equiv CCH_3 \xrightarrow[\text{quinoline}]{H_2, Pd/C}$



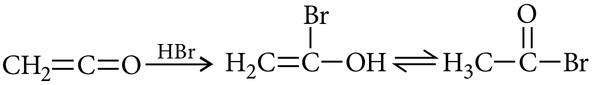
cis-2-Butene

18. (c) :



$$\underset{H_2}{\overset{H_2C-CH_2}{\diagdown C \diagup}} \xrightarrow{HBr} CH_3CH_2\underset{Br}{\underset{|}{CH_2}} \xrightarrow{\text{Elimination}} H_3CCH=CH_2$$

$$CH_3CH_2CH_2OH \xrightarrow{HBr} \xrightarrow{\text{Elimination}} H_3C\text{-}CH=CH_2$$

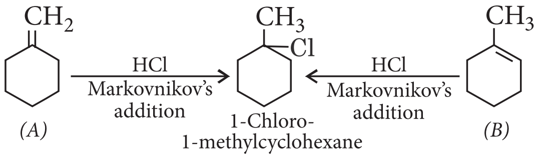


$$CH_2=C=O \xrightarrow{HBr} H_2C=\overset{Br}{\overset{|}{C}}-OH \rightleftharpoons H_3C-\overset{O}{\overset{||}{C}}-Br$$

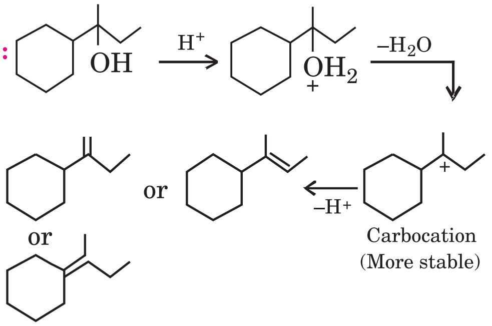
$$CH_3CH_2CH_2Br \xrightarrow{\text{Elimination}} CH_3CH=CH_2$$

19. (a) : Rate of free radical substitution with $Br_{2(g)}$ depends upon the stability of free radical. Propenyl free radical is allylic free radical which is more stable.

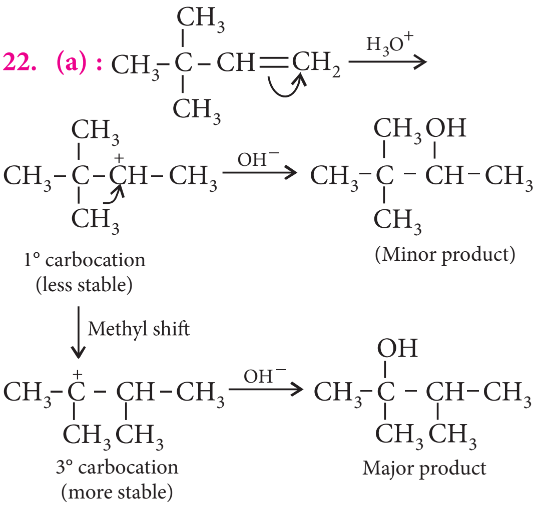
20. (c) :



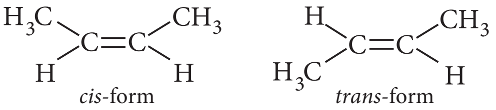
21. (a) :



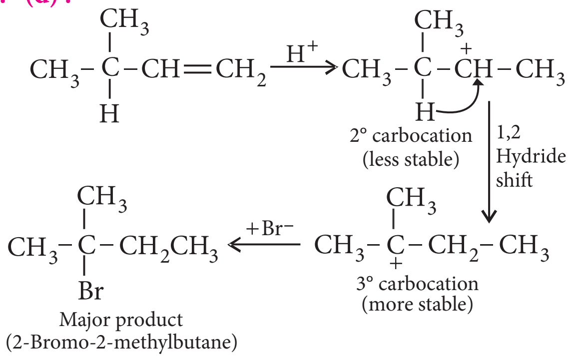
22. (a) :



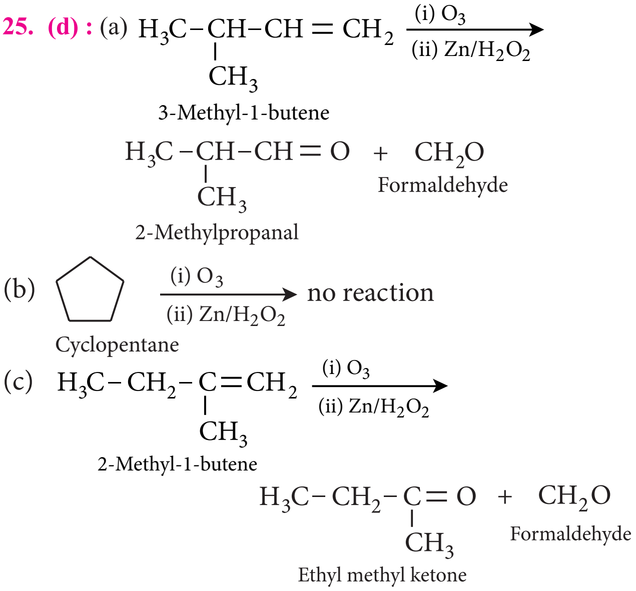
23. (d) : *Cis-trans* isomerism is exhibited by compounds having C $=$ C, C $=$ N and N $=$ N groups, due to restricted rotation around the double bond. Among the given options, only 2-butene exhibits geometrical isomerism.

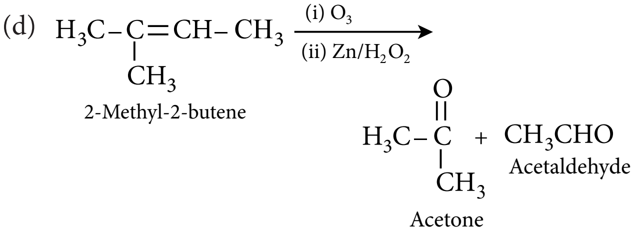


24. (d) :



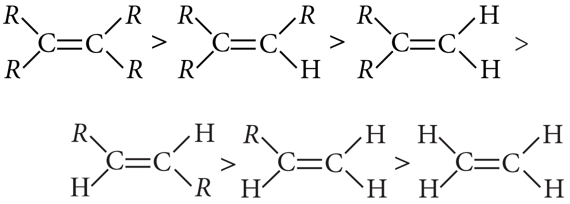
25. (d) :



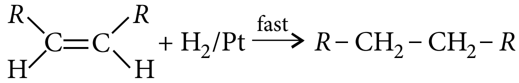


26. (a) : The relative rates of hydrogenation decrease with the increase of steric hindrance. Most stable the alkene, slowly it undergoes hydrogenation to give the product. Least substituted alkene is less stable and more reactive.

Order of stability is :



Hence, alkene which will react faster with H_2 is that which is most unstable.



27. (d) : The formation of *n*-propyl bromide in presence of peroxide can be explained as follow :

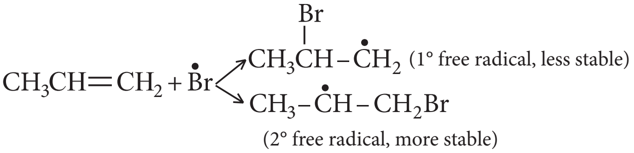
Step 1 : Peroxide undergoes fission to give free radicals.

$$R-O-O-R \longrightarrow 2R-\dot{O}$$

Step 2 : HBr combines with free radical to form bromine free radical.

$$R-\dot{O} + HBr \longrightarrow R-OH + \dot{Br}$$

Step 3 : $\dot{Br}$ attacks the double bond of the alkene to form a more stable free radical.

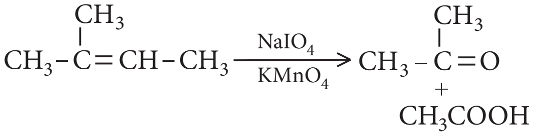


Step 4 : More stable free radical attacks on HBr.

$$CH_3\dot{C}HCH_2Br + HBr \longrightarrow \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br} + \dot{Br}$$

Step 5 : $\dot{Br} + \dot{Br} \longrightarrow Br_2$

28. (b) :



29. (c) : Geometrical isomers are those isomers which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to hindered rotation around the double bonded atoms.

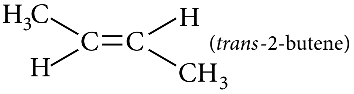
30. (b) : Temperature is an effective factor because at different temperature it forms different products.

$$CH_3CH_2OH \xrightarrow[-H_2O]{Al_2O_3,\ 620\ K} CH_2=CH_2$$

This is intramolecular dehydration. At lower temperature, intermolecular dehydration takes place between two molecules of alcohol and ether will be formed.

31. (b) : Propene adds to diborane (B_2H_6) giving an addition product. The addition compound on oxidation gives 1-propanol. Here addition of water takes place according to anti-Markownikoff's rule.

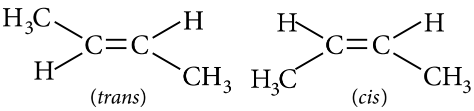
32. (c) :



(*trans*-2-butene)

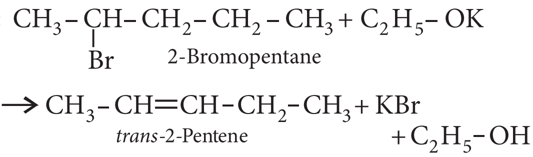
This is most stable as the repulsion between two methyl groups is least.

33. (a) : Due to restricted rotation about double bond, 2-butene shows geometrical isomerism.



(*trans*) (*cis*)

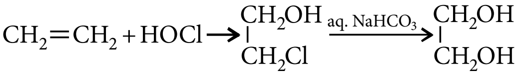
34. (a) :



$$CH_3-\underset{\substack{|\\ Br}}{CH}-CH_2-CH_2-CH_3+C_2H_5-OK \quad \text{2-Bromopentane}$$

$$\longrightarrow \underset{trans\text{-2-Pentene}}{CH_3-CH=CH-CH_2-CH_3}+KBr+C_2H_5-OH$$

35. (d) :



$$CH_2=CH_2+HOCl\longrightarrow \begin{matrix}CH_2OH\\ |\\ CH_2Cl\end{matrix} \xrightarrow{\text{aq. NaHCO}_3} \begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}$$

Therefore, $M = CH_2Cl—CH_2OH$ and
R = aq. $NaHCO_3$

36. (d) : In this reaction, HBr undergoes heterolytic fission as $HBr \longrightarrow H^+ + Br^-$

$$CH_2=CH-CH_3+HBr\longrightarrow CH_3-\overset{+}{C}H-CH_3$$

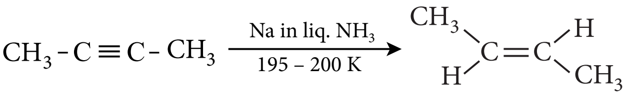
$$\xrightarrow{Br^-} CH_3-CHBr-CH_3$$

This is an example of electrophilic addition reaction.

37. (d)

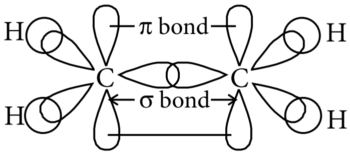
38. (c) : In case of but-2-ene ($CH_3-CH=CH-CH_3$) both double bonded carbons are identical. Therefore, it does not observe the anti-Markownikoff's addition of HBr.

39. (c) : Reduction of non-terminal alkynes with Na in liq. NH_3 at 195 - 200 K gives *trans*-2-butene.



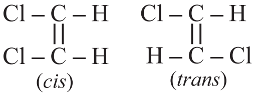
trans-But-2-ene
(Birch reduction)

40. (d) : $>C=C<$,



Restricted rotation is due to sideways overlap of two *p*-orbitals.

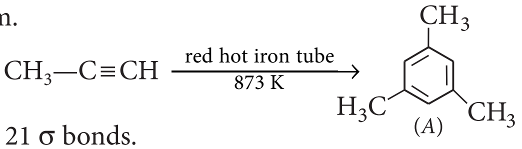
41. (c) :



$$\underset{(cis)}{\begin{matrix}Cl-C-H\\ \|\\ Cl-C-H\end{matrix}} \qquad \underset{(trans)}{\begin{matrix}Cl-C-H\\ \|\\ H-C-Cl\end{matrix}}$$

1, 2-Dichloroethene exhibits *cis-trans* (geometrical) isomerism.

42. (a) :



There are 21 σ bonds.

43. (a) : Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

$$\overset{sp}{HC}\equiv\overset{sp}{CH} > \overset{sp^2}{H_2C}=\overset{sp^2}{CH_2} > \overset{sp^3}{CH_3}—\overset{sp^3}{CH_3}$$

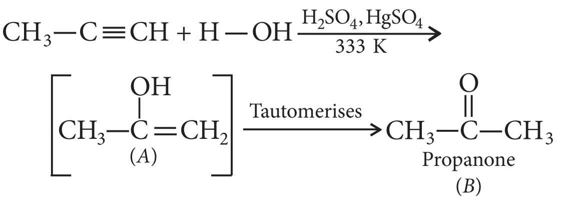
This is because *sp*-hybridised carbon is more electronegative than sp^2-hybridised carbon which is further more electronegative than sp^3-hybridised carbon. Hence, in ethyne proton can be released more easily than ethene and ethane.

Among alkynes the order of acidity is :

$$HC\equiv CH > CH_3—C\equiv CH > CH_3—C\equiv C—CH_3$$

This is due to $+I$ effect of — CH_3 group.

44. (c) : In case of unsymmetrical alkynes addition of H_2O occurs in accordance with Markownikoff's rule.



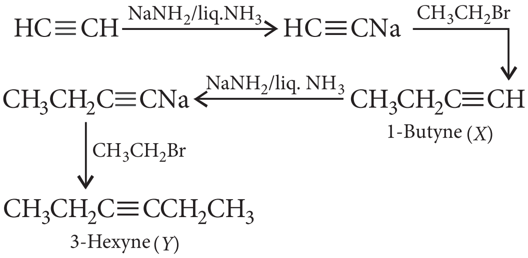
$$CH_3—C\equiv CH + H—OH \xrightarrow[333\ K]{H_2SO_4,\ HgSO_4}$$

$$\left[\underset{(A)}{CH_3—\overset{\overset{OH}{|}}{C}=CH_2}\right] \xrightarrow{\text{Tautomerises}} \underset{\substack{\text{Propanone}\\ (B)}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_3}$$

45. (b) : $CH_3—\overset{sp}{C}\equiv\overset{sp}{C^-}$

Thus, pair of electrons is present in *sp*-hybridised orbital.

46. (c) :



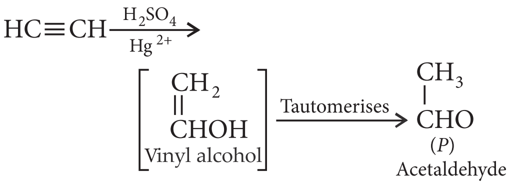
$$\begin{tikzcd}
HC\equiv CH \arrow[r, "NaNH_2/liq.NH_3"] & HC\equiv CNa \arrow[dr, "CH_3CH_2Br"] & \\
CH_3CH_2C\equiv CNa \arrow[d, "CH_3CH_2Br"] & & \underset{\text{1-Butyne }(X)}{CH_3CH_2C\equiv CH} \arrow[ll, "NaNH_2/liq.\ NH_3"'] \\
\underset{\text{3-Hexyne }(Y)}{CH_3CH_2C\equiv CCH_2CH_3} & &
\end{tikzcd}$$

47. (b) : $C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$

Both ethyne and CO_2 have *sp*-hybridisation.

$$O{=}\overset{sp}{C}{=}O \qquad H\overset{sp}{C}{\equiv}\overset{sp}{C}H$$

48. (c) :



$$HC{\equiv}CH \xrightarrow[Hg^{2+}]{H_2SO_4} \left[\begin{array}{c}CH_2\\ \|\\ CHOH\\ \text{Vinyl alcohol}\end{array}\right] \xrightarrow{\text{Tautomerises}} \begin{array}{c}CH_3\\ |\\ CHO\\ (P)\\ \text{Acetaldehyde}\end{array}$$

Acetaldehyde does not give Victor Meyer test.

49. (a) : Terminal alkynes (1-butyne) react with $NaNH_2$ to form sodium acetylide and evolve hydrogen but 2-butyne do not.

50. (b) : $CH_3-C{\equiv}C-CH_3$

In case of sp^3 hybridised carbon, bond angle is 109° 28′; sp^2 hybridised carbon, bond angle is 120° and *sp* hybridised carbon, bond angle is 180°.

So, only $CH_3-\underset{\substack{\downarrow\\ sp}}{C}{\equiv}\underset{\substack{\downarrow\\ sp}}{C}-CH_3$ is linear.

51. (b) : $H-\underset{sp}{C}{\equiv}\underset{sp}{C}-H > \underset{sp^2}{CH_2}{=}\underset{sp^2}{CH_2} > \underset{sp^3}{CH_3}\underset{sp^3}{CH_3}$

(Acidic character)

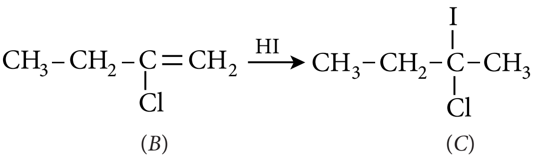
Conjugate base of the given acid :

$\bar{C}{\equiv}C-H < \bar{C}H{=}CH_2 < \bar{C}H_2CH_3$

(Basic character)

Conjugate base of stronger acid is weaker and vice-versa.

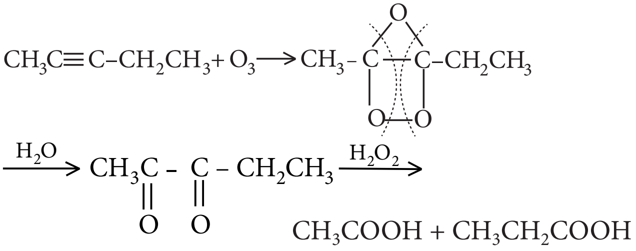
52. (c) : $CH_3-CH_2-C{\equiv}CH + HCl \longrightarrow$



$$\underset{(B)}{CH_3-CH_2-\underset{\substack{|\\ Cl}}{C}{=}CH_2} \xrightarrow{HI} \underset{(C)}{CH_3-CH_2-\overset{\substack{I\\ |}}{\underset{\substack{|\\ Cl}}{C}}-CH_3}$$

According to Markownikoff's rule, during hydrohalogenation to unsymmetrical alkene, the negative part of the addendum adds to less hydrogenated (*i.e.* more substituted) carbon atom.

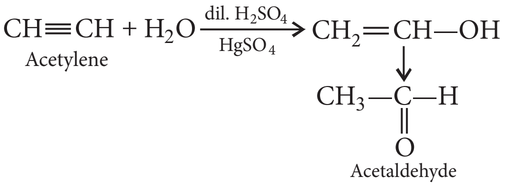
53. (b) : On ozonolysis, higher alkynes form diketones which are further oxidised to dicarboxylic acid.



$$CH_3C{\equiv}C-CH_2CH_3 + O_3 \longrightarrow CH_3-C-C-CH_2CH_3 \xrightarrow{H_2O} CH_3\underset{\substack{\|\\ O}}{C}-\underset{\substack{\|\\ O}}{C}-CH_2CH_3 \xrightarrow{H_2O_2} CH_3COOH + CH_3CH_2COOH$$

54. (b) : $CH_3CH_2CHCl_2 \xrightarrow{NaNH_2} CH_3C{\equiv}CH$

55. (d) :



$$\underset{\text{Acetylene}}{CH{\equiv}CH} + H_2O \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} CH_2{=}CH-OH \longrightarrow \underset{\text{Acetaldehyde}}{CH_3-\underset{\substack{\|\\ O}}{C}-H}$$

56. (b) : In alkyne, two carbon atoms constituting the triple bond are *sp*-hybridised.Carbon undergoes *sp*-hybridisation to form two *sp*-hybrid orbitals. The two 2*p*-orbitals remain unhybridised. Hybrid orbitals form one sigma bond while two π-bonds are formed by unhybridised orbitals.

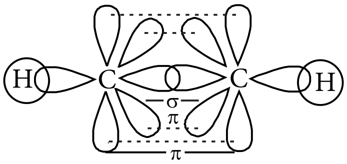
57. (c) : A powerful base is needed to carry out second dehydrohalogenation reaction *e.g.*, hot alcoholic KOH solution or alkoxide ion.

58. (a) : Alkynes react with strong bases like $NaNH_2$ to form sodium acetylide derivative known as acetylides.

$H-C{\equiv}C-H + NaNH_2 \longrightarrow H-C{\equiv}\bar{C}\overset{+}{Na} + 1/2H_2$

59. (d) : Shortest C– C distance (1.20 Å) is in acetylene.

60. (a) :

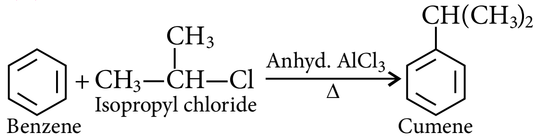


The formation of C – H bond in acetylene involves *sp*-hybridised carbon atom. Since *s*-electrons are closer to the nucleus than *p*-electrons, the electrons present in a bond having more *s*-character will be more closer to the nucleus. In alkynes *s* character is 50%, the electrons constituting this bond are more strongly bonded by the carbon nucleus. Thus, acetylenic C-atom becomes more electronegative in comparison to sp^2, sp^3 and hence the hydrogen atom present on carbon atom (≡ C – H) can be easily removed.

61. (d) : All the three reagents except ammoniacal $AgNO_3$ reacts with 1, 2 and 4 compounds. The compound 3 possessing the terminal alkyne only reacts with ammoniacal $AgNO_3$ and thus can be distinguished from 1, 2 and 4 compounds.

62. (c) : The attacking species in the reaction given in option (c) is an electrophile *i.e.*, $\overset{\delta+}{Cl}$. Therefore, it is an electrophilic substitution reaction.

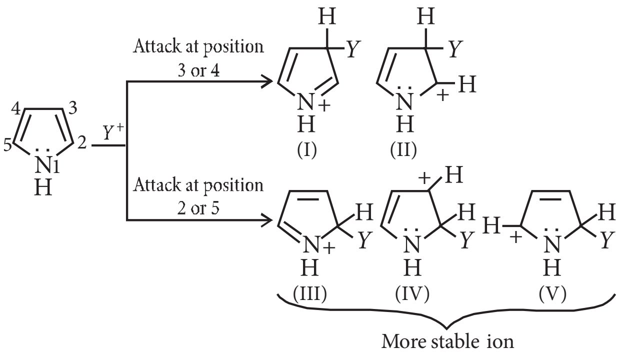
63. (d) : Friedel–Crafts reaction :



Chlorobenzene, bromobenzene and chloroethene are not suitable halide components as C–*X* bond acquires some double bond character due to resonance of lone pair of electrons with π-bond.

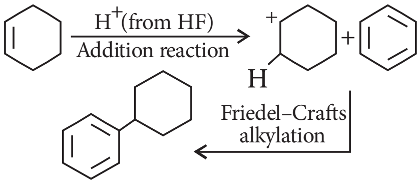
64. (a) : Biphenyl is coplanar as all C-atoms are sp^2 hybridised.

65. (d) : Pyrrole has maximum electron density on 2 and 5. It generally reacts with electrophiles at the C-2 or C-5 due to the highest degree of stability of the protonated intermediate.



Attack at position 3 or 4 yields a carbocation that is a hybrid of structures (I) and (II). Attack at position 2 or 5 yields a carbocation that is a hybrid not only of structures (III) and (IV) (analogous to I and II) but also of structure (V). The extra stabilization conferred by (V) makes this ion the more stable one. Also, attack at position 2 or 5 is faster because the developing positive charge is accommodated by three atoms of the ring instead of only two.

66. (c) :

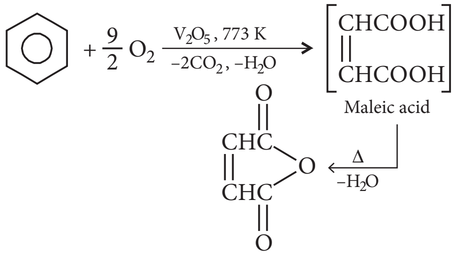


67. (d) : Mechanism of nitration is :

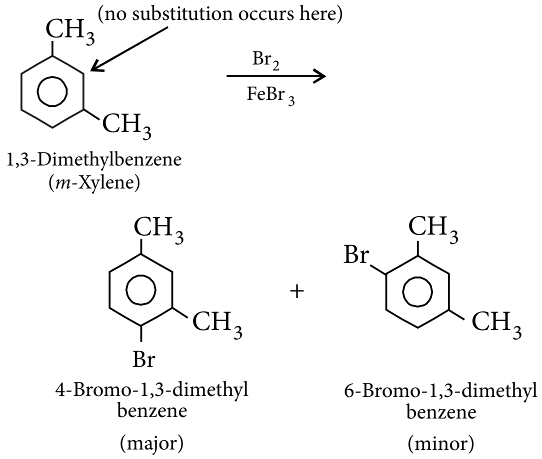
$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

If a large amount of $KHSO_4$ is added then conc. of HSO_4^- ions increases and the reaction will be shifted in backward direction hence, the rate of nitration will be slower.

68. (a) :



69. (c) : — CH_3 group is *o*,*p*-directing. Because of crowding, no substitution occurs at the carbon atom between the two — CH_3 groups in *m*-xylene, even though two — CH_3 groups activate that position.

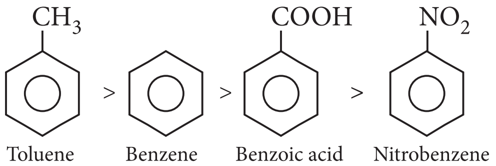


70. (b) : —NO_2 is most deactivating due to – *I* and – *M* effect.

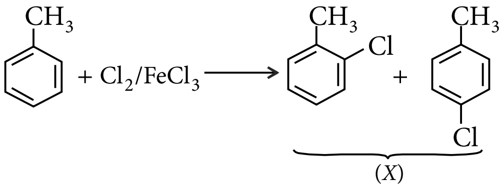
71. (a) : Nitrobenzene is strongly deactivated, hence will not undergo Friedel-Crafts reaction.

72. (d) : The molecules which do not satisfy Huckel rule or $(4n + 2)\pi$-electron rule are said to be non-aromatic. The compound (d) has total $4\pi e^-$. It does not follow $(4n + 2)\pi$ rule. So, it is non-aromatic compound.

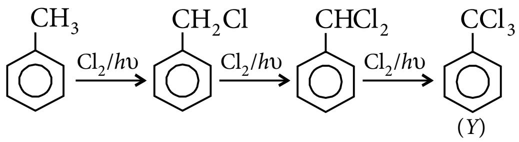
73. (c) : As the +*I* effect increases reactivity towards electrophilic reactions increases and as –*I* or –*M* effect increases, reactivity towards electrophilic reactions decreases. Thus, the order is



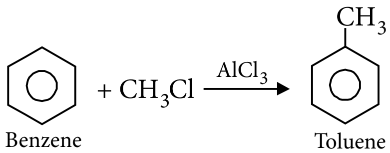
74. (c) : The reaction of Cl_2, in presence of $FeCl_3$, with toluene yields a ring substitution product.



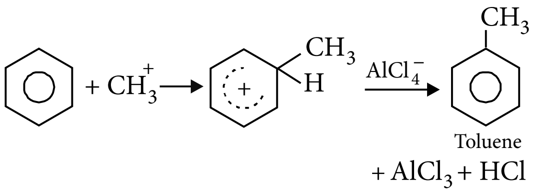
In presence of sunlight, free radical reaction takes place.



75. (d) : This is Friedel-Crafts alkylation.



Mechanism: $CH_3Cl + \underset{\text{Lewis acid}}{AlCl_3} \rightarrow AlCl_4^- + \underset{\text{Electrophile}}{CH_3^+}$



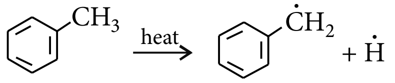
76. (b) : $\underset{(\text{From } H_2SO_4)}{H^+} + \underset{(\text{Base})}{H\ddot{O}-NO_2} \longrightarrow [H_2O^+-NO_2] \longrightarrow H_2O + NO_2^+$

77. (a) : Groups like, —Cl and —NO_2 shows –*I* effect. –*I* groups attached to the benzene ring decrease the electron density and hence less prone to electrophilic attack. —OH not only shows –*I* effect but also +*M* effect which predominates the –*I* character and electron density is increased in the benzene ring which facilitates electrophilic attack.

78. (c) : Benzene having any activating group *i.e.*, —OH, —*R* undergoes electrophilic substitution easily as compared to benzene itself. Thus, toluene and phenol undergo electrophilic substitution easily. Chlorine due to –*I*-effect deactivates the ring. So, it is difficult to carry out the electrophilic substitution in chlorobenzene. Hence, the order is $C_6H_5OH > C_6H_5CH_3 > C_6H_6 > C_6H_5Cl$.

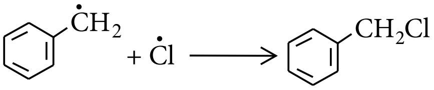
79. (c) : $C_6H_5H + H_2C = CH_2 \xrightarrow[95°C,\ \text{pressure}]{AlCl_3,\ HCl} C_6H_5CH_2CH_3$

80. (a) :

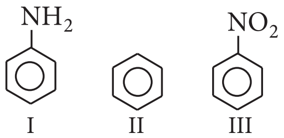


Benzyl free radical

$Cl_2 \xrightarrow[\text{sunlight}]{\text{Energy}} 2\dot{Cl}$

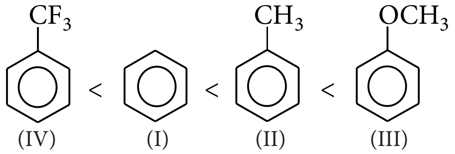


81. (d) :

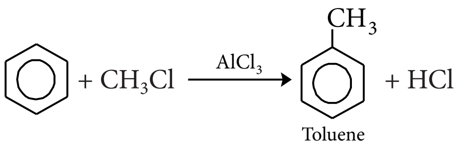


—NH_2 group is electron donating hence increases electron density on ring. Benzene is also electron rich due to delocalisation of electrons. —NO_2 group is electron withdrawing hence, decreases electron density on ring. Thus, correct order for electrophilic substitution is I > II > III.

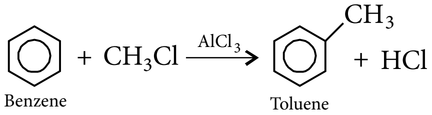
82. (a) : Due to –*I* effect of F atom, —CF_3 on benzene ring, deactivates the ring and does not favour electrophilic substitution. While —CH_3 and —OCH_3 are electron-donating group which favours electrophilic substitution in the benzene ring at '*ortho*' and '*para*' positions. The +*I* effect of —OCH_3 is more than —CH_3, therefore the correct order for electrophilic substitution is



83. (a) : In Friedel-Crafts reaction toluene is obtained by the action of CH_3Cl on benzene in presence of $AlCl_3$.



84. (a) : In Friedel-Crafts reaction, an alkyl group is introduced into the benzene ring in presence of a Lewis acid ($AlCl_3$) catalyst. The reaction is



85. (a) : —OH, —Cl and —CH_3 groups in benzene are *ortho, para* directing groups. But among these —OH group is strongly activating while —CH_3 is weakly activating and —Cl is deactivating. Thus, phenol will be most easily attacked by an electrophile.

86. (a) : Arenes undergo electrophilic substitution reactions and are resistant to addition reactions, due to delocalisation of π-electrons. These are also stabilized by resonance.

87. (a) : In structure III, withdrawal of electrons by —NO_2 causes decrease in reaction rate while in structure I, there is electron releasing effect by —OCH_3 group which accelerates the reaction.

The order of reactivity towards electrophile is :

I > II > III

88. (c) : $Cl_2 + FeCl_3 \longrightarrow FeCl_4^- + Cl^+$

89. (c) : Nitronium ion (NO_2^+) is an electrophile that actually attacks the benzene ring.

90. (d) : Benzene shows Kekule structures which are resonating structures and these structures are separated by a double headed arrow (↔).

91. (c) : Due to resonance all the C – C bonds in the benzene possess same nature and the resonating structures are obtained because of the delocalisation of π-electrons.

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CHAPTER

14

Environmental Chemistry

14.2 Atmospheric Pollution

1. Which of the following is not correct about carbon monoxide?
(a) It forms carboxyhaemoglobin.
(b) It reduces oxygen carrying ability of blood.
(c) The carboxyhaemoglobin (haemoglobin bound to CO) is less stable than oxyhaemoglobin.
(d) It is produced due to incomplete combustion.
(NEET 2020)

2. Among the following, the one that is not a greenhouse gas is
(a) sulphur dioxide (b) nitrous oxide
(c) methane (d) ozone. *(NEET 2019)*

3. Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity?
(a) N_2O_5 (b) NO_2
(c) N_2O (d) NO *(NEET 2018)*

4. Which of the following is a sink for CO?
(a) Microorganisms present in the soil
(b) Oceans
(c) Plants
(d) Haemoglobin *(NEET 2017)*

5. Which one of the following is not a common component of photochemical smog?
(a) Ozone
(b) Acrolein
(c) Peroxyacetyl nitrate
(d) Chlorofluorocarbons *(2014)*

6. Which one of the following statements regarding photochemical smog is not correct?
(a) Carbon monoxide does not play any role in photochemical smog formation.
(b) Photochemical smog is an oxidising agent in character.
(c) Photochemical smog is formed through photochemical reaction involving solar energy.
(d) Photochemical smog does not cause irritation in eyes and throat. *(2012)*

7. Which one of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?
(a) Polyhalogens (b) Ferrocene
(c) Fullerenes (d) Freons *(2004)*

8. About 20 km above the earth, there is an ozone layer. Which one of the following statements about ozone and ozone layer is true?
(a) It is beneficial to us as it stops U.V. radiation.
(b) Conversion of O_3 to O_2 is an endothermic reaction.
(c) Ozone is a triatomic linear molecule.
(d) It is harmful as it stops useful radiation. *(1995)*

14.3 Water Pollution

9. Which one of the following statements is not true?
(a) Clean water would have a BOD value of 5 ppm.
(b) Fluoride deficiency in drinking water is harmful. Soluble fluoride is often used to bring its concentration upto 1 ppm.
(c) When the pH of rain water is higher than 6.5, it is called acid rain.
(d) Dissolved Oxygen (DO) in cold water can reach a concentration upto 10 ppm.
(Karnataka NEET 2013)

10. Which one of the following statement is not true?
(a) pH of drinking water should be between 5.5 – 9.5.
(b) Concentration of DO below 6 ppm is good for the growth of fish.
(c) Clean water would have a BOD value of less than 5 ppm.

(d) Oxides of sulphur, nitrogen and carbon, are the most widespread air pollutant. *(2011)*

14.7 Green Chemistry

11. Green chemistry means such reactions which

(a) are related to the depletion of ozone layer

(b) study the reactions in plants

(c) produce colour during reactions

(d) reduce the use and production of hazardous chemicals. *(2008)*

ANSWER KEY

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

Hints & Explanations

1. (c) : The carboxyhaemoglobin is about 300 times more stable than oxyhaemoglobin.

2. (a) : Besides carbon dioxide, ether greenhouse gases are methane, water vapours, nitrous oxide, CFCs and ozone.

3. (a)

4. (a) : Microorganisms present in the soil consume atmospheric CO.

5. (d)

6. (d) : Photochemical smog causes irritation in eyes and throat.

7. (d) : Chlorofluorocarbons such as freon-11 ($CFCl_3$) and freon-12 (CF_2Cl_2) emitted as propellants in aerosol spray cans, refrigerators, fire fighting reagents etc. are stable compounds and chemically inert. They do not react with any substance with which they come in contact and thus float through the atmosphere unchanged and eventually enter the stratosphere. There they absorb UV radiations and break down liberating free atomic chlorine which causes decomposition of ozone. This results in the depletion of the ozone layer.

$$\dot{C}l + O_3 \rightarrow Cl\dot{O} + O_2$$

$$Cl\dot{O} + O_3 \rightarrow \dot{C}l + 2O_2$$

8. (a) : Ozone layer is very beneficial to us, because it stops harmful ultraviolet radiations to reach the earth.

9. (c) : When pH of rain water drops below 5.6 it is called acid rain.

10. (b) : Fish dies in water bodes polluted by sewage due to decrease in dissolved oxygen (D.O.)

11. (d) : Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment. Green chemistry also refers to the redesign of chemical products and processes with the goal of reducing or eliminating any negative environmental or health effects.

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CLASS

XII


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CHAPTER
1

The Solid State

1.2 Amorphous and Crystalline Solids

1. The pure crystalline substance on being heated gradually first forms a turbid liquid at constant temperature and still at higher temperature turbidity completely disappears. The behaviour is a characteristic of substance forming
(a) allotropic crystals (b) liquid crystals
(c) isomeric crystals (d) isomorphous crystals. *(1993)*

2. Glass is a
(a) liquid
(b) solid
(c) supercooled liquid
(d) transparent organic polymer. *(1991)*

3. Most crystals show good cleavage because their atoms, ions or molecules are
(a) weakly bonded together
(b) strongly bonded together
(c) spherically symmetrical
(d) arranged in planes. *(1991)*

4. The ability of a substance to assume two or more crystalline structures is called
(a) isomerism (b) polymorphism
(c) isomorphism (d) amorphism. *(1990)*

1.3 Classification of Crystalline Solids

5. Cation and anion combines in a crystal to form following type of compound
(a) ionic (b) metallic
(c) covalent (d) dipole-dipole. *(2000)*

6. For two ionic solids CaO and KI, identify the wrong statement among the following.
(a) CaO has high melting point.
(b) Lattice energy of CaO is much larger than that of KI.
(c) KI has high melting point.
(d) KI is soluble in benzene. *(1997)*

1.4 Crystal Lattice and Unit Cells

7. For orthorhombic system axial ratios are $a \neq b \neq c$ and the axial angles are
(a) $\alpha = \beta = \gamma \neq 90^\circ$ (b) $\alpha = \beta = \gamma = 90^\circ$
(c) $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ (d) $\alpha \neq \beta \neq \gamma \neq 90^\circ$ *(1991)*

1.5 Number of Atoms in a Unit Cell

8. The number of carbon atoms per unit cell of diamond unit cell is
(a) 6 (b) 1
(c) 4 (d) 8 *(NEET 2013)*

9. In a face-centred cubic lattice, a unit cell is shared equally by how many unit cells?
(a) 2 (b) 4
(c) 6 (d) 8 *(2005)*

10. When Zn converts from melted state to its solid state, it has *hcp* structure, then find the number of nearest atoms.
(a) 6 (b) 8
(c) 12 (d) 4 *(2001)*

11. The *fcc* crystal contains how many atoms in each unit cell?
(a) 6 (b) 8
(c) 4 (d) 5 *(1996)*

12. The number of atoms contained in a *fcc* unit cell of a monatomic substance is
(a) 1 (b) 2
(c) 4 (d) 6 *(1993)*

1.6 Closed Packed Structures

13. A compound is formed by cation C and anion A. The anions form hexagonal close packed (*hcp*) lattice and the cations occupy 75% of octahedral voids. The formula of the compound is
(a) C_4A_3 (b) C_2A_3
(c) C_3A_2 (d) C_3A_4 *(NEET 2019)*

14. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are
(a) 4 and 2 (b) 6 and 6
(c) 8 and 4 (d) 4 and 8 *(NEET-II 2016)*

15. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is
(a) 8 (b) 2
(c) 6 (d) 4 *(NEET-I 2016)*

16. The number of octahedral void(s) per atom present in a cubic close-packed structure is
(a) 1 (b) 3
(c) 2 (d) 4 *(2012)*

17. Structure of a mixed oxide is cubic close packed (*ccp*). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is
(a) ABO_2 (b) A_2BO_2
(c) $A_2B_3O_4$ (d) AB_2O_2 *(Mains 2012)*

18. A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion (Y^-) will be
(a) 275.1 pm (b) 322.5 pm
(c) 241.5 pm (d) 165.7 pm *(Mains 2011)*

19. A compound formed by elements X and Y crystallises in a cubic structure in which the X atoms are at the corners of a cube and the Y atoms are at the face-centres. The formula of the compound is
(a) XY_3 (b) X_3Y
(c) XY (d) XY_2 *(2004)*

20. In cube of any crystal A-atom placed at every corners and B-atom placed at every centre of face. The formula of compound is
(a) AB (b) AB_3
(c) A_2B_2 (d) A_2B_3 *(2000)*

21. In crystals of which one of the following ionic compounds would you expect maximum distance between centres of cations and anions?
(a) CsI (b) CsF
(c) LiF (d) LiI *(1998)*

22. The second order Bragg diffraction of X-rays with $\lambda = 1.00$ Å from a set of parallel planes in a metal occurs at an angle 60°. The distance between the scattering planes in the crystal is
(a) 2.00 Å (b) 1.00 Å
(c) 0.575 Å (d) 1.15 Å *(1998)*

23. The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is
(a) face-centred cube (b) simple cube
(c) body-centred cube (d) none of these. *(1997)*

24. In the fluorite structure, the coordination number of Ca^{2+} ion is
(a) 4 (b) 6
(c) 8 (d) 3 *(1993)*

1.7 Packing Efficiency

25. An element has a body centered cubic (*bcc*) structure with a cell edge of 288 pm. The atomic radius is
(a) $\frac{\sqrt{3}}{4} \times 288$ pm (b) $\frac{\sqrt{2}}{4} \times 288$ pm
(c) $\frac{4}{\sqrt{3}} \times 288$ pm (d) $\frac{4}{\sqrt{2}} \times 288$ pm
(NEET 2020)

26. The vacant space in *bcc* lattice unit cell is
(a) 48% (b) 23%
(c) 32% (d) 26% *(2015, 2008)*

27. If a is the length of the side of a cube, the distance between the body-centred atom and one corner atom in the cube will be
(a) $\frac{2}{\sqrt{3}}a$ (b) $\frac{4}{\sqrt{3}}a$
(c) $\frac{\sqrt{3}}{4}a$ (d) $\frac{\sqrt{3}}{2}a$ *(2014)*

28. A metal crystallises with a face-centred cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is
(a) 288 pm (b) 408 pm
(c) 144 pm (d) 204 pm *(2012)*

29. AB crystallizes in a body-centred cubic lattice with edge length 'a' equal to 387 pm. The distance between two oppositely charged ions in the lattice is
(a) 335 pm (b) 250 pm
(c) 200 pm (d) 300 pm *(2010)*

30. Lithium metal crystallises in a body-centred cubic crystal. If the length of the side of the unit cell of lithium is 351 pm, the atomic radius of lithium will be
(a) 151.8 pm (b) 75.5 pm
(c) 300.5 pm (d) 240.8 pm *(2009)*

31. Copper crystallises in a face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm?
(a) 157 (b) 181
(c) 108 (d) 128 *(2009)*

32. Which of the following statements is not correct?

(a) The number of carbon atoms in a unit cell of diamond is 8.

(b) The number of Bravais lattices in which a crystal can be categorized is 14.

(c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.

(d) Molecular solids are generally volatile. *(2008)*

33. If a stands for the edge length of the cubic systems: simple cubic, body-centred cubic and face-centred cubic, then the ratio of radii of the spheres in these systems will be respectively

(a) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$

(b) $1a : \sqrt{3}a : \sqrt{2}a$

(c) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$

(d) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

(2008)

34. The fraction of total volume occupied by the atoms present in a simple cube is

(a) $\frac{\pi}{3\sqrt{2}}$

(b) $\frac{\pi}{4\sqrt{2}}$

(c) $\frac{\pi}{4}$

(d) $\frac{\pi}{6}$

(2007)

35. The pyknometric density of sodium chloride crystal is $2.165 \times 10^3\,\text{kg m}^{-3}$ while its X-ray density is $2.178 \times 10^3\,\text{kg m}^{-3}$. The fraction of unoccupied sites in sodium chloride crystal is

(a) 5.96

(b) 5.96×10^{-2}

(c) 5.96×10^{-1}

(d) 5.96×10^{-3} *(2003)*

36. The edge length of face-centred unit cubic cells is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is

(a) 144 pm

(b) 398 pm

(c) 288 pm

(d) 618 pm *(1998)*

1.8 Calculations Involving Unit Cell Dimensions

37. Iron exhibits *bcc* structure at room temperature. Above 900°C, it transforms to *fcc* structure. The ratio of density of iron at room temperature to that at 900°C (assuming molar mass and atomic radii of iron remains constant with temperature) is

(a) $\frac{\sqrt{3}}{\sqrt{2}}$

(b) $\frac{4\sqrt{3}}{3\sqrt{2}}$

(c) $\frac{3\sqrt{3}}{4\sqrt{2}}$

(d) $\frac{1}{2}$

(NEET 2018)

38. Lithium has a *bcc* structure. Its density is $530\ \text{kg m}^{-3}$ and its atomic mass is $6.94\ \text{g mol}^{-1}$. Calculate the edge length of a unit cell of lithium metal. ($N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$)

(a) 527 pm

(b) 264 pm

(c) 154 pm

(d) 352 pm

(NEET-I 2016)

39. A metal has a *fcc* lattice. The edge length of the unit cell is 404 pm. The density of the metal is $2.72\ \text{g cm}^{-3}$. The molar mass of the metal is

(N_A Avogadro's constant = $6.02 \times 10^{23}\ \text{mol}^{-1}$)

(a) $27\ \text{g mol}^{-1}$

(b) $20\ \text{g mol}^{-1}$

(c) $40\ \text{g mol}^{-1}$

(d) $30\ \text{g mol}^{-1}$

(NEET 2013)

40. CsBr crystallises in a body-centred cubic lattice. The unit cell length is 436.6 pm. Given that the atomic mass of Cs = 133 and that of Br = 80 amu and Avogadro number being $6.02 \times 10^{23}\ \text{mol}^{-1}$, the density of CsBr is

(a) $4.25\ \text{g/cm}^3$

(b) $42.5\ \text{g/cm}^3$

(c) $0.425\ \text{g/cm}^3$

(d) $8.25\ \text{g/cm}^3$ *(2006)*

41. An element (atomic mass = 100 g/mol) having *bcc* structure has unit cell edge 400 pm. The density of element is

(a) $7.289\ \text{g/cm}^3$

(b) $2.144\ \text{g/cm}^3$

(c) $10.376\ \text{g/cm}^3$

(d) $5.188\ \text{g/cm}^3$ *(1996)*

1.9 Imperfections in Solids

42. Formula of nickel oxide with metal deficiency defect in its crystal is $Ni_{0.98}O$. The crystal contains Ni^{2+} and Ni^{3+} ions. The fraction of nickel existing as Ni^{2+} ions in the crystal is

(a) 0.96

(b) 0.04

(c) 0.50

(d) 0.3

(Odisha NEET 2019)

43. The correct statement regarding defects in crystalline solids is

(a) Frenkel defects decrease the density of crystalline solids

(b) Frenkel defect is a dislocation defect

(c) Frenkel defect is found in halides of alkaline metals

(d) Schottky defects have no effect on the density of crystalline solids. *(2015)*

44. The appearance of colour in solid alkali metal halides is generally due to

(a) interstitial positions

(b) *F*-centres

(c) Schottky defect

(d) Frenkel defect. *(2006)*

45. Schottky defect in crystals is observed when

(a) density of the crystal is increased

(b) unequal number of cations and anions are missing from the lattice

(c) an ion leaves its normal site and occupies an interstitial site

(d) equal number of cations and anions are missing from the lattice. *(1998)*

46. Ionic solids, with Schottky defects, contain in their structure
(a) cation vacancies only
(b) cation vacancies and interstitial cations
(c) equal number of cation and anion vacancies
(d) anion vacancies and interstitial anions. *(1994)*

1.10 Electrical Properties

47. Which is the incorrect statement?
(a) Density decreases in case of crystals with Schottky defect.
(b) $NaCl_{(s)}$ is insulator, silicon is semiconductor, silver is conductor, quartz is piezoelectric crystal.
(c) Frenkel defect is favoured in those ionic compounds in which sizes of cation and anions are almost equal.
(d) $FeO_{0.98}$ has non-stoichiometric metal deficiency defect. *(NEET 2017)*

48. With which one of the following elements silicon should be doped so as to give *p*-type of semiconductor?
(a) Selenium (b) Boron
(c) Germanium (d) Arsenic *(2008)*

49. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 6.02×10^{16} mol^{-1} (b) 6.02×10^{17} mol^{-1}
(c) 6.02×10^{14} mol^{-1} (d) 6.02×10^{15} mol^{-1} *(2007)*

50. If we mix a pentavalent impurity in a crystal lattice of germanium, what type of semiconductor formation will occur?
(a) *n*-type semiconductor
(b) *p*-type semiconductor
(c) Both (a) and (b)
(d) None of these *(1996)*

51. On doping Ge metal with a little of In or Ga, one gets
(a) *p*-type semiconductor
(b) *n*-type semiconductor
(c) insulator
(d) rectifier. *(1993)*

ANSWER KEY

1.	(b)	**2.**	(c)	**3.**	(d)	**4.**	(b)	**5.**	(a)	**6.**	(d)	**7.**	(b)	**8.**	(d)	**9.**	(c)	**10.**	(c)
11.	(c)	**12.**	(c)	**13.**	(d)	**14.**	(c)	**15.**	(c)	**16.**	(a)	**17.**	(d)	**18.**	(c)	**19.**	(a)	**20.**	(b)
21.	(a)	**22.**	(d)	**23.**	(c)	**24.**	(c)	**25.**	(a)	**26.**	(c)	**27.**	(d)	**28.**	(a)	**29.**	(a)	**30.**	(a)
31.	(d)	**32.**	(c)	**33.**	(c)	**34.**	(d)	**35.**	(d)	**36.**	(a)	**37.**	(c)	**38.**	(d)	**39.**	(a)	**40.**	(a)
41.	(d)	**42.**	(a)	**43.**	(b)	**44.**	(b)	**45.**	(d)	**46.**	(c)	**47.**	(c, d)	**48.**	(b)	**49.**	(b)	**50.**	(a)
51.	(a)																		

Hints & Explanations

1. (b) : Liquid crystals on heating first become turbid and then on further heating turbidity completely disappears.

2. (c) : Glass is a supercooled liquid which forms a non-crystalline solid without a regular lattice.

3. (d) : Crystals show good cleavage because their constituent particles are arranged in planes.

4. (b) : The phenomenon of existence of a substance in two or more crystalline structures is called polymorphism.

5. (a) : The electrostatic force of attraction which exists between oppositely charged ions is called as ionic bond.

6. (d) : KI is an ionic compound while benzene is not.

7. (b) : For orthorhombic system, $\alpha = \beta = \gamma = 90°$

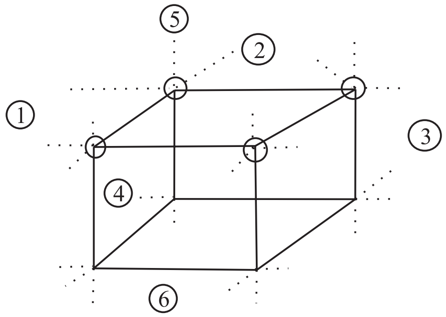
8. (d) : Diamond is like ZnS (Zinc blende).

Carbon forming *ccp* (*fcc*) and also occupying half of tetrahedral voids.

Total no. of carbon atoms per unit cell

$$= \underset{\text{(Corners)}}{8\times\frac{1}{8}} + \underset{\text{(Face centred)}}{6\times\frac{1}{2}} + \underset{\text{(Tetrahedral void)}}{4} = 8$$

9. (c) : Here given unit cell is shared equally by six faces in the *fcc* which is shared equally by six different unit cells.

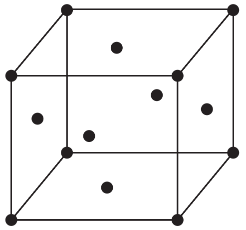


10. (c) : *hcp* is a closed packed arrangement in which the unit cell is hexagonal and coordination number is 12.

11. (c) : The contribution of eight atoms of face-centred cubic unit cell = $8 \times \frac{1}{8}$ = 1 atom. There is one atom at each of six faces, which is shared by 2 unit cells each. The contribution of 6 face-centred atoms = $6 \times \frac{1}{2}$ = 3.
Therefore $n = 1 + 3 = 4$

12. (c) : *fcc* crystal contains

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \text{ atoms in a unit cell}$$



13. (d) : Number of atoms per unit cell in *hcp* = 6
Number of octahedral void in *hcp* = 6
Number of anions per unit cell = 6
Number of octahedral voids occupied by cations

$$= 6 \times \frac{75}{100} = \frac{9}{2}$$

∴ Formula of compound = $C_{9/2}A_6 = C_3A_4$

14. (c) : In fluorite structure, Ca^{2+} ions are in the face-centred cubic arrangement. Each Ca^{2+} is connected to 4 F^- ions below it and to another set of 4 F^- ions above it *i.e.* Ca^{2+} has a coordination number of 8 and each F^- ion has a coordination number 4.

15. (c) : Radius ratio, $\frac{r_+}{r_-} = \frac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.541$

It lies in the range of 0.414 to 0.732 hence, coordination number of each ion will be 6 as the compound will have NaCl type structure *i.e.*, octahedral arrangement.

16. (a) : Number of octahedral voids is same as number of atoms.

17. (d) : Number of atoms in *ccp* = 4 = O^{2-}
Number of tetrahedral voids = 2 × N = 2 × 4 = 8
Number of A^{2+} ions $= 8 \times \frac{1}{4} = 2$
Number of octahedral voids = Number of B^+ ions = $N = 4$
Ratio, $O^{2-} : A^{2+} : B^+ = 4 : 2 : 4 = 2 : 1 : 2$
Formula of oxide = AB_2O_2

18. (c) : For NaCl, $\frac{r_+}{r_-} = 0.414$
Given : radius of cation = 100 pm

$$\frac{100}{r_-} = 0.414 \Rightarrow \frac{100}{0.414} = r_- \Rightarrow r_- = 241.5 \text{ pm}$$

19. (a) : In a unit cell, X atoms at the corners $= \frac{1}{8} \times 8 = 1$
Y atoms at the face centres = $\frac{1}{2} \times 6 = 3$
Ratio of X and Y = 1 : 3. Hence formula is XY_3.

20. (b) : 'A' atoms are at '8' corners of the cube. Thus, no. of 'A' atoms per unit cell = $8 \times \frac{1}{8} = 1$
'B' atoms are at the face centre of six faces. Thus, no. of 'B' atoms per unit cell = $6 \times \frac{1}{2} = 3$
The formula is AB_3.

21. (a) : As Cs^+ ion has larger size than Li^+ and I^- has larger size than F^-, so maximum distance between centres of cations and anions is in CsI.

22. (d) : According to Bragg's equation, $n\lambda = 2d \sin\theta$
As, $n = 2$, $\lambda = 1.00$Å, $\theta = 60°$, d = ?

$$2d\sin\theta = n\lambda$$

$$2d\sin 60° = 2 \times 1 \text{ Å}$$

$$2d \times \frac{\sqrt{3}}{2} = 2 \Rightarrow d = \frac{2}{\sqrt{3}} = 1.15 \text{ Å} \quad \left(\because \sin 60° = \frac{\sqrt{3}}{2} \right)$$

23. (c) : A body-centred cubic unit cell consists of 8 atoms at the corners and one atom at the centre.

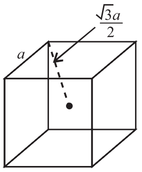
24. (c) : In fluorite (CaF_2) structure, C.N. of Ca^{2+} = 8, C.N. of F^- = 4.

25. (a) : For *bcc* structure, $r = \frac{\sqrt{3}}{4}a$, where a is the unit cell edge length and r is the radius of the sphere (atom).

$$r = \frac{\sqrt{3}}{4} \times 288 \text{ pm}$$

26. (c) : Packing efficiency of *bcc* lattice = 68%
Hence, empty space = 32%.

27. (d) : The distance between the body-centred atom and one corner atom is $\frac{\sqrt{3}a}{2}$ *i.e.* half of the body diagonal.



28. (a) : For a face-centred cubic (*fcc*) structure,

$$r=\frac{a}{2\sqrt{2}},\ a = 408\text{ pm},\ r=\frac{408}{2\sqrt{2}}=144\text{ pm}$$

Diameter = $2r = 2 \times 144 = 288$ pm

29. (a) : For a *bcc* lattice, $2(r_+ + r_-) = \sqrt{3}\,a$

where r_+ = radius of cation, r_- = radius of anion

a = edge length

$$\therefore\ (r_+ + r_-)=\frac{\sqrt{3}\times 387}{2} = 335.15\text{ pm} \approx 335\text{ pm}$$

30. (a) : Since Li crystallises in body-centred cubic crystal, atomic radius,

$$r=\frac{\sqrt{3}a}{4}\quad (a = \text{edge length})$$

$$\therefore\ r=\frac{\sqrt{3}}{4}\times 351=151.8\text{ pm}\quad (\text{Given}: a=351\text{ pm})$$

31. (d) : Since Cu crystallises in a face-centred cubic lattice,

$$\text{Atomic radius, } r=\frac{a}{2\sqrt{2}}\quad (a = \text{edge length} = 361\text{ pm})$$

$$\therefore\ r=\frac{361}{2\sqrt{2}}=127.6 \approx 128\text{ pm}$$

32. (c) : Packing fraction for a cubic unit cell is given by

$$f=\frac{Z\times\frac{4}{3}\pi r^3}{a^3}$$

where a = edge length, r = radius of cation and anion.

Efficiency of packing in simple cubic or primitive cell = $\pi/6 = 0.52$ *i.e.* 52% of unit cell is occupied by atoms and 48% is empty.

33. (c) : For simple cubic : $r = a/2$

For body centred : $r = a\sqrt{3}/4$

For face-centred: $r=\dfrac{a}{2\sqrt{2}}$

where a = edge length, r = radius.

$\therefore$ Ratio of radii of the three will be $\dfrac{a}{2}:\dfrac{a\sqrt{3}}{4}:\dfrac{a}{2\sqrt{2}}$

34. (d)

35. (d) : Molar volume from pyknometric density

$$=\frac{M}{2.165\times 10^3}\text{ m}^3$$

Molar volume from X-ray density $=\dfrac{M}{2.178\times 10^3}\text{ m}^3$

$$\text{Volume occupied} = \frac{M}{10^3}\left(\frac{1}{2.165}-\frac{1}{2.178}\right)\text{m}^3$$

Fraction unoccupied

$$=\left(\frac{0.013\,M\times 10^{-3}}{2.165\times 2.178}\right)\bigg/\left(\frac{M\times 10^{-3}}{2.165}\right)= 5.96 \times 10^{-3}$$

36. (a) : In the face–centred cubic lattice, the edge length of the unit cell, $a = r + 2R + r$

where r = Radius of cation, R = Radius of anion

$\Rightarrow\ 508 = 2 \times 110 + 2R \Rightarrow R = 144$ pm

37. (c) : For *bcc* lattice : $Z = 2,\ a=\dfrac{4r}{\sqrt{3}}$

For *fcc* lattice : $Z = 4,\ a=2\sqrt{2}\,r$

$$\therefore\ \frac{d_{\text{R.T.}}}{d_{900\,°\text{C}}}=\frac{\left(\dfrac{ZM}{N_A a^3}\right)_{bcc}}{\left(\dfrac{ZM}{N_A a^3}\right)_{fcc}}$$

Given, molar mass and atomic radii are constant.

$$=\frac{2}{4}\left(\frac{2\sqrt{2}r}{\frac{4r}{\sqrt{3}}}\right)^3=\frac{3\sqrt{3}}{4\sqrt{2}}$$

38. (d) : For *bcc*, $Z = 2$, $\rho = 530$ kg m^{-3},

at. mass of Li = 6.94 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}

$$\rho = 530\text{ kg m}^{-3} = \frac{530\times 1000\text{ g}}{1\times(100)^3\text{cm}^3} = 0.53\text{ g cm}^{-3}$$

$$\rho=\frac{Z\times\text{At. mass}}{N_A\ \times a^3}$$

$$a^3=\frac{Z\times\text{At. mass}}{N_A\ \times\rho}=\frac{2\times 6.94}{6.02\times 10^{23}\times 0.53}$$

$= 43.5 \times 10^{-24}$ cm^3

$\Rightarrow\ a = 352 \times 10^{-10}$ cm = 352 pm

39. (a) : $d=\dfrac{ZM}{N_A a^3}\quad (Z = 4 \text{ for } fcc)$

$$M=\frac{d\times N_A\times a^3}{Z}=\frac{2.72\times 6.023\times 10^{23}\times\left(404\times 10^{-10}\right)^3}{4}$$

$M = 27$ g mol^{-1}

40. (a) : Density of CsBr = $\dfrac{Z\times M}{a^3\times N_A}$

$$=\frac{1\times 213}{(436.6\times 10^{-10})^3\times 6.023\times 10^{23}}=4.25\text{ g/cm}^3$$

(It has one formula unit in the unit cell, so $Z = 1$.)

41. (d) : Cell edge = 400 pm; number of atoms in *bcc* (Z) = 2 and atomic mass = 100 g/mol.

Since atomic mass is 100 g/mol, therefore mass of each atom (m) = $\dfrac{100}{6.023\times 10^{23}}$ = 16.6×10^{-23} g

We know that volume of unit cell = $(400 \text{ pm})^3$
$= (64 \times 10^6)\text{pm}^3 = 64 \times 10^{-24} \text{ cm}^3$ and
mass of unit cell $= Z \times m = 2 \times (16.6 \times 10^{-23})$
$= 33.2 \times 10^{-23}$ g

$$\text{Therefore density} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{33.2 \times 10^{-23}}{64 \times 10^{-24}} = 5.188 \text{ g/cm}^3$$

42. (a) : Let the fraction of metal which exists as Ni^{2+} ion be x. Then the fraction of metal as $Ni^{3+} = 0.98 - x$

$\therefore \quad 2x + 3(0.98 - x) = 2$

$\Rightarrow \quad 2x + 2.94 - 3x = 2 \Rightarrow x = 0.94$

43. (b) : Frenkel defect is a dislocation defect as smaller ions (usually cations) are dislocated from normal sites to interstitial sites. Frenkel defect is shown by compounds having large difference in the size of cations and anions hence, alkali metal halides do not show Frenkel defect. Also, Schottky defect decreases the density of crystal while Frenkel defect has no effect on the density of crystal.

44. (b) : *F*-centres are the sites where anions are missing and instead electrons are present. They are responsible for colours.

45. (d) : In Schottky defect, equal no. of cations and anions are missing from the lattice. So, the crystal remains neutral. Such defect is more common in highly ionic compounds of similar cationic and anionic size, *i.e.* NaCl.

46. (c) : When an atom is missing from its normal lattice site, a lattice vacancy is created. Such a defect, which involves equal number of cation and anion vacancies in the crystal lattice is called a Schottky defect.

47. (c, d) : Frenkel defect is favoured in those ionic compounds in which there is large difference in the size of cations and anions.

Non-stoichiometric defects due to metal deficiency is shown by Fe_xO where $x = 0.93$ to 0.96.

48. (b) : If silicon is doped with any of the elements of group 13 (B, Al, Ga, In, Tl) of the periodic table, *p*-type of semiconductor will be obtained.

49. (b) : As each Sr^{2+} ion introduces one cation vacancy, therefore, concentration of cation vacancies = mole % of $SrCl_2$ added.

$\therefore$ Concentration of cation vacancies $= 10^{-4}$ mole%

$$= \frac{10^{-4}}{100} \times 6.023 \times 10^{23} = 6.023 \times 10^{17}$$

50. (a) : When an impurity atom with 5 valence electrons (as arsenic) is introduced in a germanium crystal, it replaces one of the germanium atoms. Four of the five valence electrons of the impurity atom form covalent bonds with each valence electron of four germanium atoms and fifth valence electron becomes free to move in the crystal structure. This free electron acts as a charge carrier. Such as an impure germanium crystal is called *n*-type semiconductor because in it charge carriers are negative (free electrons).

51. (a) : *p*-type of semiconductors are produced (a) due to metal deficiency defects (b) by adding impurity containing less electrons (*i.e.* atoms of group 13). Ge belongs to Group 14 and In or Ga to Group 13. Hence on doping *p*-type semiconductor is obtained. This doping of Ge with In increase the electrical conductivity of the Ge crystal.

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CHAPTER 2

Solutions

2.2 Expressing Concentration of Solutions

1. Which of the following is dependent on temperature?
(a) Molarity
(b) Mole fraction
(c) Weight percentage
(d) Molality *(NEET 2017)*

2. What is the mole fraction of the solute in a 1.00 m aqueous solution?
(a) 1.770
(b) 0.0354
(c) 0.0177
(d) 0.177 *(2015, 2011)*

3. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3? The concentrated acid is 70% HNO_3.
(a) 70.0 g conc. HNO_3
(b) 54.0 g conc. HNO_3
(c) 45.0 g conc. HNO_3
(d) 90.0 g conc. HNO_3 *(NEET 2013)*

4. Which of the following compounds can be used as antifreeze in automobile radiators?
(a) Methyl alcohol
(b) Glycol
(c) Nitrophenol
(d) Ethyl alcohol *(2012)*

5. Concentrated aqueous sulphuric acid is 98% H_2SO_4 by mass and has a density of 1.80 g mL^{-1}. Volume of acid required to make one litre of 0.1 M H_2SO_4 solution is
(a) 16.65 mL
(b) 22.20 mL
(c) 5.55 mL
(d) 11.10 mL *(2007)*

6. The mole fraction of the solute in one molal aqueous solution is
(a) 0.009
(b) 0.018
(c) 0.027
(d) 0.036 *(2005)*

7. 2.5 litre of 1 M NaOH solution is mixed with another 3 litre of 0.5 M NaOH solution. Then find out molarity of resultant solution.
(a) 0.80 M
(b) 1.0 M
(c) 0.73 M
(d) 0.50 M *(2002)*

8. How many g of dibasic acid (mol. weight 200) should be present in 100 mL of the aqueous solution to give strength of 0.1 N?
(a) 10 g
(b) 2 g
(c) 1 g
(d) 20 g *(1999)*

9. What is the molarity of H_2SO_4 solution, that has a density 1.84 g/cc at 35°C and contains 98% by weight?
(a) 18.4 M
(b) 18 M
(c) 4.18 M
(d) 8.14 M *(1996)*

10. The concentration unit, independent of temperature, would be
(a) normality
(b) weight volume percent
(c) molality
(d) molarity. *(1995, 1992)*

11. How many grams of CH_3OH should be added to water to prepare 150 mL solution of 2 M CH_3OH?
(a) 9.6×10^3
(b) 2.4×10^3
(c) 9.6
(d) 2.4 *(1994)*

2.4 Vapour Pressure of Liquid Solutions

12. In water saturated air, the mole fraction of water vapour is 0.02. If the total pressure of the saturated air is 1.2 atm, the partial pressure of dry air is
(a) 1.18 atm
(b) 1.76 atm
(c) 1.176 atm
(d) 0.98 atm. *(Odisha NEET 2019)*

13. p_A and p_B are the vapour pressures of pure liquid components, A and B, respectively of an ideal binary solution. If x_A represents the mole fraction of component A, the total pressure of the solution will be
(a) $p_A + x_A(p_B - p_A)$
(b) $p_A + x_A(p_A - p_B)$
(c) $p_B + x_A(p_B - p_A)$
(d) $p_B + x_A(p_A - p_B)$ *(2012)*

14. Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 25°C are 200 mm Hg and 41.5 mm Hg respectively. Vapour pressure of the solution obtained by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at the same temperature will be

(Molecular mass of $CHCl_3$ = 119.5 u and molecular mass of CH_2Cl_2 = 85 u)
(a) 173.9 mm Hg (b) 615.0 mm Hg
(c) 347.9 mm Hg (d) 285.5 mm Hg
(Mains 2012)

15. A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20 °C are 440 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in the vapour phase would be
(a) 0.200 (b) 0.549
(c) 0.786 (d) 0.478 *(2005)*

16. The vapour pressure of two liquids *P* and *Q* are 80 and 60 torr, respectively. The total vapour pressure of solution obtained by mixing 3 mole of *P* and 2 mol of *Q* would be
(a) 72 torr (b) 140 torr
(c) 68 torr (d) 20 torr *(2005)*

2.5 Ideal and Non-Ideal Solutions

17. The mixture which shows positive deviation from Raoult's law is
(a) ethanol + acetone (b) benzene + toluene
(c) acetone + chloroform
(d) chloroethane + bromoethane. *(NEET 2020)*

18. For an ideal solution, the correct option is
(a) $\Delta_{mix}G = 0$ at constant T and P
(b) $\Delta_{mix}S = 0$ at constant T and P
(c) $\Delta_{mix}V \neq 0$ at constant T and P
(d) $\Delta_{mix}H = 0$ at constant T and P. *(NEET 2019)*

19. The mixture that forms maximum boiling azeotrope is
(a) heptane + octane (b) water + nitric acid
(c) ethanol + water
(d) acetone + carbon disulphide. *(NEET 2019)*

20. Which of the following statements is correct regarding a solution of two components *A* and *B* exhibiting positive deviation from ideal behaviour?
(a) Intermolecular attractive forces between *A*-*A* and *B*-*B* are stronger than those between *A*-*B*.
(b) $\Delta_{mix}H = 0$ at constant T and P.
(c) $\Delta_{mix}V = 0$ at constant T and P.
(d) Intermolecular attractive forces between *A*-*A* and *B*-*B* are equal to those between *A*-*B*.
(Odisha NEET 2019)

21. Which one of the following is incorrect for ideal solution?
(a) $\Delta H_{mix} = 0$ (b) $\Delta U_{mix} = 0$
(c) $\Delta P = P_{obs} - P_{\text{calculated by Raoult's law}} = 0$
(d) $\Delta G_{mix} = 0$ *(NEET-II 2016)*

22. Which of the following statements about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C. (Given, vapour pressure data at 25°C, benzene = 12.8 kPa, toluene = 3.85 kPa)
(a) The vapour will contain equal amounts of benzene and toluene.
(b) Not enough information is given to make a prediction.
(c) The vapour will contain a higher percentage of benzene.
(d) The vapour will contain a higher percentage of toluene. *(NEET-I 2016)*

23. Which condition is not satisfied by an ideal solution?
(a) $\Delta_{mix}V = 0$ (b) $\Delta_{mix}S = 0$
(c) Obeyance to Raoult's Law
(d) $\Delta_{mix}H = 0$ *(Karnataka NEET 2013)*

24. A solution of acetone in ethanol
(a) obeys Raoult's law
(b) shows a negative deviation from Raoult's law
(c) shows a positive deviation from Raoult's law
(d) behaves like a near ideal solution. *(2006)*

25. A solution containing components *A* and *B* follows Raoult's law
(a) *A* - *B* attraction force is greater than *A* - *A* and *B* - *B*
(b) *A* - *B* attraction force is less than *A* - *A* and *B* - *B*
(c) *A* - *B* attraction force remains same as *A* - *A* and *B* - *B*
(d) volume of solution is different from sum of volume of solute and solvent. *(2002)*

26. All form ideal solution except
(a) C_6H_6 and $C_6H_5CH_3$ (b) C_2H_6 and C_2H_5I
(c) C_6H_5Cl and C_6H_5Br (d) C_2H_5I and C_2H_5OH
(1988)

27. An ideal solution is formed when its components
(a) have no volume change on mixing
(b) have no enthalpy change on mixing
(c) have both the above characteristics
(d) have high solubility. *(1988)*

2.6 Colligative Properties and Determination of Molar Mass

28. The freezing point depression constant (K_f) of benzene is 5.12 K kg mol^{-1}. The freezing point depression for the solution of molality 0.078 m containing a non-electrolyte solute in benzene is (rounded off upto two decimal places)
(a) 0.20 K (b) 0.80 K
(c) 0.40 K (d) 0.60 K *(NEET 2020)*

29. If molality of the dilute solution is doubled, the value of molal depression constant (K_f) will be

(a) halved (b) tripled

(c) unchanged (d) doubled. *(NEET 2017)*

30. At 100°C the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If $K_b = 0.52$, the boiling point of this solution will be

(a) 102 °C (b) 103 °C

(c) 101 °C (d) 100 °C

(NEET-I 2016)

31. 200 mL of an aqueous solution of a protein contains its 1.26 g. The osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. The molar mass of protein will be ($R = 0.083$ L bar mol^{-1} K^{-1})

(a) 51022 g mol^{-1} (b) 122044 g mol^{-1}

(c) 31011 g mol^{-1} (d) 61038 g mol^{-1}

(Mains 2011)

32. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be (K_f for water = 1.86 K kg mol^{-1})

(a) – 0.372 °C (b) – 0.520 °C

(c) + 0.372 °C (d) – 0.570 °C *(2010)*

33. During osmosis, flow of water through a semipermeable membrane is

(a) from solution having lower concentration only

(b) from solution having higher concentration only

(c) from both sides of semipermeable membrane with equal flow rates

(d) from both sides of semipermeable membrane with unequal flow rates. *(2006)*

34. 1.00 g of a non-electrolyte solute (molar mass 250 g mol^{-1}) was dissolved in 51.2 g of benzene. If the freezing point constant, K_f of benzene is 5.12 K kg mol^{-1}, the freezing point of benzene will be lowered by

(a) 0.2 K (b) 0.4 K

(c) 0.3 K (d) 0.5 K *(2006)*

35. A solution containing 10 g per dm^3 of urea (molecular mass = 60 g mol^{-1}) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is

(a) 200 g mol^{-1} (b) 250 g mol^{-1}

(c) 300 g mol^{-1} (d) 350 g mol^{-1} *(2006)*

36. A solution of urea (mol. mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol^{-1} respectively, the above solution will freeze at

(a) 0.654°C (b) – 0.654°C

(c) 6.54°C (d) – 6.54°C *(2005)*

37. A solution contains non-volatile solute of molecular mass M_2. Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure?

(a) $M_2 = \left(\frac{m_2}{\pi}\right)VRT$ (b) $M_2 = \left(\frac{m_2}{V}\right)\frac{RT}{\pi}$

(c) $M_2 = \left(\frac{m_2}{V}\right)\pi RT$ (d) $M_2 = \left(\frac{m_2}{V}\right)\frac{\pi}{RT}$

(m_2 = mass of solute, V = volume of solution, π = osmotic pressure) *(2002)*

38. Pure water can be obtained from sea water by

(a) centrifugation (b) plasmolysis

(c) reverse osmosis (d) sedimentation.

(2001)

39. From the colligative properties of solution, which one is the best method for the determination of molecular weight of proteins and polymers?

(a) Osmotic pressure

(b) Lowering in vapour pressure

(c) Lowering in freezing point

(d) Elevation in boiling point *(2000)*

40. The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A non-volatile and non-electrolyte solid, weighing 2.175 g is added to 39.08 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molecular weight of solid substance?

(a) 69.5 (b) 59.6

(c) 49.50 (d) 79.8 *(1999)*

41. If 0.15 g of a solute, dissolved in 15 g of solvent, is boiled at a temperature higher by 0.216°C, than that of the pure solvent. The molecular weight of the substance (Molal elevation constant for the solvent is 2.16°C) is

(a) 10.1 (b) 100

(c) 1.01 (d) 1000 *(1999)*

42. A 5% solution of cane sugar (mol. wt. = 342) is isotonic with 1% solution of a substance X. The molecular weight of X is

(a) 68.4 (b) 171.2

(c) 34.2 (d) 136.8 *(1998)*

43. The vapour pressure of a solvent decreased by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent if the decrease in the vapour pressure is to be 20 mm of mercury?

(a) 0.4 (b) 0.6

(c) 0.8 (d) 0.2 *(1998)*

44. The vapour pressure of CCl_4 at 25°C is 143 mm Hg. If 0.5 g of a non-volatile solute (mol. weight = 65) is dissolved in 100 g CCl_4, the vapour pressure of the solution will be
(a) 199.34 mm Hg (b) 143.99 mm Hg
(c) 141.43 mm Hg (d) 94.39 mm Hg. *(1996)*

45. The relationship between osmotic pressure at 273 K when 10 g glucose (p_1), 10 g urea (p_2), and 10 g sucrose (p_3) are dissolved in 250 mL of water is
(a) $p_2 > p_1 > p_3$ (b) $p_2 > p_3 > p_1$
(c) $p_1 > p_2 > p_3$ (d) $p_3 > p_1 > p_2$ *(1996)*

46. According to Raoult's law, the relative lowering of vapour pressure for a solution is equal to
(a) mole fraction of solute
(b) mole fraction of solvent
(c) moles of solute (d) moles of solvent. *(1995)*

47. If 0.1 M solution of glucose and 0.1 M solution of urea are placed on two sides of the semipermeable membrane to equal heights, then it will be correct to say that
(a) there will be no net movement across the membrane
(b) glucose will flow towards glucose solution
(c) urea will flow towards glucose solution
(d) water will flow from urea solution to glucose. *(1992)*

48. Which one is a colligative property?
(a) Boiling point (b) Vapour pressure
(c) Osmotic pressure (d) Freezing point *(1992)*

49. Blood cells retain their normal shape in solution which are
(a) hypotonic to blood (b) isotonic to blood
(c) hypertonic to blood (d) equinormal to blood. *(1991)*

50. The relative lowering of the vapour pressure is equal to the ratio between the number of
(a) solute molecules to the solvent molecules
(b) solute molecules to the total molecules in the solution
(c) solvent molecules to the total molecules in the solution
(d) solvent molecules to the total number of ions of the solute. *(1991)*

2.7 Abnormal Molar Masses

51. The van't Hoff factor (i) for a dilute aqueous solution of the strong electrolyte barium hydroxide is
(a) 0 (b) 1 (c) 2 (d) 3 *(NEET-II 2016)*

52. The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolal solution of Y in water. Which one of the following statements is true in this case?
(a) Molecular mass of X is less than the molecular mass of Y.
(b) Y is undergoing dissociation in water while X undergoes no change.
(c) X is undergoing dissociation in water.
(d) Molecular mass of X is greater than the molecular mass of Y. *(2015, Cancelled)*

53. Of the following 0.10 m aqueous solutions, which one will exhibit the largest freezing point depression?
(a) KCl (b) $C_6H_{12}O_6$
(c) $Al_2(SO_4)_3$ (d) K_2SO_4 *(2014)*

54. The van't Hoff factor i for a compound which undergoes dissociation in one solvent and association in other solvent is respectively
(a) less than one and greater than one
(b) less than one and less than one
(c) greater than one and less than one
(d) greater than one and greater than one. *(2011)*

55. The freezing point depression constant for water is −1.86 °C m^{-1}. If 5.00 g Na_2SO_4 is dissolved in 45.0 g H_2O, the freezing point is changed by −3.82 °C. Calculate the van't Hoff factor for Na_2SO_4.
(a) 2.05 (b) 2.63
(c) 3.11 (d) 0.381 *(2011)*

56. A 0.1 molal aqueous solution of a weak acid is 30% ionized. If K_f for water is 1.86°C/m, the freezing point of the solution will be
(a) – 0.18 °C (b) – 0.54 °C
(c) – 0.36 °C (d) – 0.24 °C *(Mains 2011)*

57. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase?
(a) Addition of NaCl (b) Addition of Na_2SO_4
(c) Addition of 1.00 molal KI
(d) Addition of water *(2010)*

58. A 0.0020 m aqueous solution of an ionic compound $[Co(NH_3)_5(NO_2)]Cl$ freezes at −0.00732 °C. Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be (K_f = −1.86 °C/m)
(a) 3 (b) 4 (c) 1 (d) 2 *(2009)*

59. 0.5 molal aqueous solution of a weak acid (HX) is 20% ionised. If K_f for water is 1.86 K kg mol^{-1}, the lowering in freezing point of the solution is
(a) 0.56 K (b) 1.12 K
(c) −0.56 K (d) −1.12 K *(2007)*

60. Which of the following 0.10 m aqueous solution will have the lowest freezing point?
(a) KI (b) $C_{12}H_{22}O_{11}$
(c) $Al_2(SO_4)_3$ (d) $C_5H_{10}O_5$ *(1997)*

61. Which of the following salts has the same value of van't Hoff factor (*i*) as that of $K_3[Fe(CN)_6]$?
(a) Na_2SO_4 (b) $Al(NO_3)_3$
(c) $Al_2(SO_4)_3$ (d) NaCl *(1994)*

62. At 25°C, the highest osmotic pressure is exhibited by 0.1 M solution of
(a) glucose (b) urea
(c) $CaCl_2$ (d) KCl. *(1994)*

63. Which of the following aqueous solution has minimum freezing point?
(a) 0.01 m NaCl (b) 0.005 m C_2H_5OH
(c) 0.005 m MgI_2 (d) 0.005 m $MgSO_4$ *(1991)*

ANSWER KEY

1.	(a)	**2.**	(c)	**3.**	(c)	**4.**	(b)	**5.**	(c)	**6.**	(b)	**7.**	(c)	**8.**	(c)	**9.**	(a)	**10.**	(c)
11.	(c)	**12.**	(c)	**13.**	(d)	**14.**	None	**15.**	(d)	**16.**	(a)	**17.**	(a)	**18.**	(d)	**19.**	(b)	**20.**	(a)
21.	(d)	**22.**	(c)	**23.**	(b)	**24.**	(c)	**25.**	(c)	**26.**	(d)	**27.**	(c)	**28.**	(c)	**29.**	(c)	**30.**	(c)
31.	(d)	**32.**	(a)	**33.**	(a)	**34.**	(b)	**35.**	(c)	**36.**	(b)	**37.**	(b)	**38.**	(c)	**39.**	(a)	**40.**	(a)
41.	(b)	**42.**	(a)	**43.**	(b)	**44.**	(c)	**45.**	(a)	**46.**	(a)	**47.**	(a)	**48.**	(c)	**49.**	(b)	**50.**	(b)
51.	(d)	**52.**	(c)	**53.**	(c)	**54.**	(c)	**55.**	(b)	**56.**	(d)	**57.**	(d)	**58.**	(d)	**59.**	(b)	**60.**	(c)
61.	(b)	**62.**	(c)	**63.**	(a)														

Hints & Explanations

1. (a) : Molarity is a function of temperature as volume depends on temperarure.

2. (c) : 1 molal aqueous solution means 1 mole of solute is present in 1000 g of water.

$$\therefore \quad x_{\text{solute}} = \frac{1}{1+\frac{1000}{18}} = \frac{1}{56.5} = 0.0177$$

3. (c) : $\text{Molarity} = \dfrac{w_{HNO_3} \times 1000}{M_{HNO_3} \times V_{\text{sol(mL)}}}$

$$\text{or} \quad 2 = \frac{w_{HNO_3}}{63} \times \frac{1000}{250} \Rightarrow w_{HNO_3} = \frac{63}{2}\text{ g}$$

$$\text{Mass of acid} \times \frac{70}{100} = \frac{63}{2}$$

Mass of acid = 45 g

4. (b) : A 35% (*V*/*V*) solution of ethylene glycol is used as an antifreeze in cars for cooling the engine. At this concentration, the antifreeze lowers the freezing point of water to 255.4 K (–17.6 °C).

5. (c) : H_2SO_4 is 98% by weight.
Weight of H_2SO_4 = 98 g, Weight of solution = 100 g

$$\therefore \quad \text{Volume of solution} = \frac{\text{mass}}{\text{density}} = \frac{100}{1.80}\text{ mL}$$
$$= 55.55\text{ mL} = 0.0555\text{ L}$$

$$\text{Molarity of solution} = \frac{98}{98 \times 0.0555} = 18.02\text{ M}$$

Let *V* mL of this H_2SO_4 is used to prepare 1 litre of 0.1 M H_2SO_4.
$\therefore$ mM of concentrated H_2SO_4 = mM of dilute H_2SO_4
or, $V \times 18.02 = 1000 \times 0.1$

$$\Rightarrow V = \frac{1000 \times 0.1}{18.02} = 5.55\text{ mL}$$

6. (b) : 1 molal aqueous solution means 1 mole of solute present in 1 kg of H_2O.

1 mole of solute present in $\dfrac{1000}{18}$ mole of H_2O

$$x_{\text{solute}} = \frac{1}{\frac{1000}{18}+1} = \frac{18}{1018} = 0.01768 \approx 0.018$$

7. (c) : Molecular weight of NaOH = 40 g mol^{-1}
2.5 litre of 1 M NaOH solution contain
$40\text{ g mol}^{-1} \times 1\text{ mol L}^{-1} \times 2.5\text{ L}$
$= 40 \times 2.5$ g of NaOH
3 litre of 0.5 M NaOH solution contain
$40\text{ g mol}^{-1} \times 0.5\text{ mol L}^{-1} \times 3\text{ L}$
$= 40 \times 0.5 \times 3$ g of NaOH
If these two solutions are mixed, the volume of the resultant solution = (2.5 + 3) = 5.5 litre.
5.5 litre of the resultant solution contain
= 40(2.5 + 1.5) g of NaOH
1 litre of the resultant solution contain

$$\frac{40 \times 4}{5.5}\text{ g of NaOH} = \frac{40 \times 4}{5.5 \times 40}\text{ mole of NaOH}$$

The molarity of the resultant solution = 0.727 ≈ 0.73 M

8. (c) : The strength of the solution is 0.1 N.

$$\frac{w}{E}=\frac{V\times N}{1000} \qquad \left(\text{Equivalent weight} = \frac{200}{2}=100\right)$$

$$\Rightarrow \quad w=\frac{100\times0.1\times100}{1000}=1\text{ g}$$

9. (a) : We know that 98% H_2SO_4 by weight means 98 g of H_2SO_4 is present in 100 g of solution.
Therefore, its weight is 98 and moles of H_2SO_4

$$=\frac{\text{Weight of } H_2SO_4}{\text{Molecular weight}}=\frac{98}{98}=1$$

and volume of solution = $\dfrac{\text{Mass}}{\text{Density}}$

$$=\frac{100}{1.84}=54.35\text{ mL}=\frac{54.35}{1000}\text{ L}$$

Therefore, molarity of H_2SO_4

$$=\frac{\text{Moles of } H_2SO_4}{\text{Volume (in litres)}}=\frac{1\times1000}{54.35}=18.4\text{ M}$$

10. (c) : The molality involves weights of the solute and the solvent. Since the weight does not change with the temperature, therefore molality does not depend upon the temperature.

11. (c) : Since the molecular mass of CH_3OH is 32, therefore quantity of CH_3OH to prepare 150 mL solution

of 2 M CH_3OH $=\left(\dfrac{2}{1000}\right)\times150\times32 = 9.6$ g

12. (c) : $p_{\text{water vapour}} = x_{\text{water vapour}} \times P_{\text{total}}$

$= 0.02 \times 1.2 = 0.024$ atm

$P_{\text{total}} = p_{\text{water vapour}} + p_{\text{dry air}}$

$1.2 = 0.024 + p_{\text{dry air}}$

$p_{\text{dry air}} = 1.2 - 0.024 = 1.176$ atm

Partial vapour pressure is directly proportional to mole fraction, $p \propto x$.

13. (d) : According to Raoult's law,

$P = x_Ap_A + x_Bp_B$ ... (i)

For binary solutions,

$x_A + x_B = 1, \quad x_B = 1 - x_A$ ... (ii)

Putting value of x_B from eqn. (ii) to eqn. (i)

$P = x_Ap_A + (1 - x_A)p_B = x_Ap_A + p_B - x_Ap_B$

$P = p_B + x_A(p_A - p_B)$

14. (None) :

$p^\circ_{CHCl_3} = 200$ mm Hg, $p^\circ_{CH_2Cl_2} = 41.5$ mm Hg

Moles of $CHCl_3$

$$=\frac{\text{Weight}}{\text{Molecular weight}}=\frac{25.5}{119.5}=0.213$$

Moles of $CH_2Cl_2 = \dfrac{40}{85} = 0.470$

$$x_{CHCl_3}=\frac{0.213}{0.213+0.470}=0.31$$

$$x_{CH_2Cl_2}=\frac{0.470}{0.213+0.470}=0.69$$

$P_{\text{total}} = p^\circ_{CHCl_3}x_{CHCl_3} + p^\circ_{CH_2Cl_2}x_{CH_2Cl_2}$

$= 200 \times 0.31 + 41.5 \times 0.69 = 62 + 28.63 = 90.63$ mm Hg

15. (d) : $\dfrac{n_{C_5H_{12}}}{n_{C_6H_{14}}}=\dfrac{1}{4}$

$\Rightarrow \; x_{C_5H_{12}}=\dfrac{1}{5}$ and $x_{C_6H_{14}}=\dfrac{4}{5}$

$p^\circ_{C_5H_{12}} = 440$ mm Hg; $p^\circ_{C_6H_{14}} = 120$ mm Hg

$P_{\text{total}} = p^\circ_{C_5H_{12}}x_{C_5H_{12}} + p^\circ_{C_6H_{14}}x_{C_6H_{14}}$

$=440\times\dfrac{1}{5}+120\times\dfrac{4}{5}=88+96=184$ mm of Hg

By Raoult's law, $p_{C_5H_{12}} = p^\circ_{C_5H_{12}}x_{C_5H_{12}}$ ...(1)

$x_{C_5H_{12}} \rightarrow$ mole fraction of pentane in solution.

By Dalton's law, $p_{C_5H_{12}} = x'_{C_5H_{12}}P_{\text{total}}$ ...(2)

$x'_{C_5H_{12}} \rightarrow$ mole fraction of pentane above the solution.

From (1) and (2),

$p_{C_5H_{12}} = 440\times\dfrac{1}{5} = 88$ mm of Hg

$\Rightarrow \; 88 = x'_{C_5H_{12}} \times 184$

$$x'_{C_5H_{12}}=\frac{88}{184}=0.478$$

16. (a) : By Raoult's Law, $P_T = p_P^\circ x_P^\circ + p_Q^\circ x_Q$

where $p_P^\circ = 80$ torr, $p_Q^\circ = 60$ torr, $x_P=\dfrac{3}{5}$; $x_Q=\dfrac{2}{5}$

$P_T=80\times\dfrac{3}{5}+60\times\dfrac{2}{5} = 48 + 24 = 72$ torr

17. (a) : Mixture of ethanol and acetone shows positive deviation from Raoult's law.
In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

18. (d) : For an ideal solution, $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$ at constant T and P.

19. (b) : Maximum boiling azeotropes are formed by those solutions which show negative deviations from Raoult's law. H_2O and HNO_3 mixture shows negative deviations.

20. (a) : In case of positive deviation from Raoult's law, *A-B* interactions are weaker than those between *A-A* or *B-B*, *i.e.*, in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solution, molecules of *A* (or *B*) will find it easier to escape than in pure state. This will increase the vapour pressure and result in positive deviation.

21. **(d) :** For an ideal solution,

$\Delta H_{mix} = 0, \Delta V_{mix} = 0,$

Now, $\Delta U_{mix} = \Delta H_{mix} - P\Delta V_{mix}$

$\therefore \quad \Delta U_{mix} = 0$

Also, for an ideal solution,

$$p_A = x_A p_A^\circ, \; p_B = x_B p_B^\circ$$

$\therefore \quad \Delta P = P_{obs} - P_{\text{calculated by Raoult's law}} = 0$

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

For an ideal solution, $\Delta S_{mix} \neq 0$

$\therefore \quad \Delta G_{mix} \neq 0$

22. **(c) :** $p_{\text{Benzene}} = x_{\text{Benzene}}\, p^\circ_{\text{Benzene}}$

$p_{\text{Toluene}} = x_{\text{Toluene}}\, p^\circ_{\text{Toluene}}$

For an ideal 1 : 1 molar mixture of benzene and toluene,

$$x_{\text{Benzene}} = \frac{1}{2} \text{ and } x_{\text{Toluene}} = \frac{1}{2}$$

$$p_{\text{Benzene}} = \frac{1}{2} p^\circ_{\text{Benzene}} = \frac{1}{2} \times 12.8 \text{ kPa} = 6.4 \text{ kPa}$$

$$p_{\text{Toluene}} = \frac{1}{2} p^\circ_{\text{Toluene}} = \frac{1}{2} \times 3.85 \text{ kPa} = 1.925 \text{ kPa}$$

Thus, the vapour will contain a high percentage of benzene as the partial vapour pressure of benzene is higher as compared to that of toluene.

23. **(b) :** For an ideal solution :

- Volume change (ΔV) on mixing should be zero.
- Heat change (ΔH) on mixing should be zero.
- Obeys Raoult's law at every range of concentration.
- Entropy change (ΔS) on mixing $\neq 0$.

24. **(c) :** Both the components escape easily showing higher vapour pressure than the expected value. This is due to breaking of some hydrogen bonds between ethanol molecules.

25. **(c) :** Raoult's law is valid for ideal solutions only. The element of non-ideality enters into the picture when the molecules of the solute and solvent affect each others intermolecular forces. A solution containing components of *A* and *B* behaves as ideal solution when *A* – *B* attraction force remains same as *A* – *A* and *B* – *B* attraction forces.

26. **(d) :** Because C_2H_5I and C_2H_5OH are dissimilar liquids.

27. **(c) :** For ideal solution,

$\Delta V_{mixing} = 0$ and $\Delta H_{mixing} = 0$.

28. **(c) :** Given : $K_f = 5.12$ K kg mol^{-1}, $m = 0.078$ m

$\Delta T_f = K_f \times m = 5.12 \times 0.078 = 0.39936 \approx 0.40$ K

29. **(c) :** The value of molal depression constant, K_f is constant for a particular solvent, thus, it will be unchanged when molality of the dilute solution is doubled.

30. **(c) :** Given : $W_B = 6.5$ g, $W_A = 100$ g,

$p_s = 732$ mm, $K_b = 0.52$, $T_b^\circ = 100°C$, $p^\circ = 760$ mm

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1} \Rightarrow \frac{760-732}{760} = \frac{n_2}{100/18}$$

$$\Rightarrow n_2 = \frac{28 \times 100}{760 \times 18} = 0.2046 \text{ mol}$$

$\Delta T_b = K_b \times m$

$$T_b - T_b^\circ = K_b \times \frac{n_2 \times 1000}{W_A(\text{g})}$$

$$T_b - 100°\text{C} = \frac{0.52 \times 0.2046 \times 1000}{100} = 1.06$$

$T_b = 100 + 1.06 = 101.06$ °C

31. **(d) :** We know that $pV = nRT$, where $n = \dfrac{w}{M}$

$$\pi V = \frac{w}{M} RT$$

$$M = \frac{wRT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times \frac{200}{1000}}$$

$$= \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 0.2} = 61038 \text{ g mol}^{-1}$$

32. **(a) :** We know, $\Delta T_f = K_f m$

$$m = \frac{w_B}{M_B} \times \frac{1000}{W_A} = \frac{68.5 \times 1000}{342 \times 1000} = \frac{68.5}{342}$$

$$\Delta T_f = 1.86 \times \frac{68.5}{342} = 0.372°\text{C}$$

$\therefore \quad T_f = 0 - 0.372°\text{C} = -0.372°\text{C}$

33. **(a)**

34. **(b) :** $M_B = \dfrac{1000 \times K_f \times w_B}{W_A \times \Delta T_f}$

$$\text{or,} \quad 250 = \frac{1000 \times 5.12 \times 1}{51.2 \times \Delta T_f}$$

$$\therefore \quad \Delta T_f = \frac{1000 \times 5.12 \times 1}{51.2 \times 250} = 0.4 \text{ K}$$

35. **(c) :** Molar concentration of urea $= \dfrac{10}{60}$ dm^{-3}

Molar concentration of non-volatile solution

$$= \frac{50}{M_B} \text{ L}^{-1} = \frac{50}{M_B} \text{ dm}^{-3}$$

For isotonic solutions, $\dfrac{10}{60} = \dfrac{50}{M_B}$

$\Rightarrow \quad M_B = 300$ g mol^{-1}

36. **(b) :** $\Delta T_f = K_f m$ ...(1)

$\Delta T_b = K_b m$ ...(2)

$$\Rightarrow \frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b} \quad ...(3)$$

$\Delta T_f \rightarrow$ depression in freezing point

$\Delta T_b \rightarrow$ elevation in boiling point

$K_f = 1.86$ K kg mol^{-1}

$K_b = 0.512$ K kg mol^{-1}, $\Delta T_b = 100.18 - 100 = 0.18$

$\Rightarrow$ From eq. (3), $\dfrac{\Delta T_f}{0.18} = \dfrac{1.86}{0.512}$

$\Rightarrow$ $\Delta T_f = 0.654 = T_f^\circ - T_f = 0 - T_f \Rightarrow T_f = -0.654°\text{C}$

$\Rightarrow$ Freezing point of urea in water = $-0.654°$C

37. (b) : For dilute solution, $\pi = \dfrac{n}{V}RT$

$$\Rightarrow \pi V = \frac{m_2}{M_2}RT \Rightarrow M_2 = \frac{m_2 RT}{\pi V}$$

38. (c) **39. (a)**

40. (a) : $p° = 640$ mm Hg, $p_s = 600$ mm Hg, $w_B = 2.175$ g, $W_A = 39.08$ g

From Raoult's law

$$\frac{p° - p_s}{p°} = \frac{w_B \times M_A}{W_A \times M_B} \Rightarrow \frac{640-600}{640} = \frac{2.175 \times 78}{39.08 \times M_B}$$

$\Rightarrow$ $M_B = 69.5$

41. (b) : $w_B = 0.15$ g, $W_A = 15$ g, $\Delta T_b = 0.216°$C

$K_b = 2.16$, $m = ?$

As $\Delta T_b = \dfrac{1000 \times K_b \times w_B}{M_B \times W_A}$

$$\Rightarrow M_B = \frac{1000 \times 2.16 \times 0.15}{0.216 \times 15} = 100$$

42. (a) :

Cane Sugar	***X***
$W_1 = 5$ g	$W_2 = 1$ g
$V_1 = 100$ mL	$V_2 = 100$ mL
$= 0.1$ L	$= 0.1$ L
$M_1 = 342$	$M_2 = ?$

For isotonic solutions, $C_1 = C_2$

$$\frac{W_1}{M_1 V_1} = \frac{W_2}{M_2 V_2} \Rightarrow \frac{5}{342 \times 0.1} = \frac{1}{M_2 \times 0.1}$$

$$\Rightarrow M_2 = \frac{342}{5} = 68.4$$

43. (b) : x_2 (mole fraction of solute) = 0.2

From Raoult's law,

$$\frac{p° - p_s}{p°} = x_2 \Rightarrow \frac{10}{p°} = 0.2 \Rightarrow p° = 50 \text{ mm Hg}$$

Again, when $p° - p_s = 20$ mm Hg, then

$\dfrac{p° - p_s}{p°}$ = mole fraction of solute = $\dfrac{20}{50} = 0.4$

$\Rightarrow$ mole fraction of solvent = $1 - 0.4 = 0.6$

44. (c) : Vapour pressure of pure solvent (p_A°) = 143 mm Hg, weight of solute (w_B) = 0.5 g, weight of solvent (W_A) = 100 g, molecular weight of solute (M_B) = 65 and molecular weight of solvent (M_A) = 154.

$$\frac{p_A^\circ - p_s}{p_A^\circ} = \frac{w_B M_A}{M_B W_A} \quad \text{or} \quad \frac{143 - p_s}{143} = \frac{0.5 \times 154}{65 \times 100}$$

or $p_s = 141.31$ mm Hg

45. (a) : Weight of glucose = 10 g,

Weight of urea = 10 g and weight of sucrose = 10 g

The number of moles of glucose

$$(n_1) = \frac{\text{Weight}}{\text{Molecular weight}} = \frac{10}{180} = 0.05$$

Similarly, number of moles of urea $(n_2) = \dfrac{10}{60} = 0.16$ and the number of moles of sucrose $(n_3) = \dfrac{10}{342} = 0.03$

The osmotic pressure is a colligative property and it depends upon the number of moles of a solute.

Since $n_2 > n_1 > n_3$, therefore $p_2 > p_1 > p_3$.

46. (a)

47. (a) : There is no net movement of the solvent through the semipermeable membrane between two solutions of equal concentration.

48. (c) : The properties which depend only upon the number of solute particles present in the solution irrespective of their nature are called colligative properties. Lowering in vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure are colligative properties.

49. (b) : Blood cells neither swell nor shrink in isotonic solution. The solutions having same osmotic pressure are called isotonic solutions.

50. (b) : Relative lowering of vapour pressure is equal to mole fraction of solute which is the ratio of solute molecules to the total molecules in solution.

51. (d) : Being a strong electrolyte, $Ba(OH)_2$ undergoes 100% dissociation in a dilute aqueous solution,

$$Ba(OH)_{2(aq)} \rightarrow Ba^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Thus, van't Hoff factor $i = 3$.

52. (c) : $\Delta T_b = iK_b m$

For equimolal solutions, elevation in boiling point will be higher if solution undergoes dissociation *i.e.*, $i > 1$.

53. (c) : $\Delta T_f = i \times K_f \times m$

So, $\Delta T_f \propto i$ (van't Hoff factor)

Salt	***i***
KCl	2
$C_6H_{12}O_6$	1
$Al_2(SO_4)_3$	5
K_2SO_4	3

Hence, i is maximum *i.e.*, 5 for $Al_2(SO_4)_3$.

54. (c) : From the value of van't Hoff factor i it is possible to determine the degree of dissociation or association. In case of dissociation, i is greater than 1 and in case of association i is less than 1.

55. (b) : We know that

$$\Delta T_f = i \times K_f \times \frac{w_B \times 1000}{M_B \times W_A}$$

Given : $\Delta T_f = 3.82$, $K_f = 1.86$,
$w_B = 5$, $M_B = 142$, $W_A = 45$

$$i = \frac{\Delta T_f \times M_B \times W_A}{K_f \times w_B \times 1000} = \frac{3.82 \times 142 \times 45}{1.86 \times 5 \times 1000} = 2.63$$

56. (d) : We know that $\Delta T_f = i \times K_f \times m$
Here i is van't Hoff factor.
i for weak acid is $1 + \alpha$.
Here α is degree of dissociation *i.e.*, 30/100 = 0.3
$\therefore \quad i = 1 + \alpha = 1 + 0.3 = 1.3$
$\Delta T_f = i \times K_f \times m = 1.3 \times 1.86 \times 0.1 = 0.24$
$\therefore$ Freezing point of solution, $T_f = T^\circ_f - \Delta T_f$
$= 0 - 0.24 = -0.24°C$

57. (d) : Addition of water to an aqueous solution of KI causes the concentration of the solution to decrease thereby increasing the vapour pressure. In the other three options, the electrolytes undergo ionization, which leads to lowering of vapour pressure.

58. (d) : The number of moles of ions produced by 1 mol of ionic compound = i
Applying, $\Delta T_f = i \times K_f \times m$
$0.00732 = i \times 1.86 \times 0.002$

$$\Rightarrow \quad i = \frac{0.00732}{1.86 \times 0.002} = 1.96 \approx 2$$

59. (b) :

$$\begin{array}{ccc} HX & \rightleftharpoons & H^+ + X^- \\ 1-\alpha & & \alpha \qquad \alpha \end{array}$$

Total = $1 + \alpha$
$\therefore \quad i = 1 + \alpha = 1 + 0.2 = 1.2$
$\Delta T_f = i \times K_f \times m = 1.2 \times 1.86 \times 0.5 = 1.116 \text{ K} \approx 1.12 \text{ K}$

60. (c) : Since $Al_2(SO_4)_3$ gives maximum number of ions on dissociation, therefore it will have the lowest freezing point.

$$\Delta T_f = iK_f \cdot m$$

61. (b) : $K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]^{3-}$ and $Al(NO_3)_3 \rightleftharpoons Al^{3+} + 3NO_3^-$
Since both $Al(NO_3)_3$ and $K_3[Fe(CN)_6]$ give the same number of ions, therefore they have the same van't Hoff factor.

62. (c) : In solution, $CaCl_2$ gives three ions, KCl gives two ions while glucose and urea are covalent molecules so they do not undergo ionisation. Since osmotic pressure is a colligative property and it depends upon the number of solute particles (ions), therefore, 0.1 M solution of $CaCl_2$ exhibits the highest osmotic pressure.

63. (a) : Here, $\Delta T_f = i \times K_f \times m$
van't Hoff factor, $i = 2$ for NaCl, so conc. = 0.02, which is maximum in the present case.
Hence, ΔT_f is maximum or freezing point is minimum in 0.01 m NaCl.

* * *

CHAPTER
3

Electrochemistry

3.2 Galvanic Cells

1. The standard electrode potential ($E°$) values of Al^{3+}/Al, Ag^+/Ag, K^+/K and Cr^{3+}/Cr are –1.66 V, 0.80 V, –2.93 V and –0.74 V, respectively. The correct decreasing order of reducing power of the metal is

(a) Ag > Cr > Al > K (b) K > Al > Cr > Ag
(c) K > Al > Ag > Cr (d) Al > K > Ag > Cr

(Odisha NEET 2019)

2. A button cell used in watches function as following :

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightleftharpoons 2Ag_{(s)} + Zn^{2+}_{(aq)} + 2OH^-_{(aq)}$$

If half cell potentials are

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$; $E° = -0.76$ V

$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)}$; $E° = 0.34$ V

The cell potential will be

(a) 0.84 V (b) 1.34 V
(c) 1.10 V (d) 0.42 V *(NEET 2013)*

3. Standard reduction potentials of the half reactions are given below :

$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$; $E° = +2.85$ V

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$; $E° = +1.36$ V

$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$; $E° = +1.06$ V

$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$; $E° = +0.53$ V

The strongest oxidising and reducing agents respectively are

(a) F_2 and I^- (b) Br_2 and Cl^-
(c) Cl_2 and Br^- (d) Cl_2 and I_2

(Mains 2012)

4. Standard electrode potentials of three metals *X*, *Y* and *Z* are –1.2 V, + 0.5 V and – 3.0 V respectively. The reducing power of these metals will be

(a) $Y > Z > X$ (b) $Y > X > Z$
(c) $Z > X > Y$ (d) $X > Y > Z$ *(2011)*

5. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is –0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be

(a) + 1.19 V (b) + 0.89 V
(c) + 0.18 V (d) + 1.83 V *(2011)*

6. A solution contains Fe^{2+}, Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C. $E°$ for Fe^{3+}/Fe^{2+} is + 0.77 V and $E°$ for $I_2/2I^- = 0.536$ V. The favourable redox reaction is

(a) I_2 will be reduced to I^-
(b) there will be no redox reaction
(c) I^- will be oxidised to I_2
(d) Fe^{2+} will be oxidised to Fe^{3+}. *(Mains 2011)*

7. Consider the following relations for emf of an electrochemical cell

(i) EMF of cell = (Oxidation potential of anode) – (Reduction potential of cathode)
(ii) EMF of cell = (Oxidation potential of anode) + (Reduction potential of cathode)
(iii) EMF of cell = (Reductional potential of anode) + (Reduction potential of cathode)
(iv) EMF of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)

Which of the above relations are correct?

(a) (iii) and (i) (b) (i) and (ii)
(c) (iii) and (iv) (d) (ii) and (iv)

(Mains 2010)

8. On the basis of the following $E°$ values, the strongest oxidizing agent is

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$; $E° = -0.35$ V

$Fe^{2+} \rightarrow Fe^{3+} + e^-$; $E° = -0.77$ V

(a) Fe^{3+} (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(CN)_6]^{4-}$ (d) Fe^{2+} *(2008)*

9. A hypothetical electrochemical cell is shown below :

$$A / A^+ (x\,M) \,||\, B^+ (y\,M) \,|\, B$$

The emf measured is + 0.20 V. The cell reaction is

(a) $A + B^+ \rightarrow A^+ + B$
(b) $A^+ + B \rightarrow A + B^+$

(c) $A^+ + e^- \longrightarrow A; B^+ + e^- \longrightarrow B$
(d) the cell reaction cannot be predicted. *(2006)*

10. $E^\circ_{Fe^{2+}/Fe} = -0.441$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ V, the standard EMF of the reaction $Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$ will be
(a) 0.111 V
(b) 0.330 V
(c) 1.653 V
(d) 1.212 V *(2006)*

11. Standard electrode potentials are Fe^{2+}/Fe; $E^\circ = -0.44$ and Fe^{3+}/Fe^{2+}; $E^\circ = 0.77$. Fe^{2+}, Fe^{3+} and Fe blocks are kept together, then
(a) Fe^{3+} increases
(b) Fe^{3+} decreases
(c) Fe^{2+}/Fe^{3+} remains unchanged
(d) Fe^{2+} decreases. *(2001)*

12. Electrode potential for the following half-cell reactions are
$Zn \longrightarrow Zn^{2+} + 2e^-$; $E^\circ = +0.76$ V;
$Fe \longrightarrow Fe^{2+} + 2e^-$; $E^\circ = +0.44$ V.
The EMF for the cell reaction
$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ will be
(a) – 0.32 V
(b) + 1.20 V
(c) – 1.20 V
(d) + 0.32 V *(1996)*

13. An electrochemical cell is set up as : Pt; H_2 (1 atm)|HCl(0.1 M) || CH_3COOH (0.1 M) |H_2 (1 atm); Pt. The e.m.f. of this cell will not be zero, because
(a) acids used in two compartments are different
(b) e.m.f. depends on molarities of acids used
(c) the temperature is constant
(d) pH of 0.1 M HCl and 0.1 M CH_3COOH is not same. *(1995)*

14. Standard reduction potentials at 25°C of $Li^+|Li$, $Ba^{2+}|Ba$, $Na^+|Na$ and $Mg^{2+}|Mg$ are –3.05, –2.90, –2.71 and –2.37 volt respectively. Which one of the following is the strongest oxidising agent?
(a) Ba^{2+}
(b) Mg^{2+}
(c) Na^+
(d) Li^+ *(1994)*

15. A solution of potassium bromide is treated with each of the following. Which one would liberate bromine?
(a) Hydrogen iodide
(b) Sulphur dioxide
(c) Chlorine
(d) Iodine *(1993)*

3.3 Nernst Equation

16. For the cell reaction :
$$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(aq)}$$
$E^\circ_{cell} = 0.24$ V at 298 K. The standard Gibbs' energy $(\Delta_r G^\circ)$of the cell reaction is
[Given that Faraday constant, $F = 96500$ C mol^{-1}]
(a) 23.16 kJ mol^{-1}
(b) –46.32 kJ mol^{-1}
(c) –23.16 kJ mol^{-1}
(d) 46.32 kJ mol^{-1}
(NEET 2019)

17. For a cell involving one electron, $E^\circ_{cell} = 0.59$ V at 298 K, the equilibrium constant for the cell reaction is [Given that $\frac{2.303RT}{F} = 0.059$ V at $T = 298$ K]
(a) 1.0×10^{30}
(b) 1.0×10^2
(c) 1.0×10^5
(d) 1.0×10^{10}
(NEET 2019)

18. In the electrochemical cell :
$Zn|ZnSO_4(0.01\ M)||CuSO_4(1.0\ M)|Cu$,
the emf of this Daniell cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to E_2. From the followings, which one is the relationship between E_1 and E_2? (Given, $RT/F = 0.059$)
(a) $E_1 < E_2$
(b) $E_1 > E_2$
(c) $E_2 = 0 \neq E_1$
(d) $E_1 = E_2$
(NEET 2017, 2003)

19. If the E°_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG° and K_{eq} ?
(a) $\Delta G^\circ > 0; K_{eq} < 1$
(b) $\Delta G^\circ > 0; K_{eq} > 1$
(c) $\Delta G^\circ < 0; K_{eq} > 1$
(d) $\Delta G^\circ < 0; K_{eq} < 1$
(NEET-II 2016, 2011)

20. The pressure of H_2 required to make the potential of H_2 electrode zero in pure water at 298 K is
(a) 10^{-10} atm
(b) 10^{-4} atm
(c) 10^{-14} atm
(d) 10^{-12} atm.
(NEET-I 2016)

21. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be
(a) 0.118 V
(b) 1.18 V
(c) 0.059 V
(d) 0.59 V *(NEET 2013)*

22. Consider the half-cell reduction reaction
$Mn^{2+} + 2e^- \longrightarrow Mn$, $E^\circ = -1.18$ V
$Mn^{2+} \longrightarrow Mn^{3+} + e^-$, $E^\circ = -1.51$ V
The E° for the reaction,
$3Mn^{2+} \longrightarrow Mn^0 + 2Mn^{3+}$,
and possibility of the forward reaction are respectively
(a) – 4.18 V and yes
(b) + 0.33 V and yes
(c) + 2.69 V and no
(d) – 2.69 V and no.
(Karnataka NEET 2013)

23. The Gibbs' energy for the decomposition of Al_2O_3 at 500 °C is as follows

$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2, \Delta_r G = +960$ kJ mol^{-1}

The potential difference needed for the electrolytic reduction of aluminium oxide (Al_2O_3) at 500 °C is at least

(a) 4.5 V
(b) 3.0 V
(c) 2.5 V
(d) 5.0 V *(Mains 2012)*

24. The electrode potentials for,
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$ and $Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$
are + 0.15 V and + 0.50 V respectively. The value of $E°_{Cu^{2+}/Cu}$ will be

(a) 0.500 V
(b) 0.325 V
(c) 0.650 V
(d) 0.150 V *(2011)*

25. For the reduction of silver ions with copper metal, the standard cell potential was found to be + 0.46 V at 25 °C. The value of standard Gibbs energy, $\Delta G°$ will be ($F = 96500$ C mol^{-1})

(a) – 89.0 kJ
(b) – 89.0 J
(c) – 44.5 kJ
(d) – 98.0 kJ *(2010)*

26. Given :
(i) $Cu^{2+} + 2e^- \rightarrow Cu, E° = 0.337$ V
(ii) $Cu^{2+} + e^- \rightarrow Cu^+, E° = 0.153$ V
Electrode potential, $E°$ for the reaction,
$Cu^+ + e^- \rightarrow Cu$, will be

(a) 0.90 V
(b) 0.30 V
(c) 0.38 V
(d) 0.52 V *(2009)*

27. Standard free energies of formation (in kJ/mol) at 298 K are –237.2, –394.4 and –8.2 for $H_2O_{(l)}$, $CO_{2(g)}$ and pentane$_{(g)}$ respectively. The value of $E°_{cell}$ for the pentane-oxygen fuel cell is

(a) 1.0968 V
(b) 0.0968 V
(c) 1.968 V
(d) 2.0968 V *(2008)*

28. The equilibrium constant of the reaction :
$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$;
$E° = 0.46$ V at 298 K is

(a) 2.0×10^{10}
(b) 4.0×10^{10}
(c) 4.0×10^{15}
(d) 2.4×10^{10} *(2007)*

29. The standard e.m.f. of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be

(a) 2.0×10^{11}
(b) 4.0×10^{12}
(c) 1.0×10^2
(d) 1.0×10^{10}

(Given F = 96500 C mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1})
(2004)

30. On the basis of the information available from the reaction,
$4/3Al + O_2 \rightarrow 2/3Al_2O_3$, $\Delta G = -827$ kJ mol^{-1} of O_2, the minimum e.m.f. required to carry out an electrolysis of Al_2O_3 is (F = 96500 C mol^{-1})

(a) 2.14 V
(b) 4.28 V
(c) 6.42 V
(d) 8.56 V *(2003)*

31. For the disproportionation of copper $2Cu^+ \rightarrow Cu^{2+} + Cu$, $E°$ is (Given : $E°$ for Cu^{2+}/Cu is 0.34 V and $E°$ for Cu^{2+}/Cu^+ is 0.15 V)

(a) 0.49 V
(b) –0.19 V
(c) 0.38 V
(d) –0.38 V *(2000)*

32. $E°$ for the cell, $Zn \mid Zn^{2+}_{(aq)} \| Cu^{2+}_{(aq)} \mid Cu$ is 1.10 V at 25°C, the equilibrium constant for the reaction $Zn + Cu^{2+}_{(aq)} \rightarrow Cu + Zn^{2+}_{(aq)}$ is of the order

(a) 10^{+18}
(b) 10^{+17}
(c) 10^{-28}
(d) 10^{+37} *(1997)*

3.4 Conductance of Electrolytic Solutions

33. Following limiting molar conductivities are given as :
$\lambda°_{m(H_2SO_4)} = x$ S cm^2 mol^{-1}
$\lambda°_{m(K_2SO_4)} = y$ S cm^2 mol^{-1}
$\lambda°_{m(CH_3COOK)} = z$ S cm^2 mol^{-1}
$\lambda°_m$ (in S cm^2 mol^{-1}) for CH_3COOH will be

(a) $x - y + 2z$
(b) $x + y - z$
(c) $x - y + z$
(d) $\frac{(x-y)}{2} + z$

(Odisha NEET 2019)

34. The molar conductivity of a 0.5 mol/dm^3 solution of $AgNO_3$ with electrolytic conductivity of 5.76×10^{-3} S cm^{-1} at 298 K is

(a) 2.88 S cm^2/mol
(b) 11.52 S cm^2/mol
(c) 0.086 S cm^2/mol
(d) 28.8 S cm^2/mol

(NEET-II 2016)

35. At 25 °C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 ohm^{-1} cm^2 mol^{-1} and at infinite dilution its molar conductance is 238 ohm^{-1} cm^2 mol^{-1}. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is

(a) 4.008%
(b) 40.800%
(c) 2.080%
(d) 20.800% *(NEET 2013)*

36. Limiting molar conductivity of NH_4OH [*i.e.*, $\Lambda°_{m(NH_4OH)}$] is equal to

(a) $\Lambda°_{m(NH_4Cl)} + \Lambda°_{m(NaCl)} - \Lambda°_{m(NaOH)}$
(b) $\Lambda°_{m(NaOH)} + \Lambda°_{m(NaCl)} - \Lambda°_{m(NH_4Cl)}$
(c) $\Lambda°_{m(NH_4OH)} + \Lambda°_{m(NH_4Cl)} - \Lambda°_{m(HCl)}$
(d) $\Lambda°_{m(NH_4Cl)} + \Lambda°_{m(NaOH)} - \Lambda°_{m(NaCl)}$ *(2012)*

37. Molar conductivities ($\Lambda°_m$) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. ($\Lambda°_m$) for CH_3COOH will be

(a) 425.5 S cm^2 mol^{-1} (b) 180.5 S cm^2 mol^{-1}
(c) 290.8 S cm^2 mol^{-1} (d) 390.5 S cm^2 mol^{-1}
(Mains 2012, 1997)

38. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to
(a) increase in ionic mobility of ions
(b) 100% ionisation of electrolyte at normal dilution
(c) increase in both *i.e.*, number of ions and ionic mobility of ions
(d) increase in number of ions. *(2010)*

39. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $Al_2(SO_4)_3$? Given that $\overset{\circ}{\Lambda}_{Al^{3+}}$ and $\overset{\circ}{\Lambda}_{SO_4^{2-}}$ are the equivalent conductances at infinite dilution of the respective ions.
(a) $2\overset{\circ}{\Lambda}_{Al^{3+}} + 3\overset{\circ}{\Lambda}_{SO_4^{2-}}$
(b) $\overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}$
(c) $(\overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}) \times 6$
(d) $\frac{1}{3}\overset{\circ}{\Lambda}_{Al^{3+}} + \frac{1}{2}\overset{\circ}{\Lambda}_{SO_4^{2-}}$ *(Mains 2010)*

40. The equivalent conductance of *M*/32 solution of a weak monobasic acid is 8.0 mho cm^2 and at infinite dilution is 400 mho cm^2. The dissociation constant of this acid is
(a) 1.25×10^{-6} (b) 6.25×10^{-4}
(c) 1.25×10^{-4} (d) 1.25×10^{-5} *(2009)*

41. Kohlrausch's law states that at
(a) infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte
(b) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte
(c) finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte
(d) infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte. *(2008)*

42. Equivalent conductances of Ba^{2+} and Cl^- ions are 127 and 76 ohm^{-1} cm^{-1} eq^{-1} respectively. Equivalent conductance of $BaCl_2$ at infinite dilution is
(a) 139.5 (b) 101.5
(c) 203 (d) 279 *(2000)*

43. The specific conductance of a 0.1 N KCl solution at 23°C is 0.012 ohm^{-1} cm^{-1}. The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be
(a) 0.918 cm^{-1} (b) 0.66 cm^{-1}
(c) 1.142 cm^{-1} (d) 1.12 cm^{-1} *(1999)*

44. On heating one end of a piece of a metal, the other end becomes hot because of
(a) energised electrons moving to the other end
(b) minor perturbation in the energy of atoms
(c) resistance of the metal
(d) mobility of atoms in the metal. *(1995)*

3.5 Electrolytic Cells and Electrolysis

45. On electrolysis of dil. sulphuric acid using platinum (Pt) electrode, the product obtained at anode will be
(a) hydrogen gas (b) oxygen gas
(c) H_2S gas (d) SO_2 gas. *(NEET 2020)*

46. The number of Faradays (F) required to produce 20 g of calcium from molten $CaCl_2$ (Atomic mass of Ca = 40 g mol^{-1}) is
(a) 1 (b) 2
(c) 3 (d) 4 *(NEET 2020)*

47. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is
(a) 55 minutes (b) 110 minutes
(c) 220 minutes (d) 330 minutes.
(NEET-II 2016)

48. The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = 1.60×10^{-19} C)
(a) 6×10^{23} (b) 6×10^{20}
(c) 3.75×10^{20} (d) 7.48×10^{23}
(NEET-II 2016)

49. When 0.1 mol MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is
(a) 96500 C (b) 2×96500 C
(c) 9650 C (d) 96.50 C *(2014)*

50. The weight of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be
(a) 5.4 g (b) 10.8 g
(c) 54.0 g (d) 108.0 g *(2014)*

51. How many grams of cobalt metal will be deposited when a solution of cobalt(II) chloride is electrolyzed with a current of 10 amperes for 109 minutes? (1 Faraday = 96,500 C; Atomic mass of Co = 59 u)
(a) 4.0 (b) 20.0
(c) 40.0 (d) 0.66
(Karnataka NEET 2013)

52. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency, at. mass of Al = 27 g mol^{-1})
(a) 8.1×10^4 g (b) 2.4×10^5 g
(c) 1.3×10^4 g (d) 9.0×10^3 g *(2009)*

53. 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be
(a) 44.8 L (b) 22.4 L
(c) 11.2 L (d) 5.6 L *(2005)*

54. In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam. The reason for this is
(a) Hg is more inert than Pt
(b) more voltage is required to reduce H^+ at Hg than at Pt
(c) Na is dissolved in Hg while it does not dissolve in Pt
(d) conc. of H^+ ions is larger when Pt electrode is taken. *(2002)*

55. A 5 ampere current is passed through a solution of zinc sulphate for 40 minutes. The amount of zinc deposited at the cathode is
(a) 0.4065 g (b) 65.04 g
(c) 40.65 g (d) 4.065 g *(1996)*

56. Sodium is made by the electrolysis of a molten mixture of about 40% NaCl and 60% $CaCl_2$ because
(a) Ca^{++} can reduce NaCl to Na
(b) Ca^{++} can displace Na from NaCl
(c) $CaCl_2$ helps in conduction of electricity
(d) this mixture has a lower melting point than NaCl. *(1995)*

57. When $CuSO_4$ is electrolysed using platinum electrodes,
(a) copper is liberated at cathode, sulphur at anode
(b) copper is liberated at cathode, oxygen at anode
(c) sulphur is liberated at cathode, oxygen at anode
(d) oxygen is liberated at cathode, copper at anode. *(1993)*

58. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be
(a) hydrogen (b) oxygen
(c) hydrogen sulphide (d) sulphur dioxide. *(1992)*

3.7 Fuel Cells

59. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as
(a) dynamo (b) Ni-Cd cell
(c) fuel cell (d) electrolytic cell. *(2015, Cancelled)*

60. The efficiency of a fuel cell is given by
(a) $\Delta G/\Delta S$ (b) $\Delta G/\Delta H$
(c) $\Delta S/\Delta G$ (d) $\Delta H/\Delta G$ *(2007)*

3.8 Corrosion

61. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because
(a) zinc is lighter than iron
(b) zinc has lower melting point than iron
(c) zinc has lower negative electrode potential than iron
(d) zinc has higher negative electrode potential than iron. *(NEET-II 2016)*

62. The most convenient method to protect the bottom of ship made of iron is
(a) coating it with red lead oxide
(b) white tin plating
(c) connecting it with Mg block
(d) connecting it with Pb block. *(2001)*

63. To protect iron against corrosion, the most durable metal plating on it, is
(a) copper plating (b) zinc plating
(c) nickel plating (d) tin plating. *(1994)*

ANSWER KEY

1.	(b)	**2.**	(c)	**3.**	(a)	**4.**	(c)	**5.**	(b)	**6.**	(c)	**7.**	(d)	**8.**	(a)	**9.**	(a)	**10.**	(d)
11.	(b)	**12.**	(d)	**13.**	(d)	**14.**	(b)	**15.**	(c)	**16.**	(b)	**17.**	(d)	**18.**	(b)	**19.**	(a)	**20.**	(c)
21.	(d)	**22.**	(d)	**23.**	(c)	**24.**	(b)	**25.**	(a)	**26.**	(d)	**27.**	(a)	**28.**	(c)	**29.**	(d)	**30.**	(a)
31.	(c)	**32.**	(d)	**33.**	(d)	**34.**	(b)	**35.**	(a)	**36.**	(d)	**37.**	(d)	**38.**	(a)	**39.**	(b)	**40.**	(d)
41.	(a)	**42.**	(a)	**43.**	(b)	**44.**	(a)	**45.**	(b)	**46.**	(a)	**47.**	(b)	**48.**	(c)	**49.**	(c)	**50.**	(d)
51.	(b)	**52.**	(a)	**53.**	(d)	**54.**	(b)	**55.**	(d)	**56.**	(d)	**57.**	(b)	**58.**	(b)	**59.**	(c)	**60.**	(b)
61.	(d)	**62.**	(b)	**63.**	(b)														

Hints & Explanations

1. (b) : Higher the value of E°_{red}, stronger is the oxidising power. Thus, the decreasing order of reducing power of the metal is K > Al > Cr > Ag.

2. (c) : $E^\circ_{cell} = E^\circ_{O.P.} + E^\circ_{R.P.}$

$= 0.76 + 0.34 = 1.10$ V

3. (a) : Less positive the value of reduction potential, stronger will be the reducing agent thus, I^- is strongest reducing agent. More positive, the value of reduction potential shows good oxidising properties thus, strongest oxidising agent is F_2.

4. (c) : More negative the value of reduction potential, stronger will be the reducing agent.

So, $Z\ (-3.0\text{ V}) > X\ (-1.2\text{ V}) > Y\ (+0.5\text{ V})$

5. (b) : $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.15 - (-0.74) = 0.15 + 0.74 = 0.89$ V

6. (c) : Since the reduction potential of Fe^{3+}/Fe^{2+} is greater than that of I_2/I^-, Fe^{3+} will be reduced and I^- will be oxidised.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

7. (d) : EMF of a cell = Reduction potential of cathode
– Reduction potential of anode
= Reduction potential of cathode +
Oxidation potential of anode
= Oxidation potential of anode –
Oxidation potential of cathode.

8. (a) : $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}, E^\circ = +0.35$ V

$Fe^{3+} \rightarrow Fe^{2+};\ E^\circ = +0.77$ V

Higher the +ve reduction potential, stronger will be the oxidising agent. Oxidising agent oxidises other compounds and gets itself reduced easily. Thus, Fe^{3+} is the strongest oxidising agent.

9. (a) : From the given expression :

At anode : $A \longrightarrow A^+ + e^-$ (oxidation)

At cathode : $B^+ + e^- \longrightarrow B$ (reduction)

Overall reaction is : $A + B^+ \longrightarrow A^+ + B$

10. (d) : $Fe^{2+} + 2e^- \longrightarrow Fe\ ;\ E^\circ = -0.441$ V ... (i)

$Fe^{3+} + e^- \longrightarrow Fe^{2+}\ ;\ E^\circ = 0.771$ V ... (ii)

$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}\ ;\ E^\circ = ?$

To get the above equation, (ii) × 2 – (i)

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}\ ;\ E^\circ = 0.771\text{ V}$$
$$-Fe^{2+} - 2e^- \longrightarrow -Fe\ ;\ E^\circ = +0.441\text{ V}$$
$$\overline{2Fe^{3+} + Fe \longrightarrow 3Fe^{2+}\ ;\ E^\circ = 1.212\text{ V}}$$

11. (b) : $E^\circ_{Fe^{2+}/Fe} = -0.44$ V

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77$ V

If a cell is constructed combining these two electrodes oxidation occurs at Fe^{2+}/Fe electrode.

At anode : $Fe \rightarrow Fe^{2+} + 2e^-$

At cathode : $[Fe^{3+} + e^- \rightarrow Fe^{2+}] \times 2$

Cell reaction : $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

If Fe^{2+}, Fe^{3+} and Fe blocks are kept together then Fe^{3+} reacts with Fe to yield Fe^{2+} *i.e.*, concentration of Fe^{3+} is decreased and that of Fe^{2+} is increased.

12. (d) : $E^\circ_{Zn/Zn^{2+}} = +0.76$ V

$E^\circ_{Fe/Fe^{2+}} = 0.44\text{ V} \Rightarrow E^\circ_{Fe^{2+}/Fe} = -0.44$ V

$E^\circ_{cell} = E^\circ_{O.P.} + E^\circ_{R.P.} = +0.76 - 0.44 = +0.32$ V

13. (d) : Since it is a concentration cell and the concentration of H^+ ions in two electrolyte solutions (HCl and CH_3COOH) are different *i.e.*, pH of 0.1 M HCl and 0.1 M CH_3COOH is not same, therefore e.m.f. of this cell will not be zero.

14. (b) : More positive or less negative the reduction potential value, the stronger is the oxidising agent.

15. (c) : A stronger oxidising agent (Cl_2) displaces a weaker oxidising agent (Br_2) from its salt solution.

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$

16. (b) : The standard Gibbs' energy,

$(\Delta G^\circ) = -nFE^\circ_{cell}$. Value of $n = 2$

$\therefore\ \Delta G^\circ = -2 \times 96500 \times 0.24 = -46320$ J

$= -46.32$ kJ/mol

17. (d) : According to Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q_c$$

At equilibrium $E_{cell} = 0$, $\therefore\ Q_c = K_c$

$$E^\circ_{cell} = \frac{0.059}{n}\log K_c \Rightarrow 0.59 = \frac{0.059}{1}\log K_c$$

$K_c = \text{antilog } 10 \Rightarrow K_c = 1 \times 10^{10}$

18. (b) : $E_{cell} = E^\circ_{cell} - \dfrac{0.059}{n}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$$E_1 = E^\circ - \frac{0.059}{2}\log\frac{0.01}{1}$$

$$E_1 = E^\circ - \frac{0.059}{2}(-2) = E^\circ + 0.059$$

$$E_2 = E^\circ - \frac{0.059}{2}\log\frac{1}{0.01} = E^\circ - 0.059$$

Hence, $E_1 > E_2$.

19. (a) : $\Delta G^\circ = -nFE^\circ_{cell}$

If E°_{cell} = – ve then ΔG° = +ve *i.e.*; $\Delta G^\circ > 0$.

$\Delta G^\circ = -nRT \log K_{eq}$

For ΔG° = +ve, K_{eq} = –ve *i.e.*, $K_{eq} < 1$.

20. (c) : pH = 7 for water.

$-\log[H^+] = 7 \Rightarrow [H^+] = 10^{-7}$

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{p_{H_2}}{[H^+]^2}$$

$$0 = 0 - \frac{0.0591}{2}\log\frac{p_{H_2}}{(10^{-7})^2}$$

$$\log\frac{p_{H_2}}{(10^{-7})^2} = 0 \Rightarrow \frac{p_{H_2}}{(10^{-7})^2} = 1 \qquad [\because \log 1 = 0]$$

$p_{H_2} = 10^{-14}$ atm

21. (d) : $\underset{1\text{ atm}}{H_2} \longrightarrow \underset{10^{-10}}{2H^+} + 2e^-$

$$E_{H_2/H^+} = 0 - \frac{0.059}{2}\log\frac{(10^{-10})^2}{1}$$

$$E_{H_2/H^+} = +0.59\text{ V}$$

22. (d) : $Mn^{2+} + 2e^- \longrightarrow Mn;\ E^\circ = -1.18$ V ... (i)

$2Mn^{2+} \longrightarrow 2Mn^{3+} + 2e^-;\ E^\circ = -1.51$ V ... (ii)

By adding equation (i) and (ii), we get equation for the cell,

$3Mn^{2+} \longrightarrow Mn + 2Mn^{3+};\ E^\circ = -2.69$ V

Since the E° value is negative, so the process is non-spontaneous as ΔG° is positive.

23. (c) : $\Delta G^\circ = -nFE^\circ$

$F = 96500$, $\Delta G^\circ = +960 \times 10^3$ J/mol

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$$

Total number of Al atoms in $Al_2O_3 = \frac{2}{3}\times 2 = \frac{4}{3}$

$Al^{3+} + 3e^- \longrightarrow Al$

As $3e^-$ change occur for each Al-atom

$$\therefore \quad \text{total } n = \frac{4}{3}\times 3 = 4$$

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{960\times1000}{4\times96500}$$

$\Rightarrow E^\circ = -2.48 \approx -2.5$ V

24. (b) : $Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)};\ E_1{}^\circ = 0.15$ V

$Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)};\ E_2{}^\circ = 0.50$ V

$Cu^{2+} + 2e^- \longrightarrow Cu;\ E^\circ = ?$

Now, $\Delta G^\circ = \Delta G_1{}^\circ + \Delta G_2{}^\circ$

or, $-nFE^\circ = -n_1FE_1{}^\circ - n_2FE_2{}^\circ$

$$\text{or, } E^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n} = \frac{1\times0.15 + 1\times0.50}{2} = 0.325\text{ V}$$

25. (a) : The cell reaction can be written as

$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

We know, $\Delta G^\circ = -nFE^\circ_{cell}$

$= -2 \times 96500 \times 0.46 = -88780$ J

$= -88.78$ kJ ≈ -89 kJ

26. (d) : Given,

$Cu^{2+} + 2e^- \longrightarrow Cu;\ E_1^\circ = 0.337$ V

$Cu^{2+} + e^- \longrightarrow Cu^+;\ E_2^\circ = 0.153$ V

The required reaction is

$Cu^+ + e^- \longrightarrow Cu;\quad E_3^\circ = ?$

Applying, $\Delta G^\circ = -nFE^\circ$, $\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$

$$-(n_3FE_3^\circ) = -(n_1FE_1^\circ) - (-n_2FE_2^\circ)$$

or $E_3^\circ = 2 \times E_1^\circ - E_2^\circ$

or $E_3^\circ = (2\times0.337) - 0.153 = 0.52$ V

27. (a) : $C_5H_{12(g)} + 8O_{2(g)} \longrightarrow 5CO_{2(g)} + 6H_2O_{(l)}$

$\Delta G^\circ = [(-394.4 \times 5) + (-237.2 \times 6)] - [(-8.2) + (8 \times 0)]$

$= -3387$ kJ

Note that the standard free energy change of elementary substances is taken as zero.

For the fuel cell, the complete cell reaction is :

$C_5H_{12(g)} + 8O_{2(g)} \longrightarrow 5CO_{2(g)} + 6H_2O_{(l)}$

which is the combination of the following two half reactions :

$C_5H_{12(g)} + 10H_2O_{(l)} \longrightarrow 5CO_{2(g)} + 32H^+ + 32e^-$ and

$8O_{2(g)} + 32H^+ + 32e^- \longrightarrow 16H_2O_{(l)}$

Therefore, the number of electrons exchanged is 32 here, *i.e.*, $n = 32$.

$\Delta G^\circ = -nFE^\circ = -3387 \times 10^3$ J

$= -32 \times 96500$ J/Volt $\times E^\circ$

Thus, $E^\circ = 1.0968$ V

28. (c) : For a cell reaction in equilibrium at 298 K,

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$$

where, K_c = equilibrium constant, n = number of electrons involved in the electrochemical cell reaction.

Given, $E^\circ_{cell} = 0.46$ V, $n = 2$

$$\therefore \quad 0.46 = \frac{0.0591}{2}\times\log K_c \text{ or, } \log K_c = \frac{2\times0.46}{0.0591} = 15.57$$

or, $K_c = 3.7 \times 10^{15} \approx 4 \times 10^{15}$

29. (d) : $E = E^\circ - \frac{0.0591}{n}\log_{10} Q$ at 25°C

At equilibrium, $E = 0$, $Q = K$

$$0 = E^\circ - \frac{0.0591}{n}\log_{10} K$$

$$\text{or, } K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$$

or, $K = \text{antilog}\left[\dfrac{2\times 0.295}{0.0591}\right] = \text{antilog}\left[\dfrac{0.590}{0.0591}\right]$

$= \text{antilog } 10 = 1 \times 10^{10}$

30. (a) : $\Delta G° = -nFE°$

$$E° = \frac{\Delta G°}{-nF} = \frac{-827000}{-4\times 96500} = 2.14 \text{ V}$$

$$\left(\because\ 1\text{ Al} \equiv 3e^-, \frac{4}{3}\text{Al} = \frac{4}{3}\times 3e^- = 4e^-\right)$$

31. (c) : For the reaction, $2Cu^+ \longrightarrow Cu^{2+} + Cu$ the cathode is Cu^+/Cu and anode is Cu^+/Cu^{2+}.

Given, $Cu^{2+} + 2e^- \longrightarrow Cu;\ E_1° = 0.34$ V ...(1)

$Cu^{2+} + e^- \longrightarrow Cu^+;\ E_2° = 0\cdot 15$ V ...(2)

$Cu^+ + e^- \longrightarrow Cu;\quad E_3° = ?$ ...(3)

Now $\Delta G_1° = -nFE_1° = -2\times 0\cdot 34\times F = -0.68$ V

$\Delta G_2° = -1\times 0\cdot 15\times F, \Delta G_3° = -1\times E_3°\times F,$

Again $\Delta G_1° = \Delta G_2° + \Delta G_3°$

$\Rightarrow\ -0.68\ F = -0.15\ F - E_3° \times F$

$\Rightarrow\ E_3° = 0\cdot 68 - 0\cdot 15 = 0\cdot 53$ V

As, $E°_{cell} = E°_{cathode(Cu^+/Cu)} - E°_{anode\ (Cu^{2+}/Cu^+)}$

$= 0.53 - 0.15 = 0.38$ V

32. (d) : Nernst equation is

$$E = E° - \frac{0.059}{2}\log K$$

$\Rightarrow\ E° = \dfrac{0.059}{2}\log K\quad (E = 0$ at equilibrium condition)

$\Rightarrow\ 1.1 = \dfrac{0.059}{2}\log K\quad \Rightarrow K = 1.9 \times 10^{+37}$

33. (d) : According to Kohlrausch's law,

$\lambda_m°$ for $CH_3COOH = \lambda°_{CH_3COO^-} + \lambda°_{H^+}$

$\lambda°$ for $H_2SO_4 = 2\lambda°_{H^+} + \lambda°_{SO_4^{2-}} = x\ \text{S cm}^2\text{mol}^{-1}$ ...(i)

$\lambda°$ for $K_2SO_4 = 2\lambda°_{K^+} + \lambda°_{SO_4^{2-}} = y\ \text{S cm}^2\text{mol}^{-1}$ ...(ii)

$\lambda°$ for $CH_3COOK = \lambda°_{CH_3COO^-} + \lambda°_{K^+} = z\ \text{S cm}^2\text{mol}^{-1}$ ...(iii)

On adding equation (i) and 2 × (iii) and subtracting (ii), we get

$$2\lambda°_{H^+} + \lambda°_{SO_4^{2-}} + 2\lambda°_{CH_3COO^-} + 2\lambda°_{K^+} - 2\lambda°_{K+} - \lambda°_{SO_4^{2-}} = x + 2z - y$$

$$2\lambda°_{H^+} + 2\lambda°_{CH_3COO^-} = x + 2z - y$$

$$\lambda°_{H^+} + \lambda°_{CH_3COO^-} = \frac{(x-y)}{2} + z$$

34. (b) : $\Lambda_m = \dfrac{\kappa\times 1000}{\text{Molarity}(M)}$

$$= \frac{5.76\times 10^{-3}\,\text{S cm}^{-1}\times 1000}{0.5\text{ mol cm}^{-3}} = 11.52\ \text{S cm}^2\ \text{mol}^{-1}$$

35. (a) : Degree of dissociation

$$(\alpha) = \frac{\text{Molar conductivity at conc. } C(\Lambda_m^c)}{\text{Molar conductivity at infinite dilution } (\Lambda_m^\infty)}$$

$$\alpha = \frac{9.54\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}}{238\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}} = 0.04008 = 4.008\%$$

36. (d)

37. (d) : $\Lambda°_{NaCl} = 126.4\ \text{S cm}^2\ \text{mol}^{-1}$

$\Lambda°_{HCl} = 425.9\ \text{S cm}^2\ \text{mol}^{-1}$

$\Lambda°_{CH_3COONa} = 91.0\ \text{S cm}^2\ \text{mol}^{-1}$

$\Lambda°_{CH_3COOH} = \Lambda°_{CH_3COONa} + \Lambda°_{HCl} - \Lambda°_{NaCl}$

$= 91.0 + 425.9 - 126.4$

$= 390.5\ \text{S cm}^2\ \text{mol}^{-1}$

38. (a) : Strong electrolytes are completely ionised at all concentrations. On increasing dilution, the no. of ions remains the same but the ionic mobility increases and the equivalent conductance increases.

39. (b) : At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated.

Hence, $\overset{\circ}{\Lambda}_{Al_2(SO_4)_3} = \overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}$

40. (d) : Given, $\Lambda = 8$ mho cm^2, $\Lambda_\infty = 400$ mho cm^2

Degree of dissociation, $\alpha = \dfrac{\Lambda}{\Lambda_\infty}$

$\Rightarrow\ \alpha = \dfrac{8}{400} = 2\times 10^{-2}$

Dissociation constant, $K = C\alpha^2$

Given, $C = M/32$

$\therefore\quad K = \dfrac{1}{32}\times 2\times 10^{-2}\times 2\times 10^{-2} = 1.25 \times 10^{-5}$

41. (a) : At infinite dilution, when dissociation is complete each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and that the molar conductance of any electrolyte at infinite dilution is given by the sum of the contributions of two ions. This is called Kohlrausch's law.

$\Lambda_m^\infty = \Lambda_+^\infty + \Lambda_-^\infty,$

where, Λ_+^∞ and Λ_-^∞ are molar ionic conductance at infinite dilution for cation and anion, respectively.

42. (a) : $\lambda_\infty = \frac{1}{n_+}\lambda_+^\infty + \frac{1}{n_-}\lambda_-^\infty$

So, $\lambda_\infty(\text{BaCl}_2) = \frac{1}{2}\times\lambda^\infty_{\text{Ba}^{2+}} + \frac{1}{1}\times\lambda^\infty_{\text{Cl}^-}$

$$= \frac{1}{2}\times 127 + 76 = 63\cdot5 + 76 = 139\cdot5$$

43. (b) : $\kappa = 0.012\ \text{ohm}^{-1}\text{cm}^{-1}$

$R = 55\ \text{ohm} \Rightarrow C = \frac{1}{R} = \frac{1}{55}\ \text{ohm}^{-1}$

$$\text{Cell Constant}\left(\frac{l}{a}\right) = \frac{\text{Specific Conductance}}{\text{Conductance}}$$

$$= \frac{0.012}{1/55} = 55\times 0.012 = 0.66\ \text{cm}^{-1}$$

44. (a) : Conductivity of heat in metals is due to the presence of free electrons, which move due to increase in temperature.

45. (b) : During electrolysis of dilute sulphuric acid the following reaction takes place at anode.

$2H_2O_{(l)} \to O_{2(g)} + 4H^+_{(aq)} + 4e^-;\ E^\circ_{\text{cell}} = +1.23\ \text{V}$

i.e., $O_{2(g)}$ will be liberated at anode.

46. (a) : $\underset{\substack{2\text{ F}\\1\text{ F}}}{Ca^{2+}_{(aq)} + 2e^-} \longrightarrow \underset{\substack{(1\text{ mole} = 40\text{ g})\\20\text{ g}}}{Ca_{(s)}}$

Thus, one Faraday is required to produce 20 g of calcium from molten $CaCl_2$.

47. (b) : During the electrolysis of molten sodium chloride,

At cathode : $2Na^+ + 2e^- \longrightarrow 2Na$

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Net reaction : $2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2$

According to Faraday's first law of electrolysis,

$w = Z\times I\times t$

$$w = \frac{E}{96500}\times I\times t$$

No. of moles of Cl_2 gas × Mol. wt. of Cl_2 gas

$$= \frac{\text{Eq. wt. of Cl}_2\text{ gas}\times I\times t}{96500}$$

$$0.10\times 71 = \frac{35.5\times 3\times t}{96500}$$

$$t = \frac{0.10\times 71\times 96500}{35.5\times 3} = 6433.33\ \text{sec}$$

$$t = \frac{6433.33}{60}\ \text{min} = 107.22\ \text{min} \approx 110\ \text{min}$$

48. (c) : $Q = I\times t$

$Q = 1\times 60 = 60$ C

Now, 1.60×10^{-19} C ≡ 1 electron

$$\therefore\ 60\ \text{C} \equiv \frac{60}{1.6\times 10^{-19}} = 3.75\times 10^{20}\ \text{electrons}$$

49. (c) : The oxidation reaction is

$$\underset{0.1\text{ mol}}{\overset{+6}{MnO_4^{2-}}} \longrightarrow \overset{+7}{MnO_4^-} + \underset{0.1\text{ mol}}{e^-}$$

$Q = 0.1\times F = 0.1\times 96500\ \text{C} = 9650\ \text{C}$

50. (d) : According to Faraday's second law,

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{O_2}}{E_{O_2}}\ \text{ or }\ \frac{W_{Ag}}{108} = \frac{\frac{5600}{22400}\times 32}{8}$$

$$\text{or}\ \frac{W_{Ag}}{108} = \frac{8}{8} \Rightarrow W_{Ag} = 108\ \text{g}$$

51. (b) : $w = \frac{ItE}{96500}$

$$= \frac{10\times 109\times 60\times 59}{96500\times 2} = 19.99 \approx 20\ \text{g}$$

52. (a) : Applying $E = Z\times 96500$

$$\frac{27}{3} = Z\times 96500 \Rightarrow Z = \frac{9}{96500}$$

Now applying the formula, $w = Z\times I\times t$

$$w = \frac{9}{96500}\times 4\times 10^4\times 6\times 60\times 60 = 8.1\times 10^4\ \text{g}$$

53. (d) : We know that,

1 Faraday charge liberates 1 eq. of substance.

This is the Faraday law.

$$\text{eq. wt. of Al} = \frac{27}{3} = 9$$

$$\text{No. of eq. of Al} = \frac{\text{wt. of Al}}{\text{eq. wt.}} = \frac{4.5}{9} = 0.5$$

No. of Faradays required = 0.5

⇒ No. of eq. of H_2 produced = 0.5 eq.

$$\text{Volume occupied by 1 eq. of H}_2 = \frac{22.4}{2} = 11.2\ \text{L}$$

⇒ Volume occupied by 0.5 eq. of H_2 = 11.2 × 0.5
= 5.6 L at STP

54. (b) : When sodium chloride is dissolved in water, it ionises as $NaCl \rightleftharpoons Na^+ + Cl^-$.

Water also dissociates as : $H_2O \rightleftharpoons H^+ + OH^-$

During passing of electric current through this solution using platinum electrode, Na^+ and H^+ ions move towards cathode. However, only H^+ ions are discharged more readily than Na^+ ions because of their low discharge potential (in the electromotive series hydrogen is lower than sodium). These H^+ ions gain electrons and change into neutral atoms.

At cathode $H^+ + e^- \longrightarrow H, H + H \longrightarrow H_2$

Cl^- and OH^- ions move towards anode. Cl^- ions lose electrons and change into neutral atom.

At anode, $Cl^- - e^- \longrightarrow Cl, Cl + Cl \longrightarrow Cl_2$

If mercury is used as cathode, H^+ ions are not discharged at mercury cathode because mercury has a high hydrogen overvoltage. Na^+ ions are discharged at the cathode in preference to H^+ ions, yielding sodium, which dissolves in mercury to form sodium amalgam.

At cathode : $Na^+ + e^- \longrightarrow Na$

55. (d) : Current (I) = 5 ampere and

time (t) = 40 minutes = 2400 seconds.

Amount of electricity passed (Q) = $I \times t$

$= 5 \times 2400 = 12000$ C

Now, $Zn^{2+} + 2e^- \longrightarrow Zn$ (1 mole = 65.39 g)

Since, two charges (*i.e.*, 2 × 96500 C) deposits 65.39 g of zinc, therefore 12000 C will deposit

$$= \frac{65.39 \times 12000}{2 \times 96500} = 4.065 \text{ g of zinc}$$

56. (d) : Sodium is obtained by electrolytic reduction of its chloride. Melting point of chloride of sodium is high so in order to lower its melting point, calcium chloride is added to it.

57. (b) : $CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

58. (b) : During electrolysis of dilute sulphuric acid, product obtained at anode will be oxygen.

At anode : $4OH^- \rightleftharpoons 2H_2O + 2O_2 + 4e^-$

59. (c)

60. (b) : The thermal efficiency, η of a fuel conversion device is the amount of useful energy produced relative to the change in enthalpy, ΔH between the product and feed streams.

$$\eta = \frac{\text{useful energy}}{\Delta H}$$

In an ideal case of an electrochemical converter, such as a fuel cell, the change in Gibb's free energy, ΔG of the reaction is available as useful electric energy at that temperature of the conversion.

Hence, $\eta_{\text{ideal}} = \dfrac{\Delta G}{\Delta H}$

61. (d) : Reduction potential values of $E^\circ_{Zn^{2+}/Zn} = -0.76$ V and $E^\circ_{Fe^{2+}/Fe} = -0.44$ V

Thus, due to higher negative electrode potential value of zinc than iron, iron cannot be coated on zinc.

62. (b) : The most convenient method to protect the bottom of the ship made of iron is white tin plating preventing the build up of barnacles.

63. (b)

❖ ❖ ❖

CHAPTER
4

Chemical Kinetics

4.1 Rate of a Chemical Reaction

1. For the chemical reaction,
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
the correct option is

(a) $3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(b) $-\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$

(c) $-\frac{d[N_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(d) $-\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$ *(NEET 2019)*

2. The rate of the reaction : $2N_2O_5 \longrightarrow 4NO_2 + O_2$ can be written in three ways.

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k'[N_2O_5]; \quad \frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k' and between k and k'' are

(a) $k' = 2k, \ k'' = k$ (b) $k' = 2k, \ k'' = k/2$

(c) $k' = 2k, \ k'' = 2k$ (d) $k' = k, \ k'' = k$

(Mains 2011)

3. For the reaction $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + 1/2O_{2(g)}$ the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as :

(a) 6.25×10^{-3} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1}

(b) 1.25×10^{-2} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

(c) 6.25×10^{-3} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

(d) 1.25×10^{-2} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1} *(2010)*

4. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, if $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol L^{-1} s^{-1}, the value of $\frac{-d[H_2]}{dt}$ would be

(a) 4×10^{-4} mol L^{-1} s^{-1} (b) 6×10^{-4} mol L^{-1} s^{-1}

(c) 1×10^{-4} mol L^{-1} s^{-1} (d) 3×10^{-4} mol L^{-1} s^{-1}

(2009)

5. In the reaction,

$BrO_3^-{}_{(aq)} + 5Br^-{}_{(aq)} + 6H^+{}_{(aq)} \longrightarrow 3Br_{2(l)} + 3H_2O_{(l)}$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as

(a) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (b) $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$

(c) $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$ (d) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

(2009)

6. Consider the reaction :
$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$
The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is

(a) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

(b) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

(c) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

(d) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$ *(2006)*

7. For the reaction, $2A + B \longrightarrow 3C + D$, which of the following does not express the reaction rate?

(a) $-\frac{d[A]}{2dt}$ (b) $-\frac{d[C]}{3dt}$

(c) $-\frac{d[B]}{dt}$ (d) $\frac{d[D]}{dt}$ *(2006)*

8. $3A \longrightarrow 2B$, rate of reaction $\frac{+d[B]}{dt}$ is equal to

(a) $-\frac{3}{2}\frac{d[A]}{dt}$ (b) $-\frac{2}{3}\frac{d[A]}{dt}$

(c) $-\frac{1}{3}\frac{d[A]}{dt}$ (d) $+2\frac{d[A]}{dt}$ *(2002)*

9. For the reaction,

$H^+ + BrO_3^- + 3Br^- \longrightarrow 5Br_2 + H_2O$

which of the following relations correctly represents the consumption and formation of products?

(a) $\frac{d[Br^-]}{dt} = -\frac{3}{5}\frac{d[Br_2]}{dt}$ (b) $\frac{d[Br^-]}{dt} = \frac{3}{5}\frac{d[Br_2]}{dt}$

(c) $\frac{d[Br^-]}{dt} = -\frac{5}{3}\frac{d[Br_2]}{dt}$ (d) $\frac{d[Br^-]}{dt} = \frac{5}{3}\frac{d[Br_2]}{dt}$

(2000)

10. For the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, the rate of reaction is expressed as

(a) $\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[HI]}{\Delta t}$

(b) $-\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$

(c) $\frac{\Delta[I_2]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[HI]}{2\Delta t}$

(d) none of these. *(1997)*

4.2 Factors Influencing Rate of a Reaction

11. Mechanism of a hypothetical reaction,

$X_2 + Y_2 \longrightarrow 2XY$, is given below :

(i) $X_2 \longrightarrow X + X$ (fast)

(ii) $X + Y_2 \rightleftarrows XY + Y$ (slow)

(iii) $X + Y \longrightarrow XY$ (fast)

The overall order of the reaction will be

(a) 2 (b) 0

(c) 1.5 (d) 1 *(NEET 2017)*

12. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the

(a) rate is proportional to the surface coverage

(b) rate is inversely proportional to the surface coverage

(c) rate is independent of the surface coverage

(d) rate of decomposition is very slow.

(NEET-II 2016)

13. The rate constant of the reaction $A \longrightarrow B$ is 0.6×10^{-3} mol L^{-1} s^{-1}. If the concentration of A is 5 M, then concentration of B after 20 minutes is

(a) 3.60 M (b) 0.36 M

(c) 0.72 M (d) 1.08 M *(2015)*

14. For a reaction between A and B the order with respect to A is 2 and the order with respect to B is 3. The concentrations of both A and B are doubled, the rate will increase by a factor of

(a) 12 (b) 16

(c) 32 (d) 10

(Karnataka NEET 2013)

15. In a reaction, $A + B \longrightarrow$ product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentration of both the reactants (A and B) are doubled, rate law for the reaction can be written as

(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$

(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$

(2012)

16. Which one of the following statements for the order of a reaction is incorrect?

(a) Order can be determined only experimentally.

(b) Order is not influenced by stoichiometric coefficient of the reactants.

(c) Order of a reaction is sum of power to the concentration terms of reactants to express the rate of reaction.

(d) Order of reaction is always whole number.

(2011)

17. The unit of rate constant for a zero order reaction is

(a) mol L^{-1} s^{-1} (b) L mol^{-1} s^{-1}

(c) L^2 mol^{-2} s^{-1} (d) s^{-1} *(Mains 2011)*

18. During the kinetic study of the reaction, $2A + B \rightarrow C + D$, following results were obtained :

Run	**[A]/ mol L^{-1}**	**[B]/ mol L^{-1}**	**Initial rate of formation of D/mol L^{-1} min^{-1}**
I.	0.1	0.1	6.0×10^{-3}
II.	0.3	0.2	7.2×10^{-2}
III.	0.3	0.4	2.88×10^{-1}
IV.	0.4	0.1	2.40×10^{-2}

Based on the above data which one of the following is correct?

(a) Rate = $k[A]^2[B]$ (b) Rate = $k[A][B]$

(c) Rate = $k[A]^2[B]^2$ (d) Rate = $k[A][B]^2$

(2010)

19. For the reaction, $A + B \longrightarrow$ products, it is observed that

(i) on doubling the initial concentration of A only, the rate of reaction is also doubled and

(ii) on doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by

(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$

(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$ *(2009)*

20. The bromination of acetone that occurs in acid solution is represented by this equation.

$$CH_3COCH_{3(aq)} + Br_{2(aq)} \longrightarrow CH_3COCH_2Br_{(aq)} + H^+_{(aq)} + Br^-_{(aq)}$$

These kinetic data were obtained for given reaction concentrations.

Initial concentrations, *M*

$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$
0.30	0.05	0.05
0.30	0.10	0.05
0.30	0.10	0.10
0.40	0.05	0.20

Initial rate, disappearance of Br_2, M s^{-1}

5.7×10^{-5}

5.7×10^{-5}

1.2×10^{-4}

3.1×10^{-4}

Based on these data, the rate equation is

(a) Rate = $k\,[CH_3COCH_3][Br_2][H^+]^2$

(b) Rate = $k\,[CH_3COCH_3][Br_2][H^+]$

(c) Rate = $k\,[CH_3COCH_3][H^+]$

(d) Rate = $k\,[CH_3COCH_3][Br_2]$ *(2008)*

21. The reaction of hydrogen and iodine monochloride is given as :

$$H_{2(g)} + 2ICl_{(g)} \longrightarrow 2HCl_{(g)} + I_{2(g)}$$

This reaction is of first order with respect to $H_{2(g)}$ and $ICl_{(g)}$, following mechanisms were proposed.

Mechanism *A* :

$$H_{2(g)} + 2ICl_{(g)} \longrightarrow 2HCl_{(g)} + I_{2(g)}$$

Mechanism *B* :

$H_{2(g)} + ICl_{(g)} \longrightarrow HCl_{(g)} + HI_{(g)}$; slow

$HI_{(g)} + ICl_{(g)} \longrightarrow HCl_{(g)} + I_{2(g)}$; fast

Which of the above mechanism(s) can be consistent with the given information about the reaction?

(a) *A* and *B* both (b) Neither *A* nor *B*

(c) *A* only (d) *B* only *(2007)*

22. The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is

(a) 2 (b) –2

(c) 1 (d) –1 *(2005)*

23. If the rate of the reaction is equal to the rate constant, the order of the reaction is

(a) 0 (b) 1

(c) 2 (d) 3 *(2003)*

24. $2A \longrightarrow B + C$, It would be a zero order reaction when

(a) the rate of reaction is proportional to square of concentration of A

(b) the rate of reaction remains same at any concentration of A

(c) the rate remains unchanged at any concentration of B and C

(d) the rate of reaction doubles if concentration of B is increased to double. *(2002)*

25. For the reaction; $2N_2O_5 \longrightarrow 4NO_2 + O_2$ rate and rate constant are 1.02×10^{-4} and 3.4×10^{-5} sec^{-1} respectively, then concentration of N_2O_5 at that time will be

(a) 1.732 (b) 3

(c) 1.02×10^{-4} (d) 3.4×10^5 *(2001)*

26. The experimental data for the reaction, $2A + B_2 \longrightarrow 2AB$ is

Experiment	**$[A]$**	**$[B_2]$**	**Rate (mole s^{-1})**
1	0.50	0.50	1.6×10^{-4}
2	0.50	1.00	3.2×10^{-4}
3	1.00	1.00	3.2×10^{-4}

The rate equation for the above data is

(a) rate = $k\,[A]^2[B]^2$ (b) rate = $k\,[A]^2[B]$

(c) rate = $k\,[B_2]$ (d) rate = $k\,[B_2]^2$ *(1997)*

27. The given reaction,

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

is an example of

(a) third order reaction

(b) first order reaction

(c) second order reaction

(d) none of these. *(1996)*

28. The data for the reaction $A + B \longrightarrow C$, is

Exp.	**$[A]_0$**	**$[B]_0$**	**Initial rate**
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

The rate law corresponds to the above data is

(a) rate = $k[A][B]^3$ (b) rate = $k[A]^2[B]^2$

(c) rate = $k[B]^3$ (d) rate = $k[B]^4$. *(1994)*

4.3 Integrated Rate Equations

29. The rate constant for a first order reaction is 4.606×10^{-3} s^{-1}. The time required to reduce 2.0 g of the reactant to 0.2 g is

(a) 100 s (b) 200 s
(c) 500 s (d) 1000 s *(NEET 2020)*

30. If the rate constant for a first order reaction is k, the time (t) required for the completion of 99% of the reaction is given by

(a) $t = 2.303/k$ (b) $t = 0.693/k$
(c) $t = 6.909/k$ (d) $t = 4.606/k$ *(NEET 2019)*

31. A first order reaction has a rate constant of 2.303×10^{-3} s^{-1}. The time required for 40 g of this reactant to reduce to 10 g will be
[Given that $\log_{10} 2 = 0.3010$]

(a) 230.3 s (b) 301 s
(c) 2000 s (d) 602 s *(Odisha NEET 2019)*

32. The correct difference between first and second order reactions is that

(a) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
(b) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
(c) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
(d) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations. *(NEET 2018)*

33. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction

(a) is halved (b) is doubled
(c) is tripled (d) remains unchanged. *(NEET 2018)*

34. A first order reaction has a specific reaction rate of 10^{-2} sec^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g?

(a) 138.6 sec (b) 346.5 sec
(c) 693.0 sec (d) 238.6 sec *(NEET 2017)*

35. The rate of first-order reaction is 0.04 mol L^{-1} s^{-1} at 10 seconds and 0.03 mol L^{-1} s^{-1} at 20 seconds after initiation of the reaction. The half-life period of the reaction is

(a) 44.1 s (b) 54.1 s
(c) 24.1 s (d) 34.1 s *(NEET-I 2016)*

36. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is

(a) second
(b) more than zero but less than first
(c) zero (d) first. *(2015, Cancelled)*

37. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. The order of reaction is

(a) 1 (b) 2 (c) 3 (d) 0 *(Karnataka NEET 2013)*

38. The half-life of a substance in a certain enzyme-catalysed reaction is 138 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.04 mg L^{-1} is

(a) 414 s (b) 552 s
(c) 690 s (d) 276 s *(Mains 2011)*

39. Half-life period of a first order reaction is 1386 seconds. The specific rate constant of the reaction is

(a) 0.5×10^{-2} s^{-1} (b) 0.5×10^{-3} s^{-1}
(c) 5.0×10^{-2} s^{-1} (d) 5.0×10^{-3} s^{-1} *(2009)*

40. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately (log 4 = 0.60, log 5 = 0.69)

(a) 45 minutes (b) 60 minutes
(c) 40 minutes (d) 50 minutes. *(2007)*

41. In a first-order reaction, $A \longrightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is

(a) $\dfrac{\log 2}{k}$ (b) $\dfrac{\log 2}{k\sqrt{0.5}}$
(c) $\dfrac{\ln 2}{k}$ (d) $\dfrac{0.693}{0.5k}$ *(2007)*

42. For a first order reaction $A \longrightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1} s^{-1}. The half-life period of the reaction is

(a) 30 s (b) 220 s
(c) 300 s (d) 347 s *(2005)*

43. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

(a) 0.383 min (b) 23.1 min
(c) 8.73 min (d) 7.53 min *(2004)*

44. The reaction $A \longrightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B ?

(a) 1 hour (b) 0.5 hour
(c) 0.25 hour (d) 2 hours *(2003)*

45. For a first-order reaction, the half-life period is independent of
(a) first power of final concentration
(b) cube root of initial concentration
(c) initial concentration
(d) square root of final concentration. *(1999)*

4.4 Temperature Dependence of the Rate of a Reaction

46. For a reaction, activation energy $E_a = 0$ and the rate constant at 200 K is $1.6 \times 10^6\ s^{-1}$. The rate constant at 400 K will be
[Given that gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$]
(a) $3.2 \times 10^4\ s^{-1}$ (b) $1.6 \times 10^6\ s^{-1}$
(c) $1.6 \times 10^3\ s^{-1}$ (d) $3.2 \times 10^6\ s^{-1}$
(Odisha NEET 2019)

47. The addition of a catalyst during a chemical reaction alters which of the following quantities?
(a) Enthalpy (b) Activation energy
(c) Entropy (d) Internal energy
(NEET-I 2016)

48. The activation energy of a reaction can be determined from the slope of which of the following graphs?
(a) $\ln k\ vs\ \frac{1}{T}$ (b) $\frac{T}{\ln k}\ vs\ \frac{1}{T}$
(c) $\ln k\ vs\ T$ (d) $\frac{\ln k}{T}\ vs\ T$
(2015, Cancelled)

49. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20 °C to 35 °C? ($R = 8.314\ J\ mol^{-1}\ K^{-1}$)
(a) $34.7\ kJ\ mol^{-1}$ (b) $15.1\ kJ\ mol^{-1}$
(c) $342\ kJ\ mol^{-1}$ (d) $269\ kJ\ mol^{-1}$
(NEET 2013)

50. In a zero-order reaction, for every 10 °C rise of temperature, the rate is doubled. If the temperature is increased from 10 °C to 100 °C, the rate of the reaction will become
(a) 256 times (b) 512 times
(c) 64 times (d) 128 times. *(2012)*

51. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by
(a) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
(b) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
(c) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} + \frac{1}{T_1}\right)$
(d) $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ *(Mains 2012)*

52. The rate of the reaction,
$2NO + Cl_2 \longrightarrow 2NOCl$ is given by the rate equation, rate $= k[NO]^2[Cl_2]$. The value of the rate constant can be increased by
(a) increasing the temperature
(b) increasing the concentration of NO
(c) increasing the concentration of the Cl_2
(d) doing all of these. *(Mains 2010)*

53. The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{-2000/T}$ and $10^{15} \cdot e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is
(a) 2000 K (b) $\frac{1000}{2.303}$ K
(c) 1000 K (d) $\frac{2000}{2.303}$ K *(2008)*

54. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A \times e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting
(a) $k\ vs\ T$ (b) $k\ vs\ \frac{1}{\log T}$
(c) $\log k\ vs\ \frac{1}{T}$ (d) $\log k\ vs\ \frac{1}{\log T}$ *(2003)*

55. The activation energy for a simple chemical reaction $A \rightleftharpoons B$ is E_a in forward direction. The activation energy for reverse reaction
(a) is negative of E_a
(b) is always less than E_a
(c) can be less than or more than E_a
(d) is always double of E_a. *(2003)*

56. When a biochemical reaction is carried out in laboratory, outside the human body in absence of enzyme, then rate of reaction obtained is 10^{-6} times, the activation energy of reaction in the presence of enzyme is
(a) $6/RT$ (b) P is required
(c) different from E_a obtained in laboratory
(d) can't say anything. *(2001)*

57. How enzymes increases the rate of reactions?
(a) By lowering activation energy
(b) By increasing activation energy
(c) By changing equilibrium constant
(d) By forming enzyme substrate complex *(2000)*

58. Activation energy of a chemical reaction can be determined by
- (a) evaluating rate constants at two different temperatures
- (b) evaluating velocities of reaction at two different temperatures
- (c) evaluating rate constant at standard temperature
- (d) changing concentration of reactants. (1998)

59. By the action of enzymes, the rate of biochemical reaction
- (a) does not change
- (b) increases
- (c) decreases
- (d) either (a) or (c).

(1994)

4.5 Collision Theory of Chemical Reactions

60. An increase in the concentration of the reactants of a reaction leads to change in
- (a) activation energy
- (b) heat of reaction
- (c) threshold energy
- (d) collision frequency.

(NEET 2020)

ANSWER KEY

1.	(d)	**2.**	(b)	**3.**	(b)	**4.**	(d)	**5.**	(d)	**6.**	(c)	**7.**	(b)	**8.**	(b)	**9.**	(a)	**10.**	(b)
11.	(c)	**12.**	(a)	**13.**	(c)	**14.**	(c)	**15.**	(d)	**16.**	(d)	**17.**	(a)	**18.**	(d)	**19.**	(a)	**20.**	(c)
21.	(d)	**22.**	(b)	**23.**	(a)	**24.**	(b)	**25.**	(b)	**26.**	(c)	**27.**	(a)	**28.**	(c)	**29.**	(c)	**30.**	(d)
31.	(d)	**32.**	(b)	**33.**	(b)	**34.**	(a)	**35.**	(c)	**36.**	(d)	**37.**	(a).	**38.**	(c)	**39.**	(b)	**40.**	(a)
41.	(c)	**42.**	(d)	**43.**	(b)	**44.**	(a)	**45.**	(c)	**46.**	(b)	**47.**	(b)	**48.**	(a)	**49.**	(a)	**50.**	(b)
51.	(b,d)	**52.**	(a)	**53.**	(b)	**54.**	(c)	**55.**	(c)	**56.**	(c)	**57.**	(a)	**58.**	(a)	**59.**	(b)	**60.**	(d)

Hints & Explanations

1. (d) : For the given chemical reaction,

Rate of reaction $= -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

2. (b) : For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$

$$-\frac{1}{2}\underset{k}{\frac{d[N_2O_5]}{dt}} = +\frac{1}{4}\underset{k'}{\frac{d[NO_2]}{dt}} = +\underset{k''}{\frac{d[O_2]}{dt}}$$

$$\frac{1}{2}k = \frac{1}{4}k' = k'',\ k' = 2k;\ k'' = \frac{1}{2}k$$

3. (b) : $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + 1/2O_{2(g)}$

For the given reaction the rate is written as

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{2d[O_2]}{dt}$$

Given that $\frac{-d[N_2O_5]}{dt} = 6.25\times10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$

$\therefore \frac{d[NO_2]}{dt} = 2\times6.25\times10^{-3} = 1.25\times10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}$

and $\frac{d[O_2]}{dt} = \frac{6.25\times10^{-3}}{2} = 3.125\times10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$

4. (d) : For reaction, $N_2 + 3H_2 \rightarrow 2NH_3$

$$\text{Rate} = \frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{d[N_2]}{dt}$$

Given, $\frac{d[NH_3]}{dt} = 2\times10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

$\therefore -\frac{d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2}\times2\times10^{-4}$

$\Rightarrow -\frac{d[H_2]}{dt} = 3\times10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

5. (d) : For the given reaction,

$BrO_3^-{}_{(aq)} + 5Br^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$

Rate of reaction in terms of Br_2 and Br^- is,

$$\text{Rate} = \frac{1}{3}\frac{d[Br_2]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt}$$

$$\therefore \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$$

6. (c) : $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$$\text{Rate} = \frac{-d[N_2]}{dt} = -\frac{d[H_2]}{3dt} = +\frac{d[NH_3]}{2dt}$$

Hence, $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

7. (b) : $2A + B \rightarrow 3C + D$

$$\text{rate} = \frac{-d[A]}{2dt} = -\frac{d[B]}{dt} = \frac{d[C]}{3dt} = \frac{d[D]}{dt}$$

Negative sign shows the decrease in concentration.

8. (b) : $3A \rightarrow 2B$

Rate of the reaction = $\frac{1}{2}\frac{d[B]}{dt} = -\frac{1}{3}\frac{d[A]}{dt}$

$$\Rightarrow \frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$$

9. (a) : Rate of reaction $= -\frac{1}{3}\frac{d[Br^-]}{dt} = +\frac{1}{5}\frac{d[Br_2]}{dt}$

$$\Rightarrow \frac{d[Br^-]}{dt} = -\frac{3}{5}\frac{d[Br_2]}{dt}$$

10. (b) : For $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, the rate of reaction is

$$-\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

Negative sign shows disappearance of reactant and positive sign shows the appearance of product.

11. (c) : Note : Correct the reactions given in question as

$$X_2 \rightleftharpoons X + X \quad \text{(fast)}$$
$$X + Y_2 \longrightarrow XY + Y \quad \text{(slow)}$$

Slow step is the rate determining step.

Rate = $k[X][Y_2]$ ...(i)

Equilibrium constant for fast step, $K = \frac{[X]^2}{[X_2]}$

$[X] = \sqrt{K[X_2]}$

By substituting $[X]$ in equation (i), we get

Rate = $k\sqrt{K[X_2]}\ [Y_2] = k'[X_2]^{1/2}\ [Y_2]$

$\therefore$ Order of reaction $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5$

12. (a) : At low pressure, rate is proportional to the surface coverage and is of first order while at high pressure, it follows zero order kinetics due to complete coverage of surface area.

13. (c) : Reaction is of zero order as the unit of rate constant is mol L^{-1} s^{-1}.

Concentration of $B = k \times t$

$= 0.6 \times 10^{-3} \times 20 \times 60 = 0.72$ M

14. (c) : $\text{Rate}_1 = k[A]^2\ [B]^3$

$\text{Rate}_2 = k[2A]^2[2B]^3$

$\text{Rate}_2 = 32k[A]^2[B]^3$

$\therefore$ $\text{Rate}_2 = 32(\text{Rate}_1)$

15. (d) :

[A]	[B]	Rate	
x	y	R	...(i)
x	$2y$	$2R$	...(ii)
$2x$	$2y$	$8R$	...(iii)

Let the rate law ; rate = $k[A]^a\ [B]^b$

From data given, $(x)^a(y)^b = R$ ...(iv)

$(x)^a(2y)^b = 2R$ ...(v)

Dividing eqn. (v) by (iv),

$$\frac{(2y)^b}{(y)^b} = \frac{2R}{R} \Rightarrow (2)^b = 2 = 2^1$$

Thus, $b = 1$

From data of (iii) experiment,

$(2x)^a(2y)^b = 8R$ ...(vi)

From eqn. (v) and (vi),

$$\frac{(2x)^a}{(x)^a} = \frac{8R}{2R} \Rightarrow (2)^a = 4 = 2^2$$

Thus, $a = 2$. By replacing the values of a and b in rate law; rate = $k[A]^2\ [B]$

16. (d) : Order of a reaction is not always whole number. It can be zero, or fractional also.

17. (a) : Rate = $k[A]^0$

mol L^{-1} $s^{-1} = k$

Thus, the unit of rate constant is mol L^{-1} s^{-1}.

18. (d) : Let the rate of reaction be given by :

rate = $k[A]^a[B]^b$.

Now consider II and III where $[A]$ is constant.

$$\frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{[0.3]^a[0.2]^b}{[0.3]^a[0.4]^b}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^b \Rightarrow b = 2$$

Now consider I and IV,

$$\frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{[0.1]^a[0.1]^b}{[0.4]^a[0.1]^b}$$

$$\frac{1}{4} = \left(\frac{1}{4}\right)^a \Rightarrow a = 1$$

$\therefore$ Rate = $k[A][B]^2$

19. (a) : $R = k[A]^m[B]^n$ ...(i)

$2R = k[2A]^m[B]^n$ ...(ii)

$8R = k[2A]^m[2B]^n$ ...(iii)

from (i), (ii) and (iii), $m = 1$, $n = 2$

So, rate = $k[A][B]^2$

20. (c) : From the first two experiments, it is clear that when concentration of Br_2 is doubled, the initial rate of disappearance of Br_2 remains unaltered. So, order of reaction with respect to Br_2 is zero. Thus, the probable rate law for the reaction will be : $k[CH_3COCH_3][H^+]$

21. (d) : The slow step is the rate determining step and it involves 1 molecule of $H_{2(g)}$ and 1 molecule of $ICl_{(g)}$. Hence, the rate will be,

$r = k[H_{2(g)}]\ [ICl_{(g)}]$

i.e., the reaction is 1st order with respect to $H_{2(g)}$ and $ICl_{(g)}$.

22. (b) : Rate of reaction = $k\ [A]^\alpha\ [B]^\beta$

$\alpha \rightarrow$ order of reaction *w.r.t. A*

$\beta \rightarrow$ order of reaction *w.r.t. B*

$r_1 = k[A]^\alpha [B]^\beta$

$r_2 = r_1/4 = k[A]^\alpha [2B]^\beta$

$$\frac{r_1}{r_2} = \frac{k[A]^\alpha[B]^\beta}{k[A]^\alpha[2B]^\beta} \Rightarrow 4 = \left(\frac{1}{2}\right)^\beta \Rightarrow \beta = -2$$

23. (a) : $A \rightarrow$ products

If $-\frac{dx}{dt} = k$, it means $-\frac{dx}{dt} = k[A]^0 = k$

Hence, order of reaction must be zero.

24. (b) : $2A \rightarrow B + C$

The rate equation of this reaction may be expressed as $r = k[A]^0$, Order = 0, $r = k$

∴ The rate is independent of concentration of the reactant A.

25. (b) : $2N_2O_5 \rightarrow 4NO_2 + O_2$

This is a first order reaction.

∴ rate = $k[N_2O_5]$;

$$[N_2O_5] = \text{rate}/k = \frac{1.02\times10^{-4}}{3.4\times10^{-5}} = 3$$

26. (c) : For the reaction, $2A + B_2 \rightleftharpoons 2AB$,

Rate $\propto [A]^x[B_2]^y$.

On substituting the given data, we get

From experiment 1,

$1.6 \times 10^{-4} \propto [0.50]^x [0.50]^y$ ...(i)

From experiment 2,

$3.2 \times 10^{-4} \propto [0.50]^x [1.00]^y$ ...(ii)

From experiment 3,

$3.2 \times 10^{-4} \propto [1.00]^x [1.00]^y$ ...(iii)

On dividing equation (iii) by (ii), we get ,

$$1 = \left[\frac{1.00}{0.50}\right]^x \Rightarrow 1 = 2^x \Rightarrow 2^0 = 2^x \Rightarrow x = 0$$

Now, divide equation (ii) by equation (i) we get,

$$2 = \left[\frac{1.00}{0.50}\right]^y \Rightarrow 2 = 2^y \Rightarrow y = 1$$

Thus, rate equation is :

Rate = $k[A]^0 [B_2]^1 = k[B_2]$

27. (a) : For a general reaction,

$xA + yB + zC \rightarrow$ product, the order of reaction is $x + y + z$. Since three molecules undergo change in concentration, therefore it is a third order reaction.

28. (c) : $A + B \rightarrow C$

Let rate = $k[A]^x [B]^y$

where order of reaction is $(x + y)$.

Putting the values of exp. 1, 2, and 3, we get following equations.

$0.10 = k[0.012]^x[0.035]^y$ ...(i)

$0.80 = k[0.024]^x[0.070]^y$ ...(ii)

$0.10 = k[0.024]^x[0.035]^y$ ...(iii)

Dividing (ii) by (iii), we get

$$\frac{0.80}{0.10} = \left(\frac{0.070}{0.035}\right)^y \Rightarrow 2^y = 8 \Rightarrow y = 3$$

Keeping $[A]$ constant, $[B]$ is doubled, rate becomes 8 times.

Dividing eq. (iii) by eq. (i), we get

$$\frac{0.10}{0.10} = \left(\frac{0.024}{0.012}\right)^x \Rightarrow 2^x = 1 \Rightarrow x = 0$$

Keeping $[B]$ constant, $[A]$ is doubled, rate remains unaffected. Hence, rate is independent of $[A]$.

rate $\propto [B]^3$.

29. (c) : For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$\Rightarrow t = \frac{2.303}{4.606\times10^{-3}\ \text{s}^{-1}}\log\left(\frac{2}{0.2}\right) = \frac{2.303\times10^3}{4.606} = 500\ \text{s}$$

30. (d) : For 1st order reaction,

$$t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{k}\log\frac{100}{100-99}$$

$$= \frac{2.303}{k}\log 10^2 = \frac{2.303}{k}\times2\times\log10 = \frac{4.606}{k}$$

31. (d) : For a first order reaction, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

$$2.303\times10^{-3} = \frac{2.303}{t}\log\frac{40}{10}$$

$$t = \frac{1}{10^{-3}}\log 2^2 = \frac{2}{10^{-3}}\log 2 = \frac{2}{10^{-3}}\times0.3010 = 602\ \text{s}$$

32. (b) : For the first order reaction, $t_{1/2} = \frac{0.693}{k}$ which is independent of initial concentration $[A]_0$.

For second order reaction, $t_{1/2} = \frac{1}{k[A]_0}$

Half-life depends on initial concentration of reactant.

33. (b) : $(t_{1/2})_{\text{zero}} = \frac{[A]_0}{2k}$

As the half-life of a zero order reaction is directly proportional to initial concentration.

∴ If $[A]_0$ = doubled then, $t_{1/2}$ = doubled.

34. (a) : For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} \quad \text{or} \quad 10^{-2} = \frac{2.303}{t}\log\frac{20}{5}$$

$$10^{-2} = \frac{2.303\times0.6020}{t} \quad \text{or} \quad t = 138.6\ \text{sec}$$

35. (c) : For a first order reaction, $A \rightarrow$ Products and for concentration of the reactant at two different times,

$$k = \frac{2.303}{t_2 - t_1}\log\frac{[A]_1}{[A]_2}$$

$$\therefore\ k = \frac{2.303}{t_2 - t_1}\log\frac{(\text{rate})_1}{(\text{rate})_2} \qquad (\because \text{rate} \propto [A])$$

$$k = \frac{2.303}{(20-10)}\log\left(\frac{0.04}{0.03}\right) = 0.0287\ \text{sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287\ \text{sec}^{-1}} = 24.14\ \text{sec}$$

36. (d) : Half-life period of a first order reaction is independent of initial concentration,

$$t_{1/2} = \frac{0.693}{k}$$

37. (a) : As $t_{75\%} = 2 \times t_{50\%}$, the order of the reaction is one.

38. (c) : Fall of concentration from 1.28 mg L^{-1} to 0.04 mg L^{-1} requires 5 half-lives.

$\therefore$ Time required = $5 \times t_{1/2} = 5 \times 138 = 690$ s

39. (b) : Given, $t_{1/2} = 1386$ s

For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad (k = \text{rate constant})$$

$$\Rightarrow\ 1386 = \frac{0.693}{k} \quad \Rightarrow\ k = 5 \times 10^{-4}\ s^{-1} = 0.5 \times 10^{-3}\ s^{-1}$$

40. (a) : For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{60}\log\frac{100}{40} = \frac{2.303}{60} \times \log 2.5 = 0.0153$$

Again, $t_{1/2} = \frac{2.303}{k}\log\frac{100}{50} = \frac{2.303}{0.0153} \times \log 2\ = 45.31$ min.

41. (c) : For a 1st order reaction,

$$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

At $t_{1/2}$, $k = \frac{2.303}{t_{1/2}}\log_{10}\frac{a}{a-\frac{a}{2}}$

or $t_{1/2} = \frac{2.303}{k}\log_{10} 2 = \frac{\ln 2}{k}$

42. (d) : $A \longrightarrow B$

Rate of reaction = 2×10^{-5} mol L^{-1} s^{-1}

$\Rightarrow$ order of reaction is $n = 1$, rate = $k\,[A]^n = k[A]$

k is the rate constant.

$[A] = 0.01$ M

$$\Rightarrow\ k = \frac{2\times10^{-5}}{0.01} = 2\times10^{-3},\ k = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{2\times10^{-3}} = 346.5 \approx 347\ \text{s}$$

43. (b) : Rate $\left(\frac{dx}{dt}\right) = kC$

i.e., $1.5 \times 10^{-2} = k \times 0.5$ or, $k = \frac{1.5\times10^{-2}}{0.5}$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693\times0.5}{1.5\times10^{-2}} = 23.1\ \text{min.}$$

44. (a) :

In case I		**In case II**	
$A \to$	B	$A \to$	B
0.8	0	0.9	0
0.2	0.6	0.225	0.675
1	3	1	3

The time taken for the completion of same fraction of change is independent of initial concentration.

45. (c) : For the first order reaction, rate constant is given by, $k_1 = \frac{1}{t}\ln\frac{a}{a-x}$

a = initial concentration, $(a - x)$ = concentration at t time

At $t = t_{1/2}$, $x = a/2$

$$\Rightarrow\ k_1 = \frac{1}{t_{1/2}}\ln\frac{a}{a-a/2} \ \Rightarrow\ k_1 = \frac{1}{t_{1/2}}\ln 2$$

$$\Rightarrow\ k_1 = \frac{0.693}{t_{1/2}}$$

Therefore, $t_{1/2}$ is independent of initial concentration.

46. (b) : According to Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log\frac{k_2}{1.6\times10^6} = 0;\ \frac{k_2}{1.6\times10^6} = 1$$

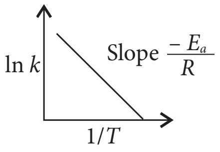
$k_2 = 1.6 \times 10^6\ s^{-1}$

47. (b) : A catalyst provides an alternate path to the reaction which has lower activation energy.

48. (a) : According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$



Hence, if ln k is plotted against $1/T$, slope of the line will be $-\frac{E_a}{R}$.

49. (a) : $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$k_2 = 2k_1$, $T_1 = 20 + 273 = 293$ K

or $T_2 = 35 + 273 = 308$ K

$R = 8.314$ J mol^{-1} K^{-1}

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{293} - \frac{1}{308}\right)$$

$$0.3010 = \frac{E_a}{19.147} \times \frac{15}{293 \times 308}$$

$E_a = 34673$ J mol^{-1} = 34.7 kJ mol^{-1}

50. (b) : At 10°C rise, rate increases by 2.

$$\frac{r_{100°\text{C}}}{r_{10°\text{C}}} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512 \text{ times}$$

51. (b, d) : $k_1 = Ae^{-E_a/RT_1}$, $k_2 = Ae^{-E_a/RT_2}$

$\ln k_1 = \ln A - E_a/RT_1$ ...(i)

$\ln k_2 = \ln A - E_a/RT_2$ ...(ii)

From eq.(i) and (ii), we have

$$\ln k_2 - \ln k_1 = \ln A - \frac{E_a}{RT_2} - \ln A + \frac{E_a}{RT_1}$$

$$\Rightarrow \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rightarrow \ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

52. (a) : Rate constant is independent of the initial concentration of the reactants. It has a constant value at fixed temperature. According to Arrhenius equation, the value of rate constant can be increased by increasing the temperature.

53. (b) : $k_1 = 10^{16} e^{-2000/T}$, $k_2 = 10^{15} e^{-1000/T}$

When, $k_1 = k_2$, $10^{16} e^{-2000/T} = 10^{15} e^{-1000/T}$

or $10e^{-2000/T} = e^{-1000/T}$

Taking natural logarithm of both sides, we get

$$\ln 10 - \frac{2000}{T} = \frac{-1000}{T}$$

or $$2.303 - \frac{2000}{T} = \frac{-1000}{T}$$

or $$\frac{1000}{T} = 2.303 \quad \text{or} \quad T = \frac{1000}{2.303}\text{ K}$$

54. (c) : On plotting log k *vs* $1/T$, we get a straight line, the slope indicates the value of activation energy.

55. (c) : Activation energy is the minimum amount of energy required to convert reactant into product. Activation energy for reverse reaction can be less than or more than E_a depending whether the reaction is exothermic or endothermic.

56. (c) : According to $k = Ae^{-E_a/RT}$ (Arrhenius equation), the activation energy of a reaction in the presence of enzyme is different from E_a obtained in laboratory.

57. (a) : Enzymes act like catalyst in biochemical reactions. Presence of an enzyme increases the rate of reaction by lowering the activation energy of the reactant.

58. (a) : According to Arrhenius equation :

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

where E_a = activation energy

R = gas constant = 8.314 J K^{-1} mol^{-1}

k_1 and k_2 are rate constants of the reaction at two different temperatures T_1 and T_2 respectively.

59. (b) : Since the enzymes are regarded as biological catalysts, therefore their action increases the rate of biological reaction.

60. (d) : Collision frequency ∝ no. of reacting molecules or atoms

Higher the concentration of reactant molecules, higher is the probability of collision and so the collision frequency.

◆ ◆ ◆

CHAPTER

5

Surface Chemistry

5.1 Adsorption

1. The correct option representing a Freundlich adsorption isotherm is
   (a) $\frac{x}{m} = kp^{0.3}$ (b) $\frac{x}{m} = kp^{2.5}$
   (c) $\frac{x}{m} = kp^{-0.5}$ (d) $\frac{x}{m} = kp^{-1}$
   (Odisha NEET 2019)

2. Which one of the following characteristics is associated with adsorption?
   (a) ΔG and ΔH are negative but ΔS is positive.
   (b) ΔG and ΔS are negative but ΔH is positive.
   (c) ΔG is negative but ΔH and ΔS are positive.
   (d) ΔG, ΔH and ΔS all are negative.
   (NEET-I 2016)

3. In Freundlich adsorption isotherm, the value of $1/n$ is
   (a) between 0 and 1 in all cases
   (b) between 2 and 4 in all cases
   (c) 1 in case of physical absorption
   (d) 1 in case of chemisorption. *(2012)*

4. If x is amount of adsorbate and m is amount of adsorbent, which of the following relations is not related to adsorption process?
   (a) $x/m = f(p)$ at constant T
   (b) $x/m = f(T)$ at constant p
   (c) $p = f(T)$ at constant (x/m)
   (d) $\frac{x}{m} = p \times T$ *(2011)*

5. The Langmuir adsorption isotherm is deduced using the assumption
   (a) the adsorption sites are equivalent in their ability to adsorb the particles
   (b) the heat of adsorption varies with coverage
   (c) the adsorbed molecules interact with each other
   (d) the adsorption takes place in multilayers. *(2007)*

6. A plot of $\log(x/m)$ versus $\log P$ for the adsorption of a gas on a solid gives a straight line with slope equal to
   (a) $\log k$ (b) $-\log k$
   (c) n (d) $1/n$ *(2006, 1994)*

7. Which is not correct regarding the adsorption of a gas on surface of a solid?
   (a) On increasing temperature adsorption increases continuously.
   (b) Enthalpy and entropy change is negative.
   (c) Adsorption is more for some specific substance.
   (d) It is a reversible reaction. *(2001)*

5.2 Catalysis

8. Which one of the following statements is not correct?
   (a) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.
   (b) Enzymes catalyse mainly biochemical reactions.
   (c) Coenzymes increase the catalytic activity of enzyme.
   (d) Catalyst does not initiate any reaction.
   (NEET 2017)

9. Which one of the following statements is incorrect about enzyme catalysis?
   (a) Enzymes are mostly proteinous in nature.
   (b) Enzyme action is specific.
   (c) Enzymes are denatured by ultraviolet rays and at high temperature.
   (d) Enzymes are least reactive at optimum temperature. *(2012)*

10. The enzyme which hydrolyses triglycerides to fatty acids and glycerol is called
    (a) maltase (b) lipase
    (c) zymase (d) pepsin. *(2004)*

11. According to the adsorption theory of catalysis, the speed of the reaction increases because
(a) the concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
(b) in the process of adsorption, the activation energy of the molecules becomes large
(c) adsorption produces heat which increases the speed of the reaction
(d) adsorption lowers the activation energy of the reaction. *(2003)*

5.3 Colloids

12. A colloidal system has particles of which of the following size?
(a) 10^{-9} m to 10^{-12} m (b) 10^{-6} m to 10^{-9} m
(c) 10^{-4} m to 10^{-10} m (d) 10^{-5} m to 10^{-7} m
(1996)

5.4 Classification of Colloids

13. Measuring zeta potential is useful in determining which property of colloidal solution?
(a) Viscosity
(b) Solubility
(c) Stability of the colloidal particles
(d) Size of the colloidal particles *(NEET 2020)*

14. Which mixture of the solutions will lead to the formation of negatively charged colloidal $[AgI]I^-$ sol?
(a) 50 mL of 0.1 M $AgNO_3$ + 50 mL of 0.1 M KI
(b) 50 mL of 1 M $AgNO_3$ + 50 mL of 1.5 M KI
(c) 50 mL of 1 M $AgNO_3$ + 50 mL of 2 M KI
(d) 50 mL of 2 M $AgNO_3$ + 50 mL of 1.5 M KI
(NEET 2019)

15. On which of the following properties does the coagulating power of an ion depend?
(a) The magnitude of the charge on the ion alone
(b) Size of the ion alone
(c) Both magnitude and sign of the charge on the ion
(d) The sign of charge on the ion alone
(NEET 2018)

16. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given below :
I. (NaCl) = 52, II. ($BaCl_2$) = 0.69,
III. ($MgSO_4$) = 0.22
The correct order of their coagulating power is
(a) I > II > III (b) II > I > III
(c) III > II > I (d) III > I > II
(NEET-II 2016)

17. Fog is a colloidal solution of
(a) solid in gas (b) gas in gas
(c) liquid in gas (d) gas in liquid.
(NEET-I 2016)

18. Which property of colloidal solution is independent of charge on the colloidal particles?
(a) Electroosmosis (b) Tyndall effect
(c) Coagulation (d) Electrophoresis
(2015, Cancelled 2014)

19. The protecting power of lyophilic colloidal sol is expressed in terms of
(a) coagulation value
(b) gold number
(c) critical micelle concentration
(d) oxidation number. *(2012)*

20. Which one of the following forms micelles in aqueous solution above certain concentration?
(a) Dodecyl trimethyl ammonium chloride
(b) Glucose
(c) Urea
(d) Pyridinium chloride *(2005)*

21. Position of non-polar and polar part in micelle
(a) polar at outer surface but non-polar at inner surface
(b) polar at inner surface non-polar at outer surface
(c) distributed over all the surface
(d) are present in the surface only. *(2002)*

22. Which one of the following method is commonly used method for destruction of colloid?
(a) Dialysis
(b) Condensation
(c) Filtration by animal membrane
(d) By adding electrolyte *(2000)*

23. At the critical micelle concentration (CMC) the surfactant molecules
(a) associate
(b) dissociate
(c) decompose
(d) become completely soluble. *(1998)*

24. The ability of anion, to bring about coagulation of a given colloid, depends upon
(a) magnitude of the charge
(b) both magnitude and charge
(c) its charge only
(d) sign of the charge alone. *(1997)*

25. When a few typical solutes are separated by a particular selective membrane such as protein particles, blood corpuscles, this process is called
(a) transpiration
(b) endosmosis
(c) dialysis
(d) diffusion. *(1996)*

ANSWER KEY

1.	(a)	**2.**	(d)	**3.**	(a)	**4.**	(d)	**5.**	(a)	**6.**	(d)	**7.**	(a)	**8.**	(a)	**9.**	(d)	**10.**	(b)
11.	(d)	**12.**	(b)	**13.**	(c)	**14.**	(b)	**15.**	(c)	**16.**	(c)	**17.**	(c)	**18.**	(b)	**19.**	(b)	**20.**	(a)
21.	(a)	**22.**	(d)	**23.**	(a)	**24.**	(b)	**25.**	(c)										

Hints & Explanations

1. (a) : Freundlich adsorption isotherm equation is $\frac{x}{m} = kp^{\frac{1}{n}} \left(1 \ge \frac{1}{n} \ge 0\right)$

2. (d) : As the molecules of the adsorbate are held on the surface of the solid adsorbent, entropy decreases *i.e.*, $\Delta S = -\text{ve}$.
As $\Delta G = \Delta H - T\Delta S$
For the adsorption to occur, $\Delta G = -\text{ve}$ and it is possible only if $\Delta H = -\text{ve}$.

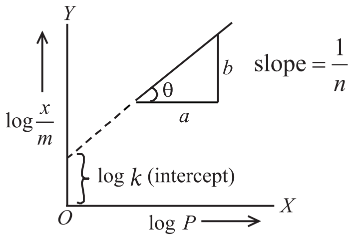
3. (a) : Freundlich adsorption isotherm :

$$\frac{x}{m} = k \cdot p^{1/n} \;;\quad 0 \le \frac{1}{n} \le 1$$

4. (d) : $\frac{x}{m} = p \times T$ is the incorrect relation.
The correct relation is
amount of absorption $\frac{x}{m} \propto \frac{P}{T}$

5. (a) : Langmuir adsorption isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether nearby sites are occupied or not occupied.

6. (d) :



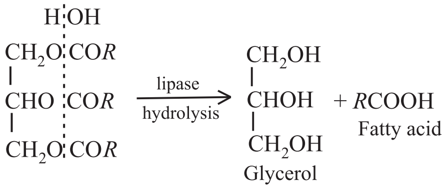
This is according to Freundlich adsorption isotherm.

7. (a) : Adsorption is the ability of a substance to concentrate or hold gases, liquids or dissolved substances upon its surface. Solids adsorb greater amounts of substances at lower temperature. In general, adsorption decreases with increase in temperature.

8. (a) : Catalyst does not change the value of equilibrium constant as they affect forward as well as backward reactions equally.

9. (d) : The enzyme activity rises rapidly with temperature and becomes maximum at definite temperature, called optimum temperature.

10. (b) :



11. (d) : Adsorption causes decrease in surface energy which appears as heat. Thus, adsorption is an exothermic process and hence lowers the activation energy of the reaction.

12. (b) : Particle size of colloids lies in the range of 10^{-6} m to 10^{-9} m. Particles themselves are invisible even under the most powerful microscope.

13. (c) : Measuring zeta potential is useful in determining stability of the colloidal particles.

14. (b) : If colloidal sol of AgI is prepared by adding KI solution to $AgNO_3$ till KI is in slight excess, iodide ion (I^-) will be adsorbed on the surface of AgI thereby, giving a negative charge to the sol.

$$\text{AgI} + \underset{\text{(From KI)}}{\text{I}^-} \longrightarrow \underset{\text{Negative sol}}{\text{AgI} : \text{I}^-}$$

15. (c) : According to Hardy-Schulze rule, the coagulating power of an electrolyte depends on both magnitude and sign of the charge of the effective ion or electrolyte.

16. (c) : Coagulating power $\propto \dfrac{1}{\text{Coagulation value}}$

Lower the coagulation value, higher is the coagulating power so, the correct order is :

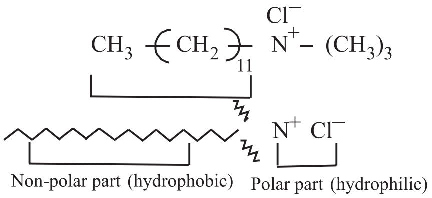
$$\underset{\text{(III)}}{MgSO_4} > \underset{\text{(II)}}{BaCl_2} > \underset{\text{(I)}}{NaCl}$$

17. (c) : Fog is an example of aerosol in which dispersed phase is liquid and dispersion medium is gas.

18. (b) : Tyndall effect is scattering of light by colloidal particles which is independent of charge on them.

19. (b)

20. (a) :



$CH_3{-}(CH_2)_{11}{-}\overset{Cl^-}{\overset{+}{N}}{-}(CH_3)_3$

21. (a) : Micelles are the clusters or aggregates formed in solution by association of colloids. Usually such molecules have a lyophobic group and a lyophilic group. The long hydrocarbon is the lyophobic portion which tries to recede away from the solvent water and the ionisable lyophilic group which tends to go into water resulting into ions. As the concentration is increased the lyophobic parts receding away from the solvent approach each other and form a cluster. Thus, the lyophobic ends are in the interior and lyophilic groups projecting outward in contact with the solvent.

22. (d) : By adding electrolytes the colloidal particles are precipitated. The electrolytes neutralise the charge of colloids leading to their coagulation and thus, destroy the colloid.

23. (a) : The soap concentration at which micelles (spherical colloid molecules) first appear is called as critical micelle concentration (CMC). At this condition, the surfactant molecules associate with each other.

24. (b) : Both magnitude of charge and nature of charge effect coagulation of a given colloid. Greater the magnitude of the charge, quicker will be the coagulation.

25. (c) : Dialysis is the process of separating the particles of colloids from the particles of crystalloids by means of diffusion through a selective membrane placed in water.

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CHAPTER
6

General Principles and Processes of Isolation of Elements

6.1 Occurrence of Metals

1. Which one is malachite from the following?
(a) $CuCO_3.Cu(OH)_2$ (b) $CuFeS_2$
(c) $Cu(OH)_2$ (d) Fe_3O_4 *(NEET 2019)*

2. Identify the incorrect statement.
(a) The scientific and technological process used for isolation of the metal from its ore is known as metallurgy.
(b) Minerals are naturally occurring chemical substances in the earth's crust.
(c) Ores are minerals that may contain a metal.
(d) Gangue is an ore contaminated with undesired materials. *(Odisha NEET 2019)*

3. "Metals are usually not found as nitrates in their ores." Out of the following two (I and II) reasons which is/are true for the above observation?
I. Metal nitrates are highly unstable.
II. Metal nitrates are highly soluble in water.
(a) I is false but II is true.
(b) I is true but II is false.
(c) I and II are true.
(d) I and II are false *(2015, Cancelled)*

4. Which one of the following is a mineral of iron?
(a) Malachite (b) Cassiterite
(c) Pyrolusite (d) Magnetite *(2012)*

5. Cassiterite is an ore of
(a) Sb (b) Ni
(c) Mn (d) Sn *(1999)*

6.2 Concentration of Ores

6. Sulphide ores of metals are usually concentrated by froth floatation process. Which one of the following sulphide ores offer an exception and is concentrated by chemical leaching?
(a) Galena (b) Copper pyrite
(c) Sphalerite (d) Argentite *(2007)*

6.3 Extraction of Crude Metal from Concentrated Ore

7. Roasting of sulphides gives the gas *X* as a byproduct. This is a colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas *X* is
(a) CO_2 (b) SO_3
(c) H_2S (d) SO_2 *(NEET 2013)*

6.4 Thermodynamic Principles of Metallurgy

8. Considering Ellingham diagram, which of the following metals can be used to reduce alumina?
(a) Fe (b) Zn
(c) Mg (d) Cu *(NEET 2018)*

9. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with
(a) carbon monoxide (b) copper (I) sulphide
(c) sulphur dioxide (d) iron (II) sulphide.
(2015, 2012)

10. The metal oxide which cannot be reduced to metal by carbon is
(a) Al_2O_3 (b) PbO (c) ZnO (d) Fe_2O_3
(Karnataka NEET 2013)

11. Which of the following elements is present as the impurity to the maximum extent in the pig iron?
(a) Manganese (b) Carbon
(c) Silicon (d) Phosphorus
(2011, 1998)

12. The following reactions take place in the blast furnace in the preparation of impure iron. Identify the reaction pertaining to the formation of the slag.
(a) $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(l)} + 3CO_{2(g)}$
(b) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
(c) $CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(s)}$
(d) $2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$ *(Mains 2011)*

13. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true?

(a) The ΔG_f° of the sulphide is greater than those for CS_2 and H_2S.

(b) The ΔG_f° is negative for roasting of sulphide ore to oxide.

(c) Roasting of the sulphide to the oxide is thermodynamically feasible.

(d) Carbon and hydrogen are suitable reducing agents for metal sulphides. *(2007)*

14. Nitriding is the process of surface hardening of steel by treating it in an atmosphere of

(a) NH_3 (b) O_3

(c) N_2 (d) H_2S *(1989)*

6.5 Electrochemical Principles of Metallurgy

15. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of

(a) $Al_2O_3 + HF + NaAlF_4$

(b) $Al_2O_3 + CaF_2 + NaAlF_4$

(c) $Al_2O_3 + Na_3AlF_6 + CaF_2$

(d) $Al_2O_3 + KF + Na_3AlF_6$ *(2012)*

16. Purification of aluminium, by electrolytic refining, is known as

(a) Hoope's process

(b) Baeyer's process

(c) Hall's process

(d) Serpeck's process. *(1999)*

17. Calcium is obtained by

(a) reduction of calcium chloride with carbon

(b) electrolysis of molten anhydrous calcium chloride

(c) roasting of limestone

(d) electrolysis of solution of calcium chloride in H_2O. *(1997)*

6.6 Oxidation Reduction

18. Extraction of gold and silver involves leaching with CN^- ion. Silver is later recovered by

(a) distillation (b) zone refining

(c) displacement with Zn

(d) liquation. *(NEET 2017)*

6.7 Refining

19. Identify the correct statement from the following :

(a) Wrought iron is impure iron with 4% carbon.

(b) Blister copper has blistered appearance due to evolution of CO_2.

(c) Vapour phase refining is carried out for Nickel by van Arkel method.

(d) Pig iron can be moulded into a variety of shapes. *(NEET 2020)*

20. Match items of Column I with the items of Column II and assign the correct code :

Column I	**Column II**
(A) Cyanide process	(i) Ultrapure Ge
(B) Froth floatation process	(ii) Dressing of ZnS
(C) Electrolytic reduction	(iii) Extraction of Al
(D) Zone refining	(iv) Extraction of Au
	(v) Purification of Ni

Code :

	A	**B**	**C**	**D**
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iii)	(iv)	(v)	(i)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(ii)	(iii)	(i)	(v)

(NEET-I 2016)

21. Which of the following pairs of metals is purified by van Arkel method?

(a) Ga and In (b) Zr and Ti

(c) Ag and Au (d) Ni and Fe *(2011)*

22. The method of zone refining of metals is based on the principle of

(a) greater mobility of the pure metal than that of the impurity

(b) higher melting point of the impurity than that of the pure metal

(c) greater noble character of the solid metal than that of the impurity

(d) greater solubility of the impurity in the molten state than in the solid. *(2003)*

ANSWER KEY

1.	(a)	**2.**	(d)	**3.**	(a)	**4.**	(d)	**5.**	(d)	**6.**	(d)	**7.**	(d)	**8.**	(c)	**9.**	(b)	**10.**	(a)
11.	(b)	**12.**	(c)	**13.**	(d)	**14.**	(a)	**15.**	(c)	**16.**	(a)	**17.**	(b)	**18.**	(c)	**19.**	(d)	**20.**	(c)
21.	(b)	**22.**	(d)																

Hints & Explanations

1. (a) : Malachite : $CuCO_3 \cdot Cu(OH)_2$

2. (d) : An ore rarely contains only a desired substance. It is usually contaminated with earthly or undesired materials known as gangue.

3. (a) : All nitrates are soluble in water and are quite stable as they do not decompose easily on heating.

4. (d) : Magnetite is Fe_3O_4 and contains upto 70% of iron metal.

5. (d) : Cassiterite is also known as tin stone (SnO_2), an ore of tin (Sn).

6. (d) : Leaching process involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical method. Argentite or silver glance, Ag_2S is an ore of silver. Silver is extracted from argentite by the Mac-Arthur and Forest cyanide process (leaching process).

$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$

$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$

7. (d)

8. (c) : Any metal oxide with lower value of $\Delta G°$ is more stable than a metal oxide with higher $\Delta G°$. This implies that the metal oxide placed higher in the Ellingham diagram can be reduced by the metal involved in the formation of the oxide placed lower in the diagram. The relative tendency of the various metals to act as reducing agents is :

$Ca > Mg > Al > Zn > Fe > Cu.$

Thus, Mg being more reducing in nature, can reduce aluminium oxide (alumina) to aluminium.

9. (b) : It is an example of auto reduction.

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

10. (a) : Oxides of less reactive metals (like PbO, ZnO, Fe_2O_3) can be reduced by carbon. While oxides of very reactive metals (like Al_2O_3) can be reduced only by the electrolytic method.

11. (b) : Pig iron contains about 4% carbon and many impurities such as S, Mn, P, Si, etc. in smaller amount.

12. (c) : Slag is formed by the reaction

$CaO + SiO_2 \longrightarrow CaSiO_3$

13. (d) : The standard free energies of formation ($\Delta G_f°$) of most of the sulphides are greater than those of CS_2 and H_2S. Hence, neither carbon nor hydrogen can reduce metal sulphides to metal. The standard free energies of formation of oxides are much lower than those of SO_2. Therefore, oxidation of metal sulphides to metal oxides is thermodynamically favourable. Hence, sulphide ore is roasted to the oxide before reduction.

14. (a) : When steel is heated in presence of NH_3, iron nitride on the surface of steel is formed which imparts a hard coating. This process is called nitriding.

15. (c) : Electrolytic mixture contains alumina (Al_2O_3), cryolite (Na_3AlF_6) and fluorspar (CaF_2) in the ratio of 20 : 40 : 20. Due to presence of these, conductivity of alumina increases and fusion temperature decreases from 2000°C to 900°C.

16. (a) : Aluminium metal obtained from Hoope's electrolytic refining process is about 99.9% pure. The cell used for this process consists of three layers. The upper layer is pure 'Al', acts as cathode, the middle layer is mixture of fluorides of Al and Ba, which acts as electrolyte. The lowest layer is impure 'Al', which acts as anode. On electrolysis pure 'Al' is transferred from the bottom to the top layer, through the middle layer.

17. (b) : Calcium is obtained by the electrolysis of a fused mixture of anhydrous $CaCl_2$ and CaF_2 in a graphite linked tank which serves as anode. The cathode is a hollow movable iron rod which is kept cool. During electrolysis, calcium is deposited at cathode while Cl_2 is liberated at anode.

18. (c) : Extraction of gold and silver involves leaching the metal with CN^- and the metals silver and gold are later recovered by displacement method.

$$4M_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)} \longrightarrow 4[M(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

$$2[M(CN)_2]^-_{(aq)} + Zn_{(s)} \longrightarrow 2M_{(s)} + [Zn(CN)_4]^{2-}_{(aq)}$$

19. (d) : (a) Pig iron is impure iron with 4% carbon.

(b) Blister copper has blistered appearance due to evolution of SO_2.

(c) Vapour phase refining is carried out for nickel by Mond's process.

(d) Pig iron can be moulded into a variety of shapes.

20. (c)

21. (b) : van Arkel method is used for purification of Zr and Ti.

22. (d) : Elements which are used as semiconductors such as Si, Ge, Ga, etc. are refined by this method, which is based on the difference in solubility of impurities in molten and solid state of the metal.

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CHAPTER 7

The *p*-Block Elements

7.1 Group 15 Elements

1. In which of the following compounds, nitrogen exhibits highest oxidation state?
(a) N_2H_4 (b) NH_3
(c) N_3H (d) NH_2OH *(2012)*

2. Nitrogen forms N_2, but phosphorus does not form P_2, however, it converts P_4, reason is
(a) triple bond present between phosphorus atom
(b) $p\pi - p\pi$ bonding is weak
(c) $p\pi - p\pi$ bonding is strong
(d) multiple bonds form easily. *(2001)*

3. Which of the following oxides is most acidic?
(a) As_2O_5 (b) P_2O_5
(c) N_2O_5 (d) Sb_2O_5 *(1999)*

4. Which of the following has the highest dipole moment?
(a) SbH_3 (b) AsH_3
(c) NH_3 (d) PH_3 *(1997)*

5. The basic character of hydrides of the V group elements decreases in the order
(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $SbH_3 > AsH_3 > PH_3 > NH_3$
(c) $SbH_3 > PH_3 > AsH_3 > NH_3$
(d) $NH_3 > SbH_3 > PH_3 > AsH_3$ *(1996)*

6. Among the following oxides, the lowest acidic is
(a) As_4O_6 (b) As_4O_{10}
(c) P_4O_6 (d) P_4O_{10} *(1996)*

7. Which of the following fluorides does not exist?
(a) NF_5 (b) PF_5
(c) AsF_5 (d) SbF_5 *(1993)*

8. Which one has the lowest boiling point?
(a) NH_3 (b) PH_3
(c) AsH_3 (d) SbH_3 *(1989)*

7.2 Dinitrogen

9. Number of electrons shared in the formation of nitrogen molecule is
(a) 6 (b) 10
(c) 2 (d) 8 *(1992)*

10. Nitrogen is relatively inactive element because
(a) its atom has a stable electronic configuration
(b) it has low atomic radius
(c) its electronegativity is fairly high
(d) dissociation energy of its molecule is fairly high. *(1992)*

11. Pure nitrogen is prepared in the laboratory by heating a mixture of
(a) $NH_4OH + NaCl$ (b) $NH_4NO_3 + NaCl$
(c) $NH_4Cl + NaOH$ (d) $NH_4Cl + NaNO_2$. *(1991)*

12. Which of the following statement is not correct for nitrogen?
(a) Its electronegativity is very high.
(b) *d*-orbitals are available for bonding.
(c) It is a typical non-metal.
(d) Its molecular size is small. *(1990)*

7.3 Ammonia

13. Urea reacts with water to form *A* which will decompose to form *B*. *B* when passed through $Cu^{2+}_{(aq)}$, deep blue colour solution *C* is formed. What is the formula of *C* from the following?
(a) $CuSO_4$ (b) $[Cu(NH_3)_4]^{2+}$
(c) $Cu(OH)_2$ (d) $CuCO_3 \cdot Cu(OH)_2$ *(NEET 2020)*

14. Aqueous solution of ammonia consists of
(a) H^+ (b) OH^-
(c) NH_4^+ (d) NH_4^+ and OH^-. *(1991)*

7.4 Oxides of Nitrogen

15. Which of the following oxides of nitrogen is paramagnetic?
(a) NO_2 (b) N_2O_3
(c) N_2O (d) N_2O_5 *(1994)*

16. Which of the following is a nitric acid anhydride?
(a) NO (b) NO_2
(c) N_2O_5 (d) N_2O_3 *(1988)*

7.5 Nitric Acid

17. When copper is heated with conc. HNO_3 it produces
(a) $Cu(NO_3)_2$, NO and NO_2
(b) $Cu(NO_3)_2$ and N_2O (c) $Cu(NO_3)_2$ and NO_2
(d) $Cu(NO_3)_2$ and NO *(NEET-I 2016)*

18. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because
(a) Zn act as oxidising agent when react with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) in electrochemical series Zn is above hydrogen
(d) NO_3^- is reduced in preference to hydronium ion. *(2002)*

19. Sugarcane on reaction with nitric acid gives
(a) CO_2 and SO_2 (b) $(COOH)_2$
(c) 2HCOOH(two moles) (d) no reaction. *(1992)*

7.6 Phosphorus - Allotropic Forms

20. Which of the following phosphorus is the most reactive?
(a) Scarlet phosphorus (b) White phosphorus
(c) Red phosphorus (d) Violet phosphorus
(1999)

21. Each of the following is true for white and red phosphorus except that they
(a) are both soluble in CS_2
(b) can be oxidised by heating in air
(c) consist of the same kind of atoms
(d) can be converted into one another. *(1989)*

7.7 Phosphine

22. A compound '*X*' upon reaction with H_2O produces a colourless gas '*Y*' with rotten fish smell. Gas '*Y*' is absorbed in a solution of $CuSO_4$ to give Cu_3P_2 as one of the products. Predict the compound '*X*'.
(a) Ca_3P_2 (b) NH_4Cl
(c) As_2O_3 (d) $Ca_3(PO_4)_2$
(Odisha NEET 2019)

23. PH_4I + NaOH forms
(a) PH_3 (b) NH_3
(c) P_4O_6 (d) P_4O_{10} *(1991)*

7.8 Phosphorus Halides

24. Identify the incorrect statement related to PCl_5 from the following :
(a) PCl_5 molecule is non-reactive.
(b) Three equatorial P – Cl bonds make an angle of 120° with each other.
(c) Two axial P – Cl bonds make an angle of 180° with each other.
(d) Axial P – Cl bonds are longer than equatorial P – Cl bonds. *(NEET 2019)*

25. PCl_3 reacts with water to form
(a) PH_3 (b) H_3PO_3, HCl
(c) $POCl_3$ (d) H_3PO_4 *(1991)*

7.9 Oxoacids of Phosphorus

26. Which of the following oxoacids of phosphorus has strongest reducing property?
(a) $H_4P_2O_7$ (b) H_3PO_3
(c) H_3PO_2 (d) H_3PO_4
(Odisha NEET 2019)

27. Which is the correct statement for the given acids?
(a) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid.
(b) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid.
(c) Both are diprotic acids.
(d) Both are triprotic acids. *(NEET-I 2016)*

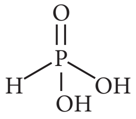
28. Strong reducing behaviour of H_3PO_2 is due to
(a) high electron gain enthalpy of phosphorus
(b) high oxidation state of phosphorus
(c) presence of two —OH groups and one P—H bond
(d) presence of one —OH group and two P—H bonds. *(2015)*

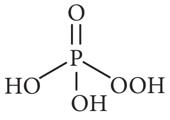
29. Which of the following statements is not valid for oxoacids of phosphorus?
(a) Orthophosphoric acid is used in the manufacture of triple superphosphate.
(b) Hypophosphorous acid is a diprotic acid.
(c) All oxoacids contain tetrahedral four coordinated phosphorus.
(d) All oxoacids contain atleast one P $=$ O unit and one P—OH group. *(2012)*

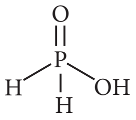
30. Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, $H_4P_2O_7$ are respectively
(a) +3, +5, +4 (b) +5, +3, +4
(c) +5, +4, +3 (d) +3, +4, +5 *(2010)*

31. How many bridging oxygen atoms are present in P_4O_{10}?
(a) 6 (b) 4
(c) 2 (d) 5 *(Mains 2010)*

32. The structural formula of hypophosphorous acid is

(a) 

(b) 

(c) 

(d) none of these. *(1997)*

33. H_3PO_2 is the molecular formula of an acid of phosphorus. Its name and basicity respectively are
(a) phosphorous acid and two
(b) hypophosphorous acid and two
(c) hypophosphorous acid and one
(d) hypophosphoric acid and two. *(1992)*

34. Which one of the following substance is used in the laboratory for fast drying of neutral gases?
(a) Phosphorus pentoxide (b) Active charcoal
(c) Anhydrous calcium chloride
(d) Na_3PO_4 *(1992)*

35. P_2O_5 is heated with water to give
(a) hypophosphorous acid
(b) phosphorous acid (c) hypophosphoric acid
(d) orthophosphoric acid. *(1991)*

36. Basicity of orthophosphoric acid is
(a) 2 (b) 3
(c) 4 (d) 5 *(1991)*

37. When orthophosphoric acid is heated to 600°C, the product formed is
(a) PH_3 (b) P_2O_5
(c) H_3PO_3 (d) HPO_3 *(1989)*

7.10 Group 16 Elements

38. Which is the correct thermal stability order for H_2E (E = O, S, Se, Te and Po) ?
(a) $H_2Se < H_2Te < H_2Po < H_2O < H_2S$
(b) $H_2S < H_2O < H_2Se < H_2Te < H_2Po$
(c) $H_2O < H_2S < H_2Se < H_2Te < H_2Po$
(d) $H_2Po < H_2Te < H_2Se < H_2S < H_2O$ *(NEET 2019)*

39. Acidity of diprotic acids in aqueous solutions increases in the order
(a) $H_2S < H_2Se < H_2Te$ (b) $H_2Se < H_2S < H_2Te$
(c) $H_2Te < H_2S < H_2Se$ (d) $H_2Se < H_2Te < H_2S$
(2014)

40. Which of the following bonds has the highest energy?
(a) S–S (b) O–O
(c) Se–Se (d) Te–Te *(1996)*

7.11 Dioxygen

41. Which of the following does not give oxygen on heating?
(a) $K_2Cr_2O_7$ (b) $(NH_4)_2Cr_2O_7$
(c) $KClO_3$ (d) $Zn(ClO_3)_2$
(NEET 2013)

42. Which would quickly absorb oxygen?
(a) Alkaline solution of pyrogallol
(b) Conc. H_2SO_4
(c) Lime water
(d) Alkaline solution of $CuSO_4$ *(1991)*

43. Oxygen will directly react with each of the following elements except
(a) P (b) Cl
(c) Na (d) S *(1989)*

44. It is possible to obtain oxygen from air by fractional distillation because
(a) oxygen is in a different group of the periodic table from nitrogen
(b) oxygen is more reactive than nitrogen
(c) oxygen has higher b.pt. than nitrogen
(d) oxygen has a lower density than nitrogen. *(1989)*

7.12 Simple Oxides

45. Match the following :

Oxide	**Nature**
(A) CO	(i) Basic
(B) BaO	(ii) Neutral
(C) Al_2O_3	(iii) Acidic
(D) Cl_2O_7	(iv) Amphoteric

Which of the following is correct option?

	(A)	**(B)**	**(C)**	**(D)**
(a)	(i)	(ii)	(iii)	(iv)
(b)	(ii)	(i)	(iv)	(iii)
(c)	(iii)	(iv)	(i)	(ii)
(d)	(iv)	(iii)	(ii)	(i)

(NEET 2020)

7.13 Ozone

46. The angular shape of ozone molecule (O_3) consists of
(a) 1σ and 1π bond (b) 2σ and 1π bond
(c) 1σ and 2π bonds (d) 2σ and 2π bonds. *(2008)*

47. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon are
(a) O_3, CH_4 (b) O_2, O_3
(c) SO_2, CH_4 (d) N_2O, O_3 *(1989)*

7.15 Sulphur Dioxide

48. Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other?
(a) Is soluble in water.
(b) Is used as a food preservative.
(c) Forms 'acid-rain'.
(d) Is a reducing agent. *(2015, Cancelled)*

49. Sulphur trioxide can be obtained by which of the following reaction?
(a) $CaSO_4 + C \xrightarrow{\Delta}$
(b) $Fe_2(SO_4)_3 \xrightarrow{\Delta}$
(c) $S + H_2SO_4 \xrightarrow{\Delta}$
(d) $H_2SO_4 + PCl_5 \xrightarrow{\Delta}$ *(2012)*

7.16 Oxoacids of Sulphur

50. Which of the following oxoacid of sulphur has — O — O — linkage
(a) H_2SO_3, sulphurous acid
(b) H_2SO_4, sulphuric acid
(c) $H_2S_2O_8$, peroxodisulphuric acid
(d) $H_2S_2O_7$, pyrosulphuric acid *(NEET 2020)*

51. Identify the correct formula of oleum from the following :
(a) $H_2S_2O_7$ (b) H_2SO_3
(c) H_2SO_4 (d) $H_2S_2O_8$
(Odisha NEET 2019)

52. In which pair of ions both the species contain S — S bond?
(a) $S_4O_6^{2-}, S_2O_3^{2-}$ (b) $S_2O_7^{2-}, S_2O_8^{2-}$
(c) $S_4O_6^{2-}, S_2O_7^{2-}$ (d) $S_2O_7^{2-}, S_2O_3^{2-}$
(NEET 2017)

53. Oleum is
(a) castor oil (b) oil of vitriol
(c) fuming H_2SO_4 (d) none of these. *(1991)*

7.17 Sulphuric Acid

54. Match List I (substances) with List II (processes) employed in the manufacture of the substances and select the correct option.

List I (Substances)	**List II (Processes)**
(A) Sulphuric acid	(i) Haber's process
(B) Steel	(ii) Bessemer's process
(C) Sodium hydroxide	(iii) Leblanc process
(D) Ammonia	(iv) Contact process

(a) A - (i), B - (iv), C - (ii), D - (iii)
(b) A - (i), B - (ii), C - (iii), D - (iv)
(c) A - (iv), B - (iii), C - (ii), D - (i)
(d) A - (iv), B - (ii), C - (iii), D - (i) *(Mains 2010)*

7.18 Group 17 Elements

55. Which of the following statements is not true for halogens?
(a) All form monobasic oxyacids.
(b) All are oxidizing agents.
(c) All but fluorine show positive oxidation states.
(d) Chlorine has the highest electron-gain enthalpy. *(NEET 2018)*

56. Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules?
(a) $Br_2 > I_2 > F_2 > Cl_2$ (b) $F_2 > Cl_2 > Br_2 > I_2$
(c) $I_2 > Br_2 > Cl_2 > F_2$ (d) $Cl_2 > Br_2 > F_2 > I_2$
(NEET-I 2016)

57. The variation of the boiling points of the hydrogen halides is in the order HF > HI > HBr > HCl.
What explains the higher boiling point of hydrogen fluoride?
(a) There is strong hydrogen bonding between HF molecules.
(b) The bond energy of HF molecules is greater than in other hydrogen halides.
(c) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.
(d) The electronegativity of fluorine is much higher than for other elements in the group. *(2015)*

58. Among the following which is the strongest oxidising agent?
(a) Br_2 (b) I_2
(c) Cl_2 (d) F_2 *(2009)*

59. Which one of the following arrangements does not give the correct picture of the trends indicated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
(b) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity
(c) $F_2 > Cl_2 > Br_2 > I_2$: Oxidizing power
(d) $F_2 > Cl_2 > Br_2 > I_2$: Electron gain enthalpy *(2008)*

60. Which one of the following orders is not in accordance with the property stated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
(b) $F_2 > Cl_2 > Br_2 > I_2$: Oxidising power
(c) HI > HBr > HCl > HF : Acidic property in water
(d) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity *(2006)*

61. Which statement is wrong?
(a) Bond energy of $F_2 > Cl_2$
(b) Electronegativity of F > Cl
(c) F is more oxidising than Cl
(d) Electron affinity of Cl > F *(2000)*

62. Which of the following has the greatest electron affinity?
(a) I (b) Br
(c) F (d) Cl *(1996)*

63. Which of the following displaces Br_2 from an aqueous solution containing bromide ions?
(a) I_2 (b) I_3^-
(c) Cl_2 (d) Cl^- *(1994)*

64. Which of the following species has four lone pairs of electrons?
(a) I (b) O
(c) Cl^- (d) He *(1993)*

7.19 Chlorine

65. Match the following :

(A) Pure nitrogen	(i) Chlorine
(B) Haber process	(ii) Sulphuric acid
(C) Contact process	(iii) Ammonia
(D) Deacon's process	(iv) Sodium azide or Barium azide

Which of the following is the correct option ?

	(A)	(B)	(C)	(D)
(a)	(iv)	(iii)	(ii)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(ii)	(iv)	(i)	(iii)
(d)	(iii)	(iv)	(ii)	(i)

(NEET 2019)

66. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from

(a) zero to +1 and zero to –5
(b) zero to –1 and zero to +5
(c) zero to –1 and zero to +3
(d) zero to +1 and zero to –3 *(2012)*

67. Which of the following is used in the preparation of chlorine?

(a) Both MnO_2 and $KMnO_4$
(b) Only $KMnO_4$
(c) Only MnO_2
(d) Either MnO_2 or $KMnO_4$ *(1999)*

68. Which of the following elements is extracted commercially by the electrolysis of an aqueous solution of its compound?

(a) Cl (b) Br
(c) Al (d) Na *(1993)*

69. When chlorine is passed over dry slaked lime at room temperature, the main reaction product is

(a) $Ca(ClO_2)_2$ (b) $CaCl_2$
(c) $CaOCl_2$ (d) $Ca(OCl)_2$ *(1992)*

70. In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with

(a) carbon dioxide (b) chlorine
(c) iodine (d) sulphur dioxide.
(1992)

71. The bleaching action of chlorine is due to

(a) reduction (b) hydrogenation
(c) chlorination (d) oxidation. *(1991)*

7.20 Hydrogen Chloride

72. Bleaching powder reacts with a few drops of conc. HCl to give

(a) chlorine (b) hypochlorous acid
(c) calcium oxide (d) oxygen. *(1989)*

7.21 Oxoacids of Halogens

73. Among the following, the correct order of acidity is

(a) $HClO_2 < HClO < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_2 < HClO < HClO_3$
(c) $HClO_3 < HClO_4 < HClO_2 < HClO$
(d) $HClO < HClO_2 < HClO_3 < HClO_4$
(NEET-I 2016, 2007, 2005)

74. Which of the statements given below is incorrect?

(a) O_3 molecule is bent.
(b) ONF is isoelectronic with O_2N^-.
(c) OF_2 is an oxide of fluorine.
(d) Cl_2O_7 is an anhydride of perchloric acid.
(2015)

75. The correct order of increasing bond angles in the following species is

(a) $Cl_2O < ClO_2 < ClO_2^-$
(b) $ClO_2 < Cl_2O < ClO_2^-$
(c) $Cl_2O < ClO_2^- < ClO_2$
(d) $ClO_2^- < Cl_2O < ClO_2$ *(2010)*

76. Which one of the following oxides is expected to exhibit paramagnetic behaviour?

(a) CO_2 (b) SiO_2
(c) SO_2 (d) ClO_2 *(2005)*

7.22 Interhalogen Compounds

77. Match the interhalogen compounds of column-I with the geometry in column-II and assign the correct code.

Column I	**Column II**
(A) XX'	(i) T-shape
(B) XX'_3	(ii) Pentagonal bipyramidal
(C) XX'_5	(iii) Linear
(D) XX'_7	(iv) Square pyramidal
	(v) Tetrahedral

Code :

	A	B	C	D
(a)	(iii)	(i)	(iv)	(ii)
(b)	(v)	(iv)	(iii)	(ii)
(c)	(iv)	(iii)	(ii)	(i)
(d)	(iii)	(iv)	(i)	(ii)

(NEET 2017)

7.23 Group-18 elements

78. Match the Xenon compounds in Column-I with its structure in Column-II and assign the correct code.

Column-I		**Column-II**	
(A)	XeF_4	(i)	pyramidal
(B)	XeF_6	(ii)	square planar
(C)	$XeOF_4$	(iii)	distorted octahedral
(D)	XeO_3	(iv)	square pyramidal

	(A)	(B)	(C)	(D)
(a)	(iii)	(iv)	(i)	(ii)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(ii)	(iii)	(iv)	(i)
(d)	(ii)	(iii)	(i)	(iv)

(NEET 2019, NEET-I 2016)

79. Identify the incorrect statement, regarding the molecule XeO_4.

(a) XeO_4 molecule is square planar.
(b) There are four $p\pi$ - $d\pi$ bonds.
(c) There are four sp^3 - p, σ bonds.
(d) XeO_4 molecule is tetrahedral.

(Karnataka NEET 2013)

80. Which compound has planar structure?

(a) XeF_4 (b) $XeOF_2$
(c) XeO_2F_2 (d) XeO_4 *(2000)*

ANSWER KEY

1.	(c)	**2.**	(b)	**3.**	(c)	**4.**	(c)	**5.**	(a)	**6.**	(a)	**7.**	(a)	**8.**	(b)	**9.**	(a)	**10.**	(d)
11.	(d)	**12.**	(b)	**13.**	(b)	**14.**	(d)	**15.**	(a)	**16.**	(c)	**17.**	(c)	**18.**	(d)	**19.**	(b)	**20.**	(b)
21.	(a)	**22.**	(a)	**23.**	(a)	**24.**	(a)	**25.**	(b)	**26.**	(c)	**27.**	(a)	**28.**	(d)	**29.**	(b)	**30.**	(d)
31.	(a)	**32.**	(c)	**33.**	(c)	**34.**	(a)	**35.**	(d)	**36.**	(b)	**37.**	(d)	**38.**	(d)	**39.**	(a)	**40.**	(a)
41.	(b)	**42.**	(a)	**43.**	(b)	**44.**	(c)	**45.**	(b)	**46.**	(b)	**47.**	(b)	**48.**	(b)	**49.**	(b)	**50.**	(c)
51.	(a)	**52.**	(a)	**53.**	(c)	**54.**	(d)	**55.**	(c)	**56.**	(d)	**57.**	(a)	**58.**	(d)	**59.**	(a,d)	**60.**	(a)
61.	(a)	**62.**	(d)	**63.**	(c)	**64.**	(c)	**65.**	(a)	**66.**	(b)	**67.**	(a)	**68.**	(a)	**69.**	(c)	**70.**	(b)
71.	(d)	**72.**	(a)	**73.**	(d)	**74.**	(c)	**75.**	(d)	**76.**	(d)	**77.**	(a)	**78.**	(c)	**79.**	(a)	**80.**	(a)

Hints & Explanations

1. **(c) :** $N_2H_4 \Rightarrow 2x + 4(+1) = 0$
$\Rightarrow\ 2x + 4 = 0$
$\Rightarrow\ x = -2$
$NH_3 \Rightarrow x + 3(+1) = 0 \Rightarrow x = -3$
$N_3H \Rightarrow 3x + 1(+1) = 0$
$\Rightarrow\ 3x + 1 = 0 \Rightarrow x = -1/3$
$NH_2OH \Rightarrow x + 2 + 1(-2) + 1 = 0$
$\Rightarrow\ x + 1 = 0 \Rightarrow x = -1$
Thus, highest oxidation state is $-1/3$.

2. **(b) :** For strong π-bonding, $p\pi$ - $p\pi$ bonding should be strong. In case of P, due to larger size as compared to N-atom, $p\pi$ - $p\pi$ bonding is not so strong.

3. **(c) :** Among N, P, As and Sb, the former has highest electronegativity (*EN*) so its oxide is most acidic.
As the electronegativity value of element increases, the acidic character of the oxide also increases.

4. **(c) :** Due to greater electronegativity of nitrogen, dipole moment for NH_3 is greater.

5. **(a) :** All the hydrides of group V elements have one lone pair of electrons on their central atom. Therefore, they can act as Lewis bases. The basic character of these hydrides decreases down the group.

6. **(a) :** The acidic character of the oxides decreases with the decrease in the oxidation state and also decreases down the group.

7. **(a) :** Nitrogen cannot form pentahalides because it cannot expand its octet due to non-availability of *d*-orbitals.

8. **(b) :** Boiling point of hydrides increases with increase in atomic number but ammonia has exceptionally high boiling point due to hydrogen bonding. Thus, the correct order of boiling point is,

$$BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$$

9. **(a) :** Nitrogen molecule is diatomic containing a triple bond between two N atoms, $\ddot{N}\equiv\ddot{N}$ therefore, nitrogen molecule is formed by sharing six electrons.

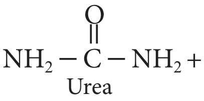
10. **(d) :** N_2 molecule contains triple bond between N atoms having very high dissociation energy (946 kJ mol^{-1}) due to which it is relatively inactive.

11. **(d) :** $NH_4Cl + NaNO_2 \xrightarrow{\text{Heat}} NH_4NO_2 + NaCl$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

12. **(b) :** In case of nitrogen, *d*-orbitals are not available for bonding. N : $1s^2\ 2s^2\ 2p^3$

13. (b) :



$$\underset{\text{Urea}}{NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + H_2O \longrightarrow \underset{(A)}{NH_2COONH_4} \longrightarrow \underset{(B)}{2NH_3 + CO_2}$$

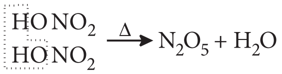
$$Cu^{2+}_{(aq)} + 4NH_3 \longrightarrow \underset{\substack{\text{(deep blue)}\\(C)}}{[Cu(NH_3)_4]^{2+}_{(aq)}}$$

14. (d) : Aqueous solution of ammonia contains NH_4^+ and OH^- ions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

15. (a) : NO_2 is paramagnetic due to the presence of one unpaired electron.

16. (c) : When two molecules of nitric acid undergoes heating, loose a water molecule to form an anhydride.



$$\begin{matrix}HO\,NO_2\\HO\,NO_2\end{matrix} \xrightarrow{\Delta} N_2O_5 + H_2O$$

Thus, N_2O_5 is nitric acid anhydride.

17. (c) : $Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

18. (d) : Zinc is on the top position of hydrogen in electrochemical series. So, Zn displaces H_2 from dilute H_2SO_4 and HCl with liberation of H_2.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

On the other hand, HNO_3 is one oxidising agent. Hydrogen obtained in the reaction is converted into H_2O.

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$2H + O \longrightarrow H_2O$$

19. (b) : $\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{From }HNO_3}{18[O]} \longrightarrow \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O$

20. (b) : White phosphorus has low ignition temperature so it is most reactive among all the allotropes.

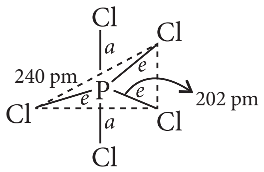
21. (a) : Red phosphorus is insoluble in CS_2 and only white P is soluble in CS_2.

22. (a) : $\underset{(X)}{Ca_3P_2} + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{\substack{(Y)\\\text{(Rotten}\\\text{fish smell)}}}{2PH_{3(g)}}$

$3CuSO_4 + \underset{(Y)}{2PH_3} \longrightarrow \underset{\substack{\text{(Copper}\\\text{phosphide)}}}{Cu_3P_2} + 3H_2SO_4$

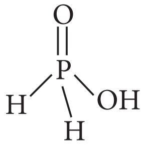
23. (a) : $PH_4I + NaOH \rightarrow NaI + PH_3 + H_2O$

24. (a) : It is a reactive gas as it easily provides Cl_2 gas.

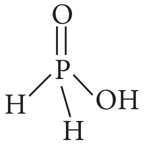


25. (b) : $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

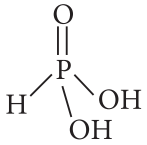
26. (c) : Acids which contain P – H bonds have strong reducing properties. Among the given compounds, H_3PO_2 is the strongest reducing agent as it contains two P – H bonds.



27. (a) :

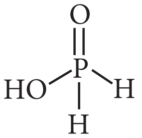


H_3PO_2
Hypophosphorous acid
or Phosphinic acid
(Monobasic)

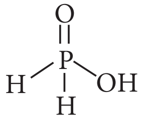


H_3PO_3
Orthophosphorous acid
or Phosphonic acid
(Dibasic)

28. (d) : All oxyacids of phosphorus which have P—H bonds act as strong reducing agents. H_3PO_2 has two P—H bonds hence, it acts as a strong reducing agent.



29. (b) : Hypophosphorous acid is a monoprotic acid.



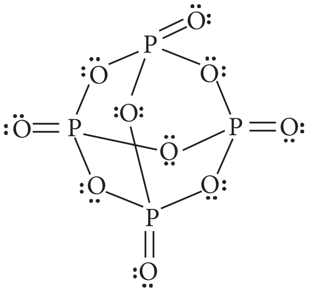
30. (d) : The oxidation state can be calculated as :

$H_4P_2O_5 : +4 + 2x + 5(-2) = 0 \Rightarrow 2x - 6 = 0 \Rightarrow x = +3$

$H_4P_2O_6 : +4 + 2x + 6(-2) = 0 \Rightarrow 2x - 8 = 0 \Rightarrow x = +4$

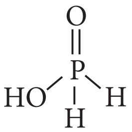
$H_4P_2O_7 : +4 + 2x + 7(-2) = 0 \Rightarrow 2x - 10 = 0 \Rightarrow x = +5$

31. (a) :



32. (c) : The formula of hypophosphorous acid is H_3PO_2 as shown in (c). It is a monobasic acid.

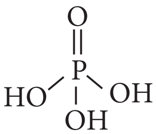
33. (c) : H_3PO_2 is named as hypophosphorous acid. As it contains only one P—OH group, its basicity is one.



34. (a) : P_2O_5 absorbs moisture much readily than anhydrous $CaCl_2$.

35. (d) : $P_2O_5 + 3H_2O \xrightarrow{\Delta} 2H_3PO_4$

36. (b) : Orthophosphoric acid, H_3PO_4 contains three P—OH groups and is therefore, tribasic.



37. (d) : On heating, it gives pyrophosphoric acid at 525 K and metaphosphoric acid at 875 K.

$$\underset{\text{Orthophosphoric acid}}{2H_3PO_4} \xrightarrow[-H_2O]{525\ K} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[-H_2O]{875\ K} \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

38. (d) : The thermal stability of hydrides decreases from H_2O to H_2Po. This is because as the size of atom E in H_2E increases, the bond H–E becomes weaker and thus, breaks on heating. Therefore, the correct order of thermal stability is $H_2Po < H_2Te < H_2Se < H_2S < H_2O$.

39. (a) : As the atomic size increases down the group, the bond length increases and the bond strength decreases and the cleavage of E–H bond becomes easier thus, more will be the acidity. Thus, the correct order is : $H_2S < H_2Se < H_2Te$.

40. (a) : Bond energy of S — S is exceptionally high due to its catenation tendency.

B.E.	O — O	S — S	Se — Se	Te — Te
(kJ mol^{-1}) :	142	226	172	126

41. (b) : $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2 + 3O_2$

$KClO_3 \xrightarrow{\Delta} KCl + 3/2O_2$

$2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + 3/2O_2$

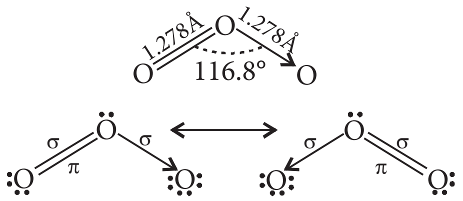
42. (a) : Alkaline solution of pyrogallol absorbs oxygen quickly.

43. (b) : Chlorine does not react directly with oxygen.

44. (c) : Air is liquefied by making use of the Joule - Thomson effect (cooling by expansion of the gas). Water vapour and CO_2 are removed by solidification. The remaining constituents of liquid air *i.e.*, liquid oxygen and liquid nitrogen are separated by means of fractional distillation as fractional distillation is a process of separation of mixture based on the difference in their boiling points. (b.pt. of O_2 = –183°C : b.pt. of N_2 = –195.8°C).

45. (b) : CO — neutral, BaO — basic, Al_2O_3 — amphoteric and Cl_2O_7 — acidic.

46. (b) : The angular shape of ozone molecule (O_3) :

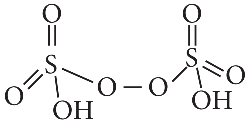


47. (b) : Alkaline pyrogallol absorbs O_2 and oil of cinnamon absorbs O_3.

48. (b) : NO_2 is not used as a food preservative.

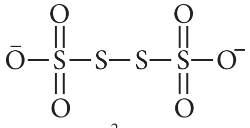
49. (b) : $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

50. (c) : Peroxodisulphuric acid, $H_2S_2O_8$ has — O — O — linkage.

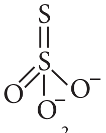


51. (a)

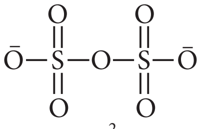
52. (a) :



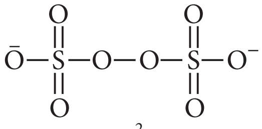
($S_4O_6^{2-}$)



($S_2O_3^{2-}$)

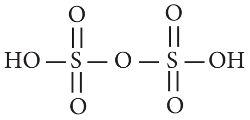


($S_2O_7^{2-}$)



($S_2O_8^{2-}$)

53. (c) : Pyrosulphuric acid or oleum (+6) is $H_2S_2O_7$ which is obtained by dissolving SO_3 and is called fuming sulphuric acid.



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

54. (d)

55. (c) : All halogens show both positive and negative oxidation states while fluorine shows only negative oxidation state except +1 in HOF.

56. (d) : The order of bond dissociation enthalpy is :

	Cl_2 >	Br_2 >	F_2 >	I_2
B.E. (in kJ mol^{-1})	242.6	192.8	158.8	151.1

A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

57. (a) : HF forms strong intermolecular H-bonding due to high electronegativity of F. Hence, the boiling point of HF is abnormally high. Boiling points of other hydrogen halides gradually increase from HCl to HI due to increase in size of halogen atoms from Cl to I which further increase the magnitude of van der Waals' forces.

58. (d) : Standard reduction potentials of halogens are positive and decrease from fluorine to iodine. So, F_2 is the strongest oxidising agent.

59. (a, d) : In case of diatomic molecules (X_2) of halogens the bond dissociation energy decreases in the order : $Cl_2 > Br_2 > F_2 > I_2$. This is due to relatively large electron-electron repulsion among the lone pairs is F_2 than in case of Cl_2.

The oxidising power, electronegativity and reactivity decrease in the order : $F_2 > Cl_2 > Br_2 > I_2$

Electron gain enthalpy of halogens follows the given order :

$$Cl_2 > F_2 > Br_2 > I_2$$

The low value of electron gain enthalpy of fluorine is probably due to small size of fluorine atom.

60. (a) :

$X-X$ bond	F – F	Cl – Cl	Br – Br	I – I
Bond dissociation energy (kcal/mol)	38	57	45.5	35.6

The lower value of bond dissociation energy of fluorine is due to the high inter-electronic repulsions between non-bonding electrons in the 2*p*-orbitals of fluorine. As a result F – F bond is weaker in comparison to Cl – Cl and Br – Br bonds.

61. (a) : Due to more repulsion in between non-bonding electron pairs (2*p*) of two fluorines (due to small size of F-atom) in comparison to non-bonding electron pairs (3*p*) in chlorine, the bond energy of F_2 is less than Cl_2.

$$B.E.\ (F_2) = 158.8 \text{ kJ/mole and}$$
$$B.E.\ (Cl_2) = 242.6 \text{ kJ/mole}$$

62. (d) : In general, the electron affinity decreases from top to bottom in a group. But in group 17, fluorine has lower electron affinity as compared to chlorine due to very small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2*s* orbitals of fluorine and thus, the incoming electron does not experience much attraction.

63. (c) : Since chlorine is stronger oxidising agent than bromine, therefore it will displace bromine from an aqueous solution containing bromide ions.

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

64. (c) : Outer electronic configuration of Cl

$$= 3s^2 3p_x^2 3p_y^2 3p_z^1$$

Outer electronic configuration of Cl^-

$= 3s^2 3p_x^2 3p_y^2 3p_z^2$, *i.e.*, 4 lone pair of electrons

65. (a)

66. (b) : $\overset{0}{3Cl_2} + \underset{\text{(hot and conc.)}}{6NaOH} \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$

This is an example of disproportionation reaction and oxidation state of chlorine changes from 0 to –1 and +5.

67. (a) : $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2\uparrow$

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$

68. (a) : Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode.

69. (c) : $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$

70. (b) : Bromide in the mother liquor (containing $MgBr_2$) is oxidised to Br_2 by passing Cl_2 which is a stronger oxidising agent.

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

71. (d) : Bleaching action of chlorine is due to oxidation in presence of moisture. Bleaching effect is permanent.

$$H_2O + Cl_2 \rightarrow 2HCl + [O]$$

Colouring matter + [O] → Colourless matter

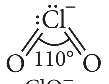
72. (a) : $CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$

73. (d) : The acidic character of the oxoacids increases with increase in oxidation number of the halogen atom *i.e.*, $HClO < HClO_2 < HClO_3 < HClO_4$.

This can be explained on the basis of relative stability of the anions left after removal of a proton. Since the stability of the anion decreases in the order : $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$, acid strength also decreases in the same order.

74. (c) : OF_2 (oxygen difluoride) is a fluoride of oxygen because fluorine is more electronegative than oxygen.

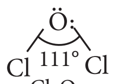
75. (d) :



ClO_2^-

(2 lone pairs)

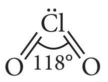
lower bond angle due to lone pair - lone pair



Cl_2O

(2 lone pairs)

High electronegativity of O than Cl so, bond pair is more closer to O atom so higher *lp* - *bp* repulsion



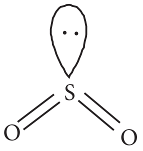
ClO_2

(1 lone pair)

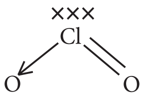
Highest bond angle due to lower lone pair - bond pair repulsion

76. (d) : $O=C=O$ Diamagnetic

$O=Si=O$ Diamagnetic



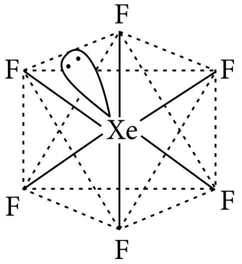
Diamagnetic



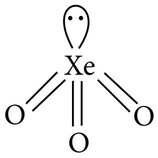
Paramagnetic

77. (a)

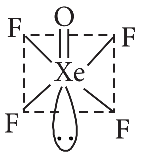
78. (c) :



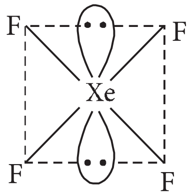
XeF_6
Distorted octahedral
sp^3d^3



XeO_3
Pyramidal
sp^3

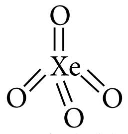


$XeOF_4$
Square pyramidal
sp^3d^2



XeF_4
Square planar
sp^3d^2

79. (a) :



Tetrahedral (sp^3)

80. (a) : In XeF_4 the 'Xe' atom is sp^3d^2 hybridised, which contains two lone pair orbitals and four bond pair orbitals. Therefore, the shape of XeF_4 molecule is square planar, with one lone pair orbital over and other below the plane.

❖❖❖

CHAPTER

8

The *d*- and *f*-Block Elements

8.2 Electronic Configurations of the *d*-Block Elements

1. Sc ($Z = 21$) is a transition element but Zn ($Z = 30$) is not because
(a) both Sc^{3+} and Zn^{2+} ions are colourless and form white compounds
(b) in case of Sc, $3d$ orbitals are partially filled but in Zn these are filled
(c) last electron is assumed to be added to $4s$ level in case of Zn
(d) both Sc and Zn do not exhibit variable oxidation states *(Karnataka NEET 2013)*

2. Which of the following ions has electronic configuration $[Ar]3d^6$?
(a) Ni^{3+} (b) Mn^{3+} (c) Fe^{3+} (d) Co^{3+}
(At. nos. Mn = 25, Fe = 26, Co = 27, Ni = 28) *(2010)*

3. Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is
[At. nos. Ti = 22, V = 23, Cr = 24, Mn = 25]
(a) $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$
(b) $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{7+}$
(c) $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$
(d) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$ *(2004)*

4. Which of the following configuration is correct for iron?
(a) $1s^22s^22p^63s^23p^64s^23d^7$ (b) $1s^22s^22p^63s^23p^64s^23d^5$
(c) $1s^22s^22p^63s^23p^63d^5$ (d) $1s^22s^22p^63s^23p^64s^23d^6$
(1999)

5. Which of the following has more unpaired *d*-electrons?
(a) N^{3+} (b) Fe^{2+} (c) Zn^{+} (d) Cu^{+}
(1999)

6. The electronic configuration of transition elements is exhibited by
(a) ns^1 (b) ns^2np^5
(c) $ns^2(n-1)d^{1-10}$ (d) $ns^2(n-1)d^{10}$ *(1996)*

7. The electronic configurations of four elements are given below. Which element does not belong to the same family as others?
(a) $[Xe]4f^{14}5d^{10}6s^2$ (b) $[Kr]4d^{10}5s^2$
(c) $[Ne]3s^23p^5$ (d) $[Ar]3d^{10}4s^2$ *(1989)*

8.3 General Properties of the Transition Elements (*d*-Block)

8. Identify the incorrect statement.
(a) Cr^{2+} (d^4) is a stronger reducing agent than Fe^{2+} (d^6) in water.
(b) The transition metals and their compounds are known for their catalytic activity due to their ability to adopt multiple oxidation states and to form complexes.
(c) Interstitial compounds are those that are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.
(d) The oxidation states of chromium in CrO_4^{2-} and $Cr_2O_7^{2-}$ are not the same. *(NEET 2020)*

9. The calculated spin only magnetic moment of Cr^{2+} ion is
(a) 3.87 BM (b) 4.90 BM
(c) 5.92 BM (d) 2.84 BM
(NEET 2020)

10. Match the metal ions given in Column-I with the spin magnetic moments of the ions given in Column-II and assign the correct code :

Column-I	**Column-II**
A. Co^{3+}	(i) $\sqrt{8}$ B.M.
B. Cr^{3+}	(ii) $\sqrt{35}$ B.M.
C. Fe^{3+}	(iii) $\sqrt{3}$ B.M.
D. Ni^{2+}	(iv) $\sqrt{24}$ B.M.
	(v) $\sqrt{15}$ B.M.

	A	B	C	D	
(a)	(iv)	(v)	(ii)	(i)	
(b)	(i)	(ii)	(iii)	(iv)	
(c)	(iv)	(i)	(ii)	(iii)	
(d)	(iii)	(v)	(i)	(ii)	*(NEET 2018)*

11. Magnetic moment 2.84 B.M. is given by
(At. nos. Ni = 28, Ti = 22, Cr = 24, Co = 27)
(a) Cr^{2+} (b) Co^{2+} (c) Ni^{2+} (d) Ti^{3+}
(2015, Cancelled)

12. Which of the following processes does not involve oxidation of iron?
(a) Formation of $Fe(CO)_5$ from Fe.
(b) Liberation of H_2 from steam by iron at high temperature.
(c) Rusting of iron sheets.
(d) Decolourisation of blue $CuSO_4$ solution by iron. *(2015, Cancelled)*

13. Which of the following statements about the interstitial compounds is incorrect?
(a) They are much harder than the pure metal.
(b) They have higher melting points than the pure metal.
(c) They retain metallic conductivity.
(d) They are chemically reactive. *(NEET 2013)*

14. Identify the alloy containing a non-metal as a constituent in it.
(a) Invar (b) Steel
(c) Bell metal (d) Bronze *(2012)*

15. The catalytic activity of transition metals and their compounds is ascribed mainly to
(a) their magnetic behaviour
(b) their unfilled *d*-orbitals
(c) their ability to adopt variable oxidation states
(d) their chemical reactivity. *(Mains 2012)*

16. Which one of the following does not correctly represent the correct order of the property indicated against it?
(a) Ti < V < Cr < Mn; increasing number of oxidation states
(b) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$: increasing magnetic moment
(c) Ti < V < Cr < Mn : increasing melting points
(d) Ti < V < Mn < Cr : increasing 2nd ionization enthalpy *(Mains 2012)*

17. Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential ($E°_{M^{2+}/M}$) value has a positive sign?
(a) Co (Z = 27) (b) Ni (Z = 28)
(c) Cu (Z = 29) (d) Fe (Z = 26)
(Mains 2012)

18. For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order?
(a) Mn > Fe > Cr > Co (b) Fe > Mn > Co > Cr
(c) Co > Mn > Fe > Cr (d) Cr > Mn > Co > Fe
(At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27) *(2011)*

19. Which of the following ions will exhibit colour in aqueous solutions?
(a) La^{3+} (Z = 57) (b) Ti^{3+} (Z = 22)
(c) Lu^{3+} (Z = 71) (d) Sc^{3+} (Z = 21) *(2010)*

20. Which of the following pairs has the same size?
(a) Fe^{2+}, Ni^{2+} (b) Zr^{4+}, Ti^{4+}
(c) Zr^{4+}, Hf^{4+} (d) Zn^{2+}, Hf^{4+} *(2010)*

21. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states?
(a) $3d^54s^1$ (b) $3d^54s^2$
(c) $3d^24s^2$ (d) $3d^34s^2$ *(2009)*

22. The correct order of decreasing second ionisation enthalpy of Ti(22), V(23), Cr(24) and Mn(25) is
(a) Mn > Cr > Ti > V (b) Ti > V > Cr > Mn
(c) Cr > Mn > V > Ti (d) V > Mn > Cr > Ti
(2008)

23. In which of the following pairs are both the ions coloured in aqueous solution?
(At. no. : Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)
(a) Ni^{2+}, Cu^{+} (b) Ni^{2+}, Ti^{3+}
(c) Sc^{3+}, Ti^{3+} (d) Sc^{3+}, Co^{2+} *(2006)*

24. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionisation enthalpy?
(a) Vanadium (Z = 23)
(b) Chromium (Z = 24)
(c) Manganese (Z = 25)
(d) Iron (Z = 26) *(2005)*

25. The aqueous solution containing which one of the following ions will be colourless?
(Atomic number : Sc = 21, Fe = 26, Ti = 22, Mn = 25)
(a) Sc^{3+} (b) Fe^{2+}
(c) Ti^{3+} (d) Mn^{2+} *(2005)*

26. Which one of the following characteristics of the transition metals is associated with their catalytic activity?
(a) High enthalpy of atomization
(b) Paramagnetic behaviour
(c) Colour of hydrated ions
(d) Variable oxidation states *(2003)*

27. The basic character of the transition metal monoxides follows the order
(Atomic no's. Ti = 22, V = 23, Cr = 24, Fe = 26)
(a) VO > CrO > TiO > FeO
(b) CrO > VO > FeO > TiO
(c) TiO > FeO > VO > CrO
(d) TiO > VO > CrO > FeO *(2003)*

28. Which of the following shows maximum number of oxidation states?
(a) Cr (b) Fe
(c) Mn (d) V *(2002, 2000, 1994)*

29. Which ion is colourless?
(a) Cr^{4+} (b) Sc^{3+}
(c) Ti^{3+} (d) V^{3+} *(2000)*

30. Bell metal is an alloy of
(a) Cu + Zn (b) Cu + Sn
(c) Cu + Pb (d) Cu + Ni *(1999)*

31. In which of the following compounds transition metal has zero oxidation state?
(a) $NOClO_4$ (b) NH_2NH_2
(c) CrO_5 (d) $[Fe(CO)_5]$ *(1999)*

32. Which one of the following ionic species will impart colour to an aqueous solution?
(a) Zn^{2+} (b) Cu^+
(c) Ti^{4+} (d) Cr^{3+} *(1998)*

33. A transition element *X* has a configuration $[Ar]3d^4$ in its +3 oxidation state. Its atomic number is
(a) 22 (b) 19
(c) 25 (d) 26 *(1996)*

34. Amongst TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$, which are the colourless species? (Atomic number of Ti = 22, Co = 27, Cu = 29, Ni = 28)
(a) CoF_6^{3-} and $NiCl_4^{2-}$ (b) TiF_6^{2-} and Cu_2Cl_2
(c) Cu_2Cl_2 and $NiCl_4^{2-}$ (d) TiF_6^{2-} and CoF_6^{3-}
(1995)

35. The mercury is the only metal which is liquid at 0°C. This is due to its
(a) high vapour pressure
(b) weak metallic bond
(c) high ionization energy
(d) both (b) and (c). *(1995)*

8.4 Some Important Compounds of Transition Elements

36. The manganate and permanganate ions are tetrahedral, due to
(a) the π-bonding involves overlap of *d*-orbitals of oxygen with *d*-orbitals of manganese
(b) the π-bonding involves overlap of *p*-orbitals of oxygen with *d*-orbitals of manganese
(c) there is no π-bonding
(d) the π-bonding involves overlap of *p*-orbitals of oxygen with *p*-orbitals of manganese.
(NEET 2019)

37. When neutral or faintly alkaline $KMnO_4$ is treated with potassium iodide, iodide ion is converted into '*X*'. '*X*' is
(a) I_2 (b) IO_4^- (c) IO_3^- (d) IO^-
(Odisha NEET 2019)

38. Which one of the following ions exhibits *d-d* transition and paramagnetism as well?
(a) CrO_4^{2-} (b) $Cr_2O_7^{2-}$
(c) MnO_4^- (d) MnO_4^{2-} *(NEET 2018)*

39. Name the gas that can readily decolourise acidified $KMnO_4$ solution.
(a) SO_2 (b) NO_2
(c) P_2O_5 (d) CO_2 *(NEET 2017)*

40. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution?
(a) SO_2 is reduced.
(b) Green $Cr_2(SO_4)_3$ is formed.
(c) The solution turns blue.
(d) The solution is decolourised. *(NEET-I 2016)*

41. Assuming complete ionisation, same moles of which of the following compounds will require the least amount of acidified $KMnO_4$ for complete oxidation?
(a) $FeSO_3$ (b) FeC_2O_4
(c) $Fe(NO_2)_2$ (d) $FeSO_4$ *(2015)*

42. The reaction of aqueous $KMnO_4$ with H_2O_2 in acidic conditions gives
(a) Mn^{4+} and O_2 (b) Mn^{2+} and O_2
(c) Mn^{2+} and O_3 (d) Mn^{4+} and MnO_2.
(2014)

43. Which of the statements is not true?
(a) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed.
(b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis.
(c) $K_2Cr_2O_7$ solution in acidic medium is orange.
(d) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7. *(2012)*

44. Acidified $K_2Cr_2O_7$ solution turns green when Na_2SO_3 is added to it. This is due to the formation of
(a) $Cr_2(SO_4)_3$ (b) CrO_4^{2-}
(c) $Cr_2(SO_3)_3$ (d) $CrSO_4$ *(2011)*

45. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is
(a) one (b) two
(c) five (d) one fifth. *(2005)*

46. $K_2Cr_2O_7$ on heating with aqueous NaOH gives
(a) $Cr_2O_7^{2-}$ (b) $Cr(OH)_2$
(c) CrO_4^{2-} (d) $Cr(OH)_3$ *(1997)*

47. $KMnO_4$ reacts with oxalic acid according to the equation
$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
Here 20 mL of 0.1 M $KMnO_4$ is equivalent to
(a) 50 mL of 0.5 M $C_2H_2O_4$
(b) 20 mL of 0.1 M $C_2H_2O_4$
(c) 20 mL of 0.5 M $C_2H_2O_4$
(d) 50 mL of 0.1 M $C_2H_2O_4$ *(1996)*

48. The oxidation state of Cr in $K_2Cr_2O_7$ is
(a) +5 (b) +3
(c) +6 (d) +7 *(1988)*

8.5 The Lanthanoids

49. Which one of the following statements related to lanthanons is incorrect?
(a) Europium shows +2 oxidation state.
(b) The basicity decreases as the ionic radius decreases from Pr to Lu.
(c) All the lanthanons are much more reactive than aluminium.
(d) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis. *(NEET-II 2016)*

50. The electronic configurations of Eu (Atomic No. 63), Gd (Atomic No. 64) and Tb (Atomic No. 65) are
(a) $[Xe]4f^6 5d^1 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^8 5d^1 6s^2$
(b) $[Xe]4f^7 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^9 6s^2$
(c) $[Xe]4f^7 6s^2$, $[Xe]4f^8 6s^2$ and $[Xe]4f^8 5d^1 6s^2$
(d) $[Xe]4f^6 5d^1 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^9 6s^2$
(NEET-I 2016)

51. Gadolinium belongs to 4*f* series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?
(a) $[Xe]\ 4f^9 5s^1$ (b) $[Xe]\ 4f^7 5d^1 6s^2$
(c) $[Xe]\ 4f^6 5d^2 6s^2$ (d) $[Xe]\ 4f^8 6d^2$
(2015, 1997)

52. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers)
(a) Zr(40) and Hf(72) (b) Zr(40) and Ta(73)
(c) Ti(22) and Zr(40) (d) Zr(40) and Nb(41)
(2015, Cancelled)

53. Reason of lanthanoid contraction is
(a) negligible screening effect of '*f*'-orbitals
(b) increasing nuclear charge
(c) decreasing nuclear charge
(d) decreasing screening effect. *(2014)*

54. Which of the following lanthanoid ions is diamagnetic?
(At. nos. Ce = 58, Sm = 62, Eu = 63, Yb = 70)
(a) Eu^{2+} (b) Yb^{2+} (c) Ce^{2+} (d) Sm^{2+}
(NEET 2013)

55. Which of the following oxidation states is the most common among the lanthanoids?
(a) 4 (b) 2 (c) 5 (d) 3
(Mains 2010)

56. Identify the incorrect statement among the following :
(a) Lanthanoid contraction is the accumulation of successive shrinkages.
(b) As a result of lanthanoid contraction, the properties of 4*d* series of the transition elements have no similarities with the 5*d* series of elements.
(c) Shielding power of 4*f* electrons is quite weak.
(d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu. *(2007)*

57. Lanthanoids are
(a) 14 elements in the sixth period (atomic no. 90 to 103) that are filling 4*f* sublevel
(b) 14 elements in the seventh period (atomic number = 90 to 103) that are filling 5*f* sublevel
(c) 14 elements in the sixth period (atomic number = 58 to 71) that are filling the 4*f* sublevel
(d) 14 elements in the seventh period (atomic number = 58 to 71) that are filling 4*f* sublevel.
(2004)

58. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is (At. nos. Y = 39, La = 57, Eu = 63, Lu = 71)
(a) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
(b) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
(c) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$
(d) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$ *(2003)*

59. General electronic configuration of lanthanides is
(a) $(n-2)f^{1-14}(n-1)s^2p^6d^{0-1}ns^2$
(b) $(n-2)f^{10-14}(n-1)d^{0-1}ns^2$
(c) $(n-2)f^{0-14}(n-1)d^{10}ns^2$
(d) $(n-2)d^{0-1}(n-1)f^{1-14}ns^2$ *(2002)*

60. Which of the following statement is not correct?
(a) $La(OH)_3$ is less basic than $Lu(OH)_3$.
(b) In lanthanide series ionic radius of Ln^{+3} ion decreases.
(c) La is actually an element of transition series rather lanthanides.
(d) Atomic radius of Zn and Hf are same because of lanthanide contraction. *(2001)*

61. The lanthanide contraction is responsible for the fact that
(a) Zr and Hf have about the same radius
(b) Zr and Zn have the same oxidation state
(c) Zr and Y have about the same radius
(d) Zr and Nb have similar oxidation state. *(1997)*

62. Which of the following statements concerning lanthanide elements is false?
(a) All lanthanides are highly dense metals.
(b) More characteristic oxidation state of lanthanide elements is +3.
(c) Lanthanides are separated from one another by ion exchange method.
(d) Ionic radii of trivalent lanthanides steadily increases with increase in the atomic number. *(1994)*

8.6 The Actinoids

63. The reason for greater range of oxidation states in actinoids is attributed to
(a) actinoid contraction
(b) 5*f*, 6*d* and 7*s* levels having comparable energies
(c) 4*f* and 5*d* levels being close in energies
(d) the radioactive nature of actinoids. *(NEET 2017)*

64. Which of the following exhibits only +3 oxidation state?
(a) U (b) Th
(c) Ac (d) Pa *(Mains 2012)*

65. More number of oxidation states are exhibited by the actinoids than by the lanthanoids. The main reason for this is
(a) more active nature of the actinoids
(b) more energy difference between 5*f* and 6*d* orbitals than that between 4*f* and 5*d* orbitals
(c) lesser energy difference between 5*f* and 6*d* orbitals than that between 4*f* and 5*d* orbitals
(d) greater metallic character of the lanthanoids than that of the corresponding actinoids. *(2006, 2005)*

66. Which one of the following elements shows maximum number of different oxidation states in its compounds?
(a) Gd (b) La
(c) Eu (d) Am *(1998)*

8.7 Some Applications of *d*- and *f*-Block Elements

67. Match the catalyst with the process :

Catalyst	**Process**
(i) V_2O_5	(p) The oxidation of ethyne to ethanal
(ii) $TiCl_4 + Al(CH_3)_3$	(q) Polymerisation of alkynes
(iii) $PdCl_2$	(r) Oxidation of SO_2 in the manufacture of H_2SO_4
(iv) Nickel complexes	(s) Polymerisation of ethylene

Which of the following is the correct option?
(a) (i)-(r), (ii)-(s), (iii)-(p), (iv)-(q)
(b) (i)-(p), (ii)-(q), (iii)-(r), (iv)-(s)
(c) (i)-(p), (ii)-(r), (iii)-(q), (iv)-(s)
(d) (i)-(r), (ii)-(p), (iii)-(s), (iv)-(q) *(Odisha NEET 2019)*

68. $HgCl_2$ and I_2 both when dissolved in water containing I^- ions, the pair of species formed is
(a) HgI_2, I^- (b) HgI_4^{2-}, I_3^-
(c) Hg_2I_2, I^- (d) HgI_2, I_3^- *(NEET 2017)*

69. Which of the following elements is responsible for oxidation of water to O_2 in biological processes?
(a) Cu (b) Mo
(c) Fe (d) Mn *(1997)*

70. When calomel reacts with NH_4OH, we get
(a) Hg_2O (b) HgO
(c) $HgNH_2Cl$ (d) $NH_2–Hg–Hg–Cl$ *(1996)*

71. Photographic films and plates have an essential ingredient of
(a) silver nitrate (b) silver bromide
(c) sodium chloride (d) oleic acid. *(1989)*

ANSWER KEY

1.	(b)	**2.**	(d)	**3.**	(d)	**4.**	(d)	**5.**	(b)	**6.**	(c)	**7.**	(c)	**8.**	(d)	**9.**	(b)	**10.**	(a)
11.	(c)	**12.**	(a)	**13.**	(d)	**14.**	(b)	**15.**	(c)	**16.**	(c)	**17.**	(c)	**18.**	(a)	**19.**	(b)	**20.**	(c)
21.	(b)	**22.**	(c)	**23.**	(b)	**24.**	(c)	**25.**	(a)	**26.**	(d)	**27.**	(d)	**28.**	(c)	**29.**	(b)	**30.**	(b)
31.	(d)	**32.**	(d)	**33.**	(c)	**34.**	(b)	**35.**	(d)	**36.**	(b)	**37.**	(c)	**38.**	(d)	**39.**	(a)	**40.**	(b)
41.	(d)	**42.**	(b)	**43.**	(b)	**44.**	(a)	**45.**	(b)	**46.**	(c)	**47.**	(d)	**48.**	(c)	**49.**	(c)	**50.**	(b)
51.	(b)	**52.**	(a)	**53.**	(a)	**54.**	(b)	**55.**	(d)	**56.**	(b)	**57.**	(c)	**58.**	(b)	**59.**	(a)	**60.**	(a)
61.	(a)	**62.**	(d)	**63.**	(b)	**64.**	(c)	**65.**	(c)	**66.**	(d)	**67.**	(a)	**68.**	(b)	**69.**	(c)	**70.**	(c)
71.	(b)																		

Hints & Explanations

1. (b) : Sc ($Z = 21$) has incompletely filled $3d$-orbitals in its ground state ($3d^1$), it is considered as a transition element but Zn ($Z = 30$) has completely filled d-orbitals ($3d^{10}$) in its ground state and its common oxidation state (+2), thus, it is not considered as a transition element.

2. (d) : The electronic configuration of the given ions is :

Ni^{3+} : $[Ar]3d^7 4s^0$, Mn^{3+} : $[Ar]3d^4 4s^0$

Fe^{3+} : $[Ar]3d^5 4s^0$, Co^{3+} : $[Ar]3d^6 4s^0$

Thus, Co^{3+} is the ion with the desired configuration.

3. (d) : ${}_{22}Ti = 3d^2\ 4s^2$; $Ti^{2+} = 3d^2$

${}_{23}V = 3d^3\ 4s^2$; $V^{3+} = 3d^2$

${}_{24}Cr = 3d^4\ 4s^2$; $Cr^{4+} = 3d^2$

${}_{25}Mn = 3d^5\ 4s^2$; $Mn^{5+} = 3d^2$

4. (d) **5. (b)**

6. (c) : General electronic configuration of transition elements is $ns^2\ (n-1)d^{1-10}$.

7. (c) : $[Ne]3s^2 3p^5$ is the electronic configuration of a p-block element whereas other configurations are those of d-block elements.

8. (d) : The oxidation states of Cr in CrO_4^{2-} and $Cr_2O_7^{2-}$ is same *i.e.*, +6.

9. (b) : Cr : $3d^5\ 4s^1$, Cr^{2+} : $3d^4$ has four unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90 \text{ B.M.}$$

10. (a) : Co^{3+} : $[Ar]3d^6$, unpaired $e^-(n) = 4$

Spin magnetic moment (μ) $= \sqrt{4(4+2)} = \sqrt{24}$ B.M.

Cr^{3+} : $[Ar]3d^3$, unpaired $e^-(n) = 3$

Spin magnetic moment (μ) $= \sqrt{3(3+2)} = \sqrt{15}$ B.M.

Fe^{3+} : $[Ar]3d^5$, unpaired $e^-(n) = 5$

Spin magnetic moment (μ) $= \sqrt{5(5+2)} = \sqrt{35}$ B.M.

Ni^{2+} : $[Ar]3d^8$, unpaired $e^-(n) = 2$

Spin magnetic moment (μ) $= \sqrt{2(2+2)} = \sqrt{8}$ B.M.

11. (c) : Magnetic moment (μ) $= \sqrt{n(n+2)}$

2.84 B.M. corresponds to 2 unpaired electrons.

Cr^{2+} – $3d^4$, 4 unpaired electrons

Co^{2+} – $3d^7$, 3 unpaired electrons

Ni^{2+} – $3d^8$, 2 unpaired electrons

Ti^{3+} – $3d^1$, 1 unpaired electron

12. (a) : Oxidation number of Fe in $Fe(CO)_5$ is zero.

13. (d) : Interstitial compounds are generally chemically inert.

14. (b) : Invar ⇒ Ni(metal) + Fe(metal)

Steel ⇒ C(non-metal) + Fe(metal)

Bell ⇒ Cu(metal) + Sn(metal) + Fe(metal)

Bronze ⇒ Cu(metal) + Sn(metal)

15. (c)

16. (c) :

Element :	Ti	< V	< Cr	< Mn
No. of oxidation states :	+3	+4	+5	+6

Hence, given order is correct.

Magnetic moment (μ) $= \sqrt{n(n+2)}$ B.M.

For Ti^{3+} $n = 1$, $\mu = \sqrt{1(1+2)} = \sqrt{3}$ B.M.

For V^{3+} $n = 2$, $\mu = \sqrt{2(2+2)} = \sqrt{8}$ B.M.

For Cr^{3+} $n = 3$, $\mu = \sqrt{3(3+2)} = \sqrt{15}$ B.M.

For Mn^{3+} $n = 4$, $\mu = \sqrt{4(4+2)} = \sqrt{24}$ B.M.

Thus, magnetic moment order : $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$

Melting point order :	Mn	< Ti	< Cr	< V
	1245°C	1668°C	1875°C	1900°C

2nd ionisation enthalpy order

	Ti	< V	< Mn	< Cr
(in kJ/mol) :	1309	1414	1509	1592

17. (c) :

Element	Co	Ni	Cu	Fe
$E^\circ_{M^{2+}/M}$ (V)	– 0.28	–0.25	+0.34	–0.44

18. (a) : Spin correlation and exchange energy gives an electronic configuration a special stability which is greatest for half-filled electronic configurations.

Mn^{2+} (d^5) gets stabilisation due to half-filled configuration.

In Fe^{2+} (d^6) the placing of one extra electron in a subshell destabilises. Placing of 2 electrons in Co^{2+} (d^7) destabilises it more. Cr^{2+} (d^4) has one vacant subshell. Fe^{2+} gets more stabilisation compared to Cr^{2+} through exchange energy. So, the order is as follows : Mn > Fe > Cr > Co.

19. (b) : Ions which have unpaired electrons exhibit colour in aqueous solution. Ti^{3+} has an outer electronic configuration of $4s^0 3d^1$, *i.e.*, 1 unpaired electron. Thus, its solution will be coloured. Others are colourless due to empty or completely filled outermost orbitals.

20. (c) : Hf^{4+} and Zr^{4+} belong to group IVB. But, Hf^{4+} has same size as Zr^{4+} due to the addition of 14 lanthanide elements before it in which electrons are added into the f-subshell which poorly shield the outer electrons and contraction in size occurs.

21. (b) : Greater the number of valence electrons, more will be the number of oxidation states exhibited by the element.

$3d^5 4s^1$, can show a maximum of 6 oxidation states.

$3d^54s^2$, can show a maximum of 7 oxidation states.
$3d^24s^2$ can show a maximum of 4 oxidation states.
$3d^34s^2$ can show a maximum of 5 oxidation states.

22. (c) : Electronic configuration of the given elements are

Mn : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Cr : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Ti : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
V : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

In general, ionization potential (both 1st and 2nd) increases from left to right across the period due to increase in effective nuclear charge. On this basis, the second IP values should exhibit the trend :

$$\text{Mn} > \text{Cr} > \text{V} > \text{Ti}$$

But the actual observed order is : Cr > Mn > V > Ti
Practically, only chromium is exceptional and rest others show the normal trend. This exceptional behaviour of chromium is due to the stable configuration ($3d^5$) that it achieves after the loss of first electron.

23. (b) :

Sc : $[Ar]\ 3d^1\ 4s^2$, Sc^{3+} :	$[Ar]$	Colourless
Ti : $[Ar]3d^2\ 4s^2$, Ti^{3+} :	$[Ar]3d^1$	Coloured
Ni : $[Ar]3d^8\ 4s^2$, Ni^{2+} :	$[Ar]3d^8$	Coloured
Cu : $[Ar]3d^{10}\ 4s^1$, Cu^+ :	$[Ar]3d^{10}$	Colourless
Co : $[Ar]3d^7\ 4s^2$, Co^{2+} :	$[Ar]3d^7$	Coloured

Ti^{3+}, Ni^{2+} and Co^{2+} are coloured due to presence of unpaired electrons.

24. (c) : V^{2+} (23) : $[Ar]3d^3\ 4s^0$
Cr^{2+} (24) : $[Ar]3d^4\ 4s^0$
Mn^{2+} (25) : $[Ar]3d^5\ 4s^0$
Fe^{2+} (26) : $[Ar]3d^5\ 4s^1$

$\Rightarrow\ I.E_3\,(\text{Mn}) > I.E_3\,(\text{Cr}) > I.E_3\,(\text{Fe}) > I.E_3\,(\text{V})$
3260 2990 2962 2833

25. (a) : If the transition metal ion has unpaired electron then it shows colour.

Sc^{3+} : $[Ar]3d^0\ 4s^0$
Fe^{2+} : $[Ar]3d^5\ 4s^1$
Ti^{3+} : $[Ar]3d^1\ 4s^0$
Mn^{2+} : $[Ar]3d^5\ 4s^0$

Sc^{3+} does not contain unpaired electron, hence it will not undergo $d - d$ transition and do not show colour.

26. (d) : The transition elements, on account of their variable valency, are able to form unstable intermediate compounds very readily.

27. (d) : The order of basicity of transition metal monoxides is, TiO > VO > CrO > FeO.

28. (c) : Each of the element in group III B to VII B can show the maximum oxidation state equal to its group number. Mn is in group seven shows a maximum oxidation state of +7 in $KMnO_4$.

29. (b) : $_{21}Sc$: $[Ar]\ 3d^14s^2$
In Sc^{3+} there is no unpaired 'd' electrons, therefore it is colourless in its solution.

30. (b) : Bell metal $\Rightarrow$ Cu = 80%, Sn = 20%
It is used for making bells, utensils, etc.

31. (d) : In iron carbonyl, the oxidation number of 'Fe' is zero.

$$[Fe(CO)_5] : x + 5 \times 0 = 0 \ \Rightarrow\ x = 0$$

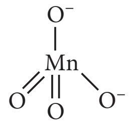
32. (d) : $Cr^{3+}(24) : 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$
As Cr^{3+} ion has three unpaired electrons in its valence shell, so it imparts colour to an aqueous solution.

33. (c) : The metal atom will have three more electrons.
Therefore, the atomic number of the metal = 18 + 4 + 3
= 25

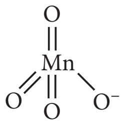
34. (b) : In TiF_6^{2-} titanium is in +4 oxidation state. In Cu_2Cl_2, the copper is in +1 state. Thus, in both cases, transition from one d-orbital to other is not possible.
Ti : $[Ar]\ 3d^24s^2 \rightarrow Ti^{4+} : [Ar]3d^04s^0$
Cu : $[Ar]\ 3d^{10}4s^1 \rightarrow Cu^+ : [Ar]3d^{10}4s^0$

35. (d) : Very high ionisation energy of Hg makes it difficult for electrons to participate in metallic bonding.

36. (b) :



Tetrahedral
Manganate ion (green)



Tetrahedral
Permanganate ion (purple)

In manganate and permanganate ions, π-bonding takes place by overlap of p -orbitals of oxygen with d-orbitals of manganese.

37. (c) : In neutral or faintly alkaline solutions :

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

38. (d) :

In CrO_4^{2-}, Cr^{+6} ($n = 0$)	diamagnetic
In $Cr_2O_7^{2-}$, Cr^{+6} ($n = 0$)	diamagnetic
In MnO_4^-, Mn^{+7} ($n = 0$)	diamagnetic
In MnO_4^{2-}, Mn^{+6}($n = 1$)	paramagnetic

In MnO_4^{2-}, one unpaired electron (n) is present in d-orbital so, d-d transition is possible.

39. (a) : SO_2 readily decolourises pink violet colour of acidified $KMnO_4$ solution.

$$\underset{\text{(Pink violet)}}{2KMnO_4} + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + \underset{\text{(Colourless)}}{2MnSO_4} + 2H_2SO_4$$

40. (b) : $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
(Green)

41. (d) : $KMnO_4$ (Mn^{7+}) changes to Mn^{2+} *i.e.*, number of electrons involved per mole of $KMnO_4$ is 5.

(a) For $FeSO_3$,
$Fe^{2+} \longrightarrow Fe^{3+}$ (No. of e^-s involved = 1)
$SO_3^{2-} \longrightarrow SO_4^{2-}$ (No. of e^-s involved = 2)
Total number of e^-s involved = 1 + 2 = 3

(b) For FeC_2O_4,
$Fe^{2+} \longrightarrow Fe^{3+}$ (No. of e^-s involved = 1)
$C_2O_4^{2-} \longrightarrow 2CO_2$ (No. of e^-s involved = 2)
Total number of e^-s involved = 1 + 2 = 3

(c) For $Fe(NO_2)_2$,
$Fe^{2+} \longrightarrow Fe^{3+}$ (No. of e^-s involved = 1)
$2NO_2^- \longrightarrow 2NO_3^-$ (No. of e^-s involved = 4)
Total number of e^-s involved = 1 + 4 = 5

(d) For $FeSO_4$,
$Fe^{2+} \longrightarrow Fe^{3+}$ (No. of e^-s involved = 1)
Total number of e^-s involved = 1

As $FeSO_4$ requires least number of electrons thus, it will require least amount of $KMnO_4$.

42. (b) : Hydrogen peroxide is oxidised to H_2O and O_2.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

or, $2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

43. (b) : Potassium dichromate is preferred over sodium dichromate in volumetric analysis, primarily because the latter is hygroscopic nature and therefore, accurate weighing is not possible in normal atmosphere.

44. (a) : $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

$[Na_2SO_3 + [O] \longrightarrow Na_2SO_4] \times 3$

$K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$

---

or $Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$

45. (b) : In alkaline medium :
$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$
$KI + 3[O] \rightarrow KIO_3$

$2KMnO_4 + KI + H_2O \rightarrow 2KOH + 2MnO_2 + KIO_3$

---

46. (c) : $K_2Cr_2O_7 + 2NaOH \rightarrow K_2CrO_4 + Na_2CrO_4 + H_2O$

or $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

47. (d) : $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

$\therefore$ 2 moles of $MnO_4^- \equiv$ 5 moles of $C_2O_4^{2-}$

20 mL of 0.1 M $KMnO_4$ = 2 mmol of $KMnO_4$
Also, 50 mL of 0.1 M $C_2H_2O_4 \equiv$ 5 mmol of $C_2O_4^{2-}$
Therefore, these are equivalent.

48. (c) : Let, oxidation state of Cr in $K_2Cr_2O_7$ is x. Then,
$2 + 2x - 14 = 0$
$\Rightarrow 2x = 12 \quad \therefore \quad x = +6$

49. (c) : The first few members of the lanthanoid series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium.

50. (b) **51. (b)**

52. (a) : Zr and Hf have nearly same radii due to lanthanoid contraction.

53. (a) : Due to poor shielding effect of 4*f*-orbitals, nucleus will exert a strong attraction and size of atom or ion goes on decreasing as move in the series with increase in atomic number.

54. (b) : Sm^{2+} ($Z = 62$) : $[Xe]4f^6$
Eu^{2+} ($Z = 63$) : $[Xe]4f^7$
Yb^{2+} ($Z = 70$) : $[Xe]4f^{14}$
Ce^{2+} ($Z = 58$) : $[Xe]4f^2$
Only Yb^{2+} is diamagnetic.

55. (d) : The common stable oxidation state of all the lanthanoids is +3. The oxidation state of +2 and +4 are also exhibited by some of the elements. These oxidation states are only stable in those cases where stable $4f^0$, $4f^7$ or $4f^{14}$ configurations are achieved.

56. (b) : In each vertical column of transition elements, the elements of second and third transition series resemble each other more closely than the elements of first and second transition series on account of lanthanide contraction. Hence, the properties of elements of 4*d* series of the transition elements resemble with the properties of the elements of 5*d* series of the transition elements.

57. (c) : As sixth period can accommodate only 18 elements in the table, 14 members of 4*f* series (atomic number 58 to 71) are separately accommodated in a horizontal row below the periodic table. These are called as lanthanides.

58. (b) : On going from La^{3+} to Lu^{3+}, the ionic radius shrinks from 1.15 Å to 0.93 Å (lanthanide contraction). The radius of La^{3+} is also larger than that of Y^{3+} ion which lies immediately above it in periodic table.

59. (a) : The general electronic structure of lanthanides is, $(n-2)f^{1-14}(n-1)s^2p^6d^{0-1}ns^2$.

60. (a) : $La(OH)_3$ is more basic than $Lu(OH)_3$. In lanthanides, the basic character of hydroxides decreases as the ionic radius decreases.

61. (a) : Due to lanthanide contraction, the elements of second and third transition series *i.e.*, Zr and Hf resemble more with each other than the elements of first and second transition series.

62. (d) : Ionic radii of trivalent lanthanides decreases with increase in atomic number.

63. (b) : Actinoids have a greater range of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* orbitals. Hence, all their electrons can take part in bond formation.

64. (c) : U exhibits + 3, + 4, + 5, + 6

Th exhibits + 3, + 4 ; Ac exhibits + 3 only

Pa exhibits + 3, + 4, + 5

65. (c) : The 5*f*-orbitals extend into space beyond the 6*s* and 6*p*-orbitals and participate in bonding. This is in direct contrast to the lanthanides where the 4*f*-orbitals are buried deep inside in the atom, totally shielded by outer orbitals and thus, unable to take part in bonding.

66. (d) : 'La' forms compounds in which its oxidation no. is +3.

'Eu' and 'Gd' exhibit +2 as well as +3 oxidation states and not higher than that, due to stable (f^7) configuration. whereas 'Am' exhibits the oxidation states +3, +4, +5, +6, etc. due to extremely large size and low ionisation energy.

67. (a)

68. (b) : $HgCl_{2(aq)} + 4I^-_{(aq)} \longrightarrow HgI_4^{2-}{}_{(aq)} + 2Cl^-_{(aq)}$

$I_{2(s)} + I^-_{(aq)} \longrightarrow I^-_{3(aq)}$

69. (c)

70. (c) : When calomel reacts with NH_4OH, it turns black due to the formation of a mixture of mercury and ammonium basic mercury (II) chloride.

$$\underset{\text{(Calomel)}}{Hg_2Cl_2} + 2\,NH_4OH \rightarrow NH_4Cl + 2H_2O + Hg + HgNH_2Cl$$

71. (b) : AgBr is highly photosensitive and is used as an ingredient for photographic films and plates.

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CHAPTER 9

Coordination Compounds

9.1 Werner's Theory of Coordination Compounds

1. The correct order of the stoichiometries of AgCl formed when $AgNO_3$ in excess is treated with the complexes : $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ respectively is
(a) 3AgCl, 1AgCl, 2AgCl
(b) 3AgCl, 2AgCl, 1AgCl
(c) 2AgCl, 3AgCl, 2AgCl
(d) 1AgCl, 3AgCl, 2AgCl *(NEET 2017)*

2. Cobalt(III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C?
(a) $CoCl_3 \cdot 5NH_3$ (b) $CoCl_3 \cdot 6NH_3$
(c) $CoCl_3 \cdot 3NH_3$ (d) $CoCl_3 \cdot 4NH_3$
(2015, Cancelled)

3. An excess of $AgNO_3$ is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium(III) chloride. The number of moles of AgCl precipitated would be
(a) 0.003 (b) 0.01
(c) 0.001 (d) 0.002 *(NEET 2013)*

4. Which of the following will exhibit maximum ionic conductivity?
(a) $K_4[Fe(CN)_6]$ (b) $[Co(NH_3)_6]Cl_3$
(c) $[Cu(NH_3)_4]Cl_2$ (d) $[Ni(CO)_4]$ *(2001)*

5. A coordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of $AgNO_3$ solution, we get two moles of AgCl precipitate. The ionic formula for this complex would be
(a) $[Co(NH_3)_5(NO_2)]Cl_2$
(b) $[Co(NH_3)_5Cl][Cl(NO_2)]$
(c) $[Co(NH_3)_4(NO_2)Cl][(NH_3)Cl]$
(d) $(Co(NH_3)_5][(NO_2)_2Cl_2]$ *(1998)*

9.2 Definitions of Some Important Terms Pertaining to Coordination Compounds

6. The correct increasing order of *trans*-effect of the following species is
(a) $NH_3 > CN^- > Br^- > C_6H_5^-$
(b) $CN^- > C_6H_5^- > Br^- > NH_3$
(c) $Br^- > CN^- > NH_3 > C_6H_5^-$
(d) $CN^- > Br^- > C_6H_5^- > NH_3$ *(NEET-II 2016)*

7. The sum of coordination number and oxidation number of the metal *M* in the complex $[M(en)_2(C_2O_4)]Cl$ (where *en* is ethylenediamine) is
(a) 6 (b) 7
(c) 8 (d) 9 *(2015)*

8. The anion of acetylacetone (*acac*) forms Co(*acac*)$_3$ chelate with Co^{3+}. The rings of the chelate are
(a) five membered (b) four membered
(c) six membered (d) three membered.
(Karnataka NEET 2013)

9. Which of the following statements is true?
(a) Silicon exhibits 4 coordination number in its compound.
(b) Bond energy of F_2 is less than Cl_2.
(c) Mn(III) oxidation state is more stable than Mn(II) in aqueous state.
(d) Elements of 15th gp shows only +3 and +5 oxidation states. *(2002)*

10. Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is
(a) 3 (b) 6
(c) 4 (d) 2 *(2001)*

11. The coordination number and oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$ are respectively
(a) 3 and + 3 (b) 3 and 0
(c) 6 and + 3 (d) 4 and + 2 *(1995)*

12. Which of the following ligands is expected to be bidentate?
(a) CH_3NH_2 (b) $CH_3C\equiv N$
(c) Br (d) $C_2O_4^{2-}$ *(1994)*

9.3 Nomenclature of Coordination Compounds

13. The name of complex ion, $[Fe(CN)_6]^{3-}$ is
(a) hexacyanitoferrate(III) ion
(b) tricyanoferrate(III) ion
(c) hexacyanidoferrate(III) ion
(d) hexacyanoiron(III) ion. *(2015)*

14. The correct IUPAC name for $[CrF_2(en)_2]Cl$ is
(a) chlorodifluoridoethylenediaminechromium (III) chloride
(b) difluoridobis(ethylene diamine)chromium (III) chloride
(c) difluorobis-(ethylene diamine)chromium (III) chloride
(d) chlorodifluoridobis(ethylene diamine) chromium (III). *(Karnataka NEET 2013)*

15. The hypothetical complex chlorodiaquatriammine cobalt(III) chloride can be represented as
(a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
(b) $[Co(NH_3)_3(H_2O)Cl_3]$
(c) $[Co(NH_2)_3(H_2O)_2Cl]$
(d) $[Co(NH_3)_3(H_2O)_3]Cl_3$ *(2002)*

16. IUPAC name of $[Pt(NH_3)_3(Br)(NO_2)Cl]Cl$ is
(a) triamminebromochloronitroplatinum(IV) chloride
(b) triamminebromonitrochloroplatinum(IV) chloride
(c) triamminechlorobromonitroplatinum(IV) chloride
(d) triamminenitrochlorobromoplatinum(IV) chloride. *(1998)*

17. The formula of dichlorobis(urea)copper(II) is
(a) $[Cu\{O=C(NH_2)_2\}Cl]Cl$
(b) $[CuCl_2]\{O=C(NH_2)_2\}$
(c) $[Cu\{O=C(NH_2)_2\}Cl_2$
(d) $[CuCl_2\{O=C(NH_2)_2\}_2]$ *(1997)*

9.4 Isomerism in Coordination Compounds

18. The type of isomerism shown by the complex $[CoCl_2(en)_2]$ is
(a) geometrical isomerism
(b) coordination isomerism
(c) ionization isomerism
(d) linkage isomerism. *(NEET 2018)*

19. Number of possible isomers for the complex $[Co(en)_2Cl_2]Cl$ will be (*en* = ethylenediamine)
(a) 1 (b) 3
(c) 4 (d) 2 *(2015)*

20. The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of which type of isomerism?
(a) Linkage isomerism
(b) Ionization isomerism
(c) Coordination isomerism
(d) Geometrical isomerism *(2011)*

21. The complex, $[Pt(py)(NH_3)BrCl]$ will have how many geometrical isomers?
(a) 3 (b) 4
(c) 0 (d) 2 *(2011)*

22. The existence of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to
(a) linkage isomerism
(b) geometrical isomerism
(c) coordination isomerism
(d) ionization isomerism. *(2010)*

23. Which one of the following complexes is not expected to exhibit isomerism?
(a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ (b) $[Pt(NH_3)_2Cl_2]$
(c) $[Ni(NH_3)_2Cl_2]$ (d) $[Ni(en)_3]^{2+}$ *(2010)*

24. Which of the following does not show optical isomerism?
(a) $[Co(NH_3)_3Cl_3]^0$
(b) $[Co(en)Cl_2(NH_3)_2]^+$
(c) $[Co(en)_3]^{3+}$
(d) $[Co(en)_2Cl_2]^+$(*en* = ethylenediamine) *(2009)*

25. Which of the following will give a pair of enantiomorphs?
(a) $[Cr(NH_3)_6][Co(CN)_6]$
(b) $[Co(en)_2Cl_2]Cl$
(c) $[Pt(NH_3)_4][PtCl_6]$
(d) $[Co(NH_3)_4Cl_2]NO_2$
(*en* = $NH_2CH_2CH_2NH_2$) *(2007)*

26. $[Co(NH_3)_4(NO_2)_2]Cl$ exhibits
(a) linkage isomerism, geometrical isomerism and optical isomerism
(b) linkage isomerism, ionization isomerism and optical isomerism
(c) linkage isomerism, ionization isomerism and geometrical isomerism
(d) ionization isomerism, geometrical isomerism and optical isomerism. *(2006)*

27. Which one of the following is expected to exhibit optical isomerism? (*en* = ethylenediamine)
(a) *cis*-$[Pt(NH_3)_2Cl_2]$
(b) *trans*-$[Pt(NH_3)_2Cl_2]$
(c) *cis*-$[Co(en)_2Cl_2]^+$
(d) *trans*-$[Co(en)_2Cl_2]^+$ *(2005)*

28. Which of the following coordination compounds would exhibit optical isomerism?
(a) Pentaamminenitrocobalt(III) iodide
(b) Diamminedichloroplatinum(II)
(c) *trans*-Dicyanobis(ethylenediamine) chromium(III) chloride
(d) *tris*-(Ethylenediamine)cobalt(III) bromide
(2004)

29. Which of the following will give maximum number of isomers?
(a) $[Co(NH_3)_4Cl_2]$ (b) $[Ni(en)(NH_3)_4]^{2+}$
(c) $[Ni(C_2O_4)(en)_2]^{2-}$ (d) $[Cr(SCN)_2(NH_3)_4]^+$
(2001)

30. Which complex compound will give four isomers?
(a) $[Fe(en)_3]Cl_3$
(b) $[Co(en)_2Cl_2]Cl$
(c) $[Fe(PPh_3)_3NH_3ClBr]Cl$
(d) $[Co(PPh_3)_3Cl]Cl_3$ *(2000)*

31. The total number of possible isomers for the complex compound $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ are
(a) 5 (b) 6
(c) 3 (d) 4 *(1998)*

32. The number of geometrical isomers of the complex $[Co(NO_2)_3(NH_3)_3]$ is
(a) 4 (b) 0
(c) 2 (d) 3 *(1997)*

33. The number of geometrical isomers for $[Pt(NH_3)_2Cl_2]$ is
(a) 3 (b) 4
(c) 1 (d) 2 *(1995)*

9.5 Bonding in Coordination Compounds

34. Which of the following is the correct order of increasing field strength of ligands to form coordination compounds?
(a) $SCN^- < F^- < C_2O_4^{2-} < CN^-$
(b) $SCN^- < F^- < CN^- < C_2O_4^{2-}$
(c) $F^- < SCN^- < C_2O_4^{2-} < CN^-$
(d) $CN^- < C_2O_4^{2-} < SCN^- < F^-$ *(NEET 2020)*

35. What is the correct electronic configuration of the central atom in $K_4[Fe(CN)_6]$ based on crystal field theory?
(a) $e^4t_2^2$ (b) $t_{2g}^4e_g^2$
(c) $t_{2g}^6e_g^0$ (d) $e^3t_2^3$ *(NEET 2019)*

36. Aluminium chloride in acidified aqueous solution forms a complex '*A*', in which hybridisation state of Al is '*B*'. What are '*A*' and '*B*', respectively ?
(a) $[Al(H_2O)_6]^{3+}$, sp^3d^2
(b) $[Al(H_2O)_4]^{3+}$, sp^3
(c) $[Al(H_2O)_4]^{3+}$, dsp^2
(d) $[Al(H_2O)_6]^{3+}$, d^2sp^3 *(Odisha NEET 2019)*

37. The crystal field stabilisation energy (CFSE) for $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for $[CoCl_4]^{2-}$ will be
(a) 6000 cm^{-1} (b) 16000 cm^{-1}
(c) 18000 cm^{-1} (d) 8000 cm^{-1}
(Odisha NEET 2019)

38. The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are
(a) square planar geometry and diamagnetic
(b) tetrahedral geometry and diamagnetic
(c) square planar geometry and paramagnetic
(d) tetrahedral geometry and paramagnetic.
(NEET 2018)

39. Correct increasing order for the wavelengths of absorption in the visible region for the complexes of Co^{3+} is
(a) $[Co(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$
(b) $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$
(c) $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(H_2O)_6]^{3+}$
(d) $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$
(NEET 2017)

40. Pick out the correct statement with respect to $[Mn(CN)_6]^{3-}$.
(a) It is sp^3d^2 hybridised and tetrahedral.
(b) It is d^2sp^3 hybridised and octahedral.
(c) It is dsp^2 hybridised and square planar.
(d) It is sp^3d^2 hybridised and octahedral.
(NEET 2017)

41. Jahn–Teller effect is not observed in high spin complexes of
(a) d^7 (b) d^8
(c) d^4 (d) d^9 *(NEET-II 2016)*

42. The hybridization involved in complex $[Ni(CN)_4]^{2-}$ is (At. No. Ni = 28)
(a) sp^3 (b) d^2sp^2
(c) d^2sp^3 (d) dsp^2 *(2015)*

43. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE) is
(a) $[Mn(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{3+}$ *(2014)*

44. A magnetic moment at 1.73 BM will be shown by one among of the following
(a) $TiCl_4$ (b) $[CoCl_6]^{4-}$
(c) $[Cu(NH_3)_4]^{2+}$ (d) $[Ni(CN)_4]^{2-}$
(NEET 2013)

45. Crystal field splitting energy for high spin d^4 octahedral complex is
(a) $-1.2\ \Delta_o$ (b) $-0.6\ \Delta_o$
(c) $-0.8\ \Delta_o$ (d) $-1.6\ \Delta_o$
(Karnataka NEET 2013)

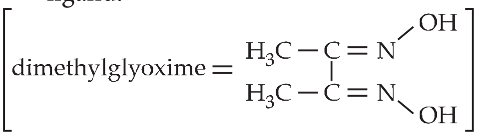
46. Which among the following is a paramagnetic complex?
(a) $[Co(NH_3)_6]^{3+}$ (b) $[Pt(en)Cl_2]$
(c) $[CoBr_4]^{2-}$ (d) $Mo(CO)_6$
(At. No. Mo = 42, Pt = 78)
(Karnataka NEET 2013)

47. Which is diamagnetic?
(a) $[CoF_6]^{3-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[NiCl_4]^{2-}$ (d) $[Fe(CN)_6]^{3-}$
(Karnataka NEET 2013)

48. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?
(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Zn(NH_3)_6]^{2+}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$ *(2012)*

49. Low spin complex of d^6-cation in an octahedral field will have the following energy
(a) $\frac{-12}{5}\Delta_o + P$ (b) $\frac{-12}{5}\Delta_o + 3P$
(c) $\frac{-2}{5}\Delta_o + 2P$ (d) $\frac{-2}{5}\Delta_o + P$
(Δ_o = crystal field splitting energy in an octahedral field, P = Electron pairing energy) *(2012)*

50. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true?
(a) Red complex has a square planar geometry.
(b) Complex has symmetrical H-bonding.
(c) Red complex has a tetrahedral geometry.
(d) Dimethylglyoxime functions as bidentate ligand.


$$\left[\text{dimethylglyoxime} = \begin{array}{l} H_3C-C=N-OH \\ \qquad\ \ | \\ H_3C-C=N-OH \end{array}\right]$$

(Mains 2012)

51. Of the following complex ions, which is diamagnetic in nature?
(a) $[NiCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[CuCl_4]^{2-}$ (d) $[CoF_6]^{3-}$ *(2011)*

52. The d-electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7 respectively. Which one of the following will exhibit minimum paramagnetic behaviour?
(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(H_2O)_6]^{2+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$
(At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27) *(2011)*

53. Which of the following complex compounds will exhibit highest paramagnetic behaviour?
(a) $[Ti(NH_3)_6]^{3+}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Zn(NH_3)_6]^{2+}$
(At. No. Ti = 22, Cr = 24, Co = 27, Zn = 30) *(2011)*

54. Which of the following complex ions is not expected to absorb visible light?
(a) $[Ni(CN)_4]^{2-}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Ni(H_2O)_6]^{2+}$ *(2010)*

55. Crystal field stabilization energy for high spin d^4 octahedral complex is
(a) $-1.8\ \Delta_o$ (b) $-1.6\ \Delta_o + P$
(c) $-1.2\ \Delta_o$ (d) $-0.6\ \Delta_o$ *(2010)*

56. Out of TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (Z of Ti = 22, Co = 27, Cu = 29, Ni = 28) the colourless species are
(a) Cu_2Cl_2 and $NiCl_4^{2-}$ (b) TiF_6^{2-} and Cu_2Cl_2
(c) CoF_6^{3-} and $NiCl_4^{2-}$ (d) TiF_6^{2-} and CoF_6^{3-}.
(2009)

57. Which of the following complex ions is expected to absorb visible light?
(a) $[Ti(en)_2(NH_3)_2]^{4+}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Zn(NH_3)_6]^{2+}$ (d) $[Sc(H_2O)_3(NH_3)_3]^{3+}$
[At. nos. Zn = 30, Sc = 21, Ti = 22, Cr = 24] *(2009)*

58. Which of the following complexes exhibits the highest paramagnetic behaviour?
(a) $[Co(ox)_2(OH)_2]^-$ (b) $[Ti(NH_3)_6]^{3+}$
(c) $[V(gly)_2(OH)_2(NH_3)_2]^+$
(d) $[Fe(en)(bpy)(NH_3)_2]^{2+}$
where *gly* = glycine, *en* = ethylenediamine and *bpy* = bipyridyl moities. (At. nos. Ti = 22, V = 23, Fe = 26, Co = 27) *(2008)*

59. In which of the following coordination entities the magnitude of Δ_o (CFSE in octahedral field) will be maximum?
(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$
(At. No. Co = 27) *(2008)*

60. The d electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Ni^{2+} are $3d^4$, $3d^5$, $3d^6$ and $3d^8$ respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?
(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Ni(H_2O)_6]^{2+}$
(c) $[Cr(H_2O)_6]^{2+}$ (d) $[Mn(H_2O)_6]^{2+}$.
(At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)
(2007)

61. $[Cr(H_2O)_6]Cl_3$ (At. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3*d* electrons in the chromium of the complex is

(a) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$

(b) $3d^1_{(x^2-y^2)}, 3d^1_{z^2}, 3d^1_{xz}$

(c) $3d^1_{xy}, 3d^1_{(x^2-y^2)}, 3d^1_{yz}$

(d) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}$ *(2006)*

62. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour?

(a) $[Zn(NH_3)_6]^{2+}$ (b) $[Cr(NH_3)_6]^{3+}$

(c) $[Co(NH_3)_6]^{3+}$ (d) $[Ni(NH_3)_6]^{2+}$

(Atomic number : Zn = 30, Cr = 24, Co = 27, Ni = 28) *(2005)*

63. Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ species, the hybridisation states at the Ni atom are, respectively

(a) sp^3, dsp^2, dsp^2 (b) sp^3, dsp^2, sp^3

(c) sp^3, sp^3, dsp^2 (d) dsp^2, sp^3, sp^3.

[Atomic number of Ni = 28] *(2004)*

64. CN^- is a strong field ligand. This is due to the fact that

(a) it carries negative charge

(b) it is a pseudohalide

(c) it can accept electrons from metal species

(d) it forms high spin complexes with metal species. *(2004)*

65. Considering H_2O as a weak field ligand, the number of unpaired electrons in $[Mn(H_2O)_6]^{2+}$ will be (atomic number of Mn = 25)

(a) three (b) five

(c) two (d) four. *(2004)*

66. In an octahedral structure, the pair of *d* orbitals involved in d^2sp^3 hybridisation is

(a) $d_{x^2-y^2}, d_{z^2}$ (b) $d_{xz}, d_{x^2-y^2}$

(c) d_{z^2}, d_{xz} (d) d_{xy}, d_{yz}. *(2004)*

67. The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$ is

(a) 2 (b) 3

(c) 4 (d) zero

(Atomic no. : Co = 27) *(2003)*

68. Atomic number of Cr and Fe are respectively 24 and 26, which of the following is paramagnetic with the spin of electron?

(a) $[Cr(CO)_6]$ (b) $[Fe(CO)_5]$

(c) $[Fe(CN)_6]^{4-}$ (d) $[Cr(NH_3)_6]^{3+}$ *(2002)*

69. Which statement is incorrect?

(a) $Ni(CO)_4$ - tetrahedral, paramagnetic

(b) $[Ni(CN)_4]^{2-}$ - square planar, diamagnetic

(c) $Ni(CO)_4$ - tetrahedral, diamagnetic

(d) $[NiCl_4]^{2-}$ - tetrahedral, paramagnetic *(2001)*

9.6 Bonding in Metal Carbonyls

70. Iron carbonyl, $Fe(CO)_5$ is

(a) tetranuclear (b) mononuclear

(c) trinuclear (d) dinuclear.

(NEET 2018)

71. An example of a sigma bonded organometallic compound is

(a) Grignard's reagent (b) ferrocene

(c) cobaltocene (d) ruthenocene.

(NEET 2017)

72. Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 Å.)

(a) $[Fe(CO)_4]^{2-}$ (b) $[Mn(CO)_6]^+$

(c) $Ni(CO)_4$ (d) $[Co(CO)_4]^-$

(NEET-I 2016)

73. Which of the following carbonyls will have the strongest C – O bond?

(a) $Mn(CO)_6^+$ (b) $Cr(CO)_6$

(c) $V(CO)_6^-$ (d) $Fe(CO)_5$ *(2011)*

74. Which of the following does not have a metal - carbon bond?

(a) $Al(OC_2H_5)_3$ (b) C_2H_5MgBr

(c) $K[Pt(C_2H_4)Cl_3]$ (d) $Ni(CO)_4$ *(2004)*

75. Among the following which is not the π-bonded organometallic compound?

(a) $K[PtCl_3(\eta^2 - C_2H_4)]$

(b) $Fe(\eta^5 - C_5H_5)_2$

(c) $Cr(\eta^6 - C_6H_6)_2$

(d) $(CH_3)_4Sn$ *(2003)*

76. Which of the following organometallic compounds is σ and π-bonded?

(a) $[Fe(\eta^5 - C_5H_5)_2]$

(b) $K[PtCl_3(\eta^2 - C_2H_4)]$

(c) $[Co(CO)_5NH_3]^{2+}$

(d) $Fe(CH_3)_3$ *(2001)*

77. Shape of $Fe(CO)_5$ is

(a) octahedral (b) square planar

(c) trigonal bipyramidal (d) square pyramidal.

(2000)

78. In metal carbonyl having general formula $M(CO)_x$ where *M* = metal, *x* = 4 and the metal is bonded to

(a) carbon and oxygen (b) $C\equiv O$

(c) oxygen (d) carbon. *(1995)*

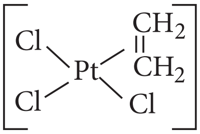
9.7 Importance and Applications of Coordination Compounds

79. Which of the following complexes is used to be as an anticancer agent?
(a) *mer*-$[Co(NH_3)_3Cl_3]$ (b) *cis*-$[PtCl_2(NH_3)_2]$
(c) *cis*-$K_2[PtCl_2Br_2]$ (d) Na_2CoCl_4 *(2014)*

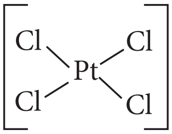
80. Copper sulphate dissolves in excess of KCN to give
(a) $Cu(CN)_2$ (b) CuCN
(c) $[Cu(CN)_4]^{3-}$ (d) $[Cu(CN)_4]^{2-}$ *(2006)*

81. Which of the following is considered to be an anticancer species?

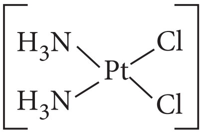
(a)



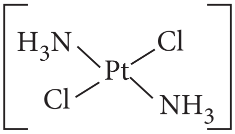
(b)



(c)



(d)



(2004)

82. In the silver plating of copper, $K[Ag(CN)_2]$ is used instead of $AgNO_3$. The reason is
(a) a thin layer of Ag is formed on Cu
(b) more voltage is required
(c) Ag^+ ions are completely removed from solution
(d) less availability of Ag^+ ions, as Cu cannot displace Ag from $[Ag(CN)_2]^-$ ion. *(2002)*

83. $CuSO_4$ when reacts with KCN forms CuCN, which is insoluble in water. It is soluble in excess of KCN, due to formation of the following complex
(a) $K_2[Cu(CN)_4]$
(b) $K_3[Cu(CN)_4]$
(c) $CuCN_2$
(d) $Cu[KCu(CN)_4]$ *(2002)*

84. Hypo is used in photography to
(a) reduce AgBr grains to metallic silver
(b) convert metallic silver to silver salt
(c) remove undecomposed silver bromide as a soluble complex
(d) remove reduced silver. *(1988)*

ANSWER KEY

1.	(b)	**2.**	(c)	**3.**	(c)	**4.**	(a)	**5.**	(a)	**6.**	(b)	**7.**	(d)	**8.**	(c)	**9.**	(b)	**10.**	(b)
11.	(c)	**12.**	(d)	**13.**	(c)	**14.**	(b)	**15.**	(a)	**16.**	(a)	**17.**	(d)	**18.**	(a)	**19.**	(b)	**20.**	(c)
21.	(a)	**22.**	(b)	**23.**	(c)	**24.**	(a)	**25.**	(b)	**26.**	(c)	**27.**	(c)	**28.**	(d)	**29.**	(d)	**30.**	(c)
31.	(d)	**32.**	(c)	**33.**	(d)	**34.**	(a)	**35.**	(c)	**36.**	(a)	**37.**	(d)	**38.**	(b)	**39.**	(d)	**40.**	(b)
41.	(b)	**42.**	(d)	**43.**	(b)	**44.**	(c)	**45.**	(b)	**46.**	(c)	**47.**	(b)	**48.**	(a)	**49.**	(b)	**50.**	(c)
51.	(b)	**52.**	(c)	**53.**	(b)	**54.**	(a)	**55.**	(d)	**56.**	(b)	**57.**	(b)	**58.**	(a)	**59.**	(a)	**60.**	(b)
61.	(d)	**62.**	(c)	**63.**	(b)	**64.**	(b)	**65.**	(b)	**66.**	(a)	**67.**	(c)	**68.**	(d)	**69.**	(a)	**70.**	(b)
71.	(a)	**72.**	(a)	**73.**	(a)	**74.**	(a)	**75.**	(d)	**76.**	(c)	**77.**	(c)	**78.**	(d)	**79.**	(b)	**80.**	(c)
81.	(c)	**82.**	(d)	**83.**	(b)	**84.**	(c)												

Hints & Explanations

1. **(b) :** $[Co(NH_3)_6]Cl_3 + 3AgNO_3 \rightarrow 3AgCl\downarrow + [Co(NH_3)_6](NO_3)_3$

$[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3 \rightarrow 2AgCl\downarrow + [Co(NH_3)_5Cl](NO_3)_2$

$[Co(NH_3)_4Cl_2]Cl + AgNO_3 \rightarrow AgCl\downarrow + [Co(NH_3)_4Cl_2]NO_3$

2. **(c) :** For octahedral complexes, coordination number is 6. Hence, $CoCl_3 \cdot 3NH_3$ *i.e.*, $[Co(NH_3)_3Cl_3]$ will not ionise and will not give test for Cl^- ion with silver nitrate.

3. **(c) :** $[Cr(H_2O)_4Cl_2]Cl + AgNO_3 \rightarrow [Cr(H_2O)_4Cl_2]NO_3 + \underset{\text{ppt.}}{AgCl}$

No. of millimoles of solution = 100 mL × 0.01 M
= 1 millimole
= 10^{-3} mole

So, mole of AgCl = 0.001

4. **(a) :** Ionic conductance increases with increasing the number of ions, produced after decomposition.

Compound	No. of ions produced
$K_4[Fe(CN)_6]$	5
$[Co(NH_3)_6]Cl_3$	4
$[Cu(NH_3)_4]Cl_2$	3
$[Ni(CO)_4]$	0

5. (a) : As the complex gives two moles of AgCl ppt. with $AgNO_3$ solution, so the complex must have two ionisable Cl atoms. Hence, the probable complex, which gives three mole ions may be $[Co(NH_3)_5NO_2]Cl_2$.

$$[Co(NH_3)_5NO_2]Cl_2 \rightarrow [Co(NH_3)_5NO_2]^{2+} + 2Cl^-$$
$$\text{one mole} \rightarrow 3 \text{ mole ions}$$

6. (b) : The intensity of the *trans*-effect (as measured by the increase in rate of substitution of the *trans* ligand) follows the sequence : $CN^- > C_6H_5^- > Br^- > NH_3$

7. (d) : $[M(en)_2(C_2O_4)]Cl$:

Oxidation number of metal = +3

Coordination number of metal = 6

∴ Sum of oxidation number and coordination number = 3 + 6 = 9

8. (c) : The ligand acetylacetone forms six membered chelate ring in the complex $[Co(acac)_3]$.

9. (b) : Bond energy of F_2 is less than Cl_2 due to inter-electronic repulsions in small sized F-atoms.

Silicon exhibits coordination number 6.

In aqueous state, Mn(II) is more stable.

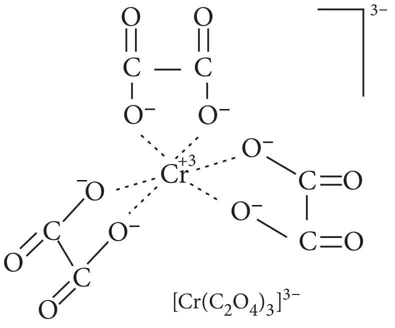
$$Mn \rightleftharpoons Mn^{2+} + 2e^-$$

The common oxidation states of 15th group elements are −3, +3 and +5.

10. (b) : $C_2O_4^{2-} \rightarrow$ bidentate ligand.

3 molecules attached from two sides with Ni makes coordination number 6.

11. (c) :



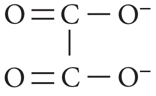
$[Cr(C_2O_4)_3]^{3-}$

As the number of atoms of the ligands that are directly bound to the central metal is known as coordination number. It is six here (see in figure).

Oxidation state : Let oxidation state of Cr be x.

$\Rightarrow \; 3(+1) + x + 3(-2) = 0 \Rightarrow 3 + x - 6 = 0 \;\Rightarrow\; x = +3$

12. (d) : When a ligand has two groups that are capable of bonding to the central atom, it is said to be bidentate. Thus, the only ligand,which is expected to be bidentate is $C_2O_4^{2-}$ as



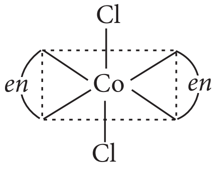
13. (c) **14. (b)**

15. (a) : Chlorodiaquatriamminecobalt(III) chloride can be represented as $[CoCl(NH_3)_3(H_2O)_2]Cl_2$.

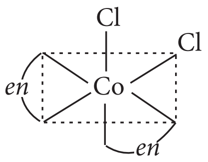
16. (a) : The ligands are named in the alphabetic order according to latest IUPAC system. So, the name of $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ is triamminebromochloronitro platinum(IV) chloride. (The oxidation no. of 'Pt' is +4).

17. (d) : The formula of dichlorobis(urea)copper(II) is $[CuCl_2\{(NH_2)_2CO\}_2]$.

18. (a) : $[CoCl_2(en)_2]$, exhibits geometrical isomerism, as the coordination number of Co is 6 and this compound has octahedral geometry.

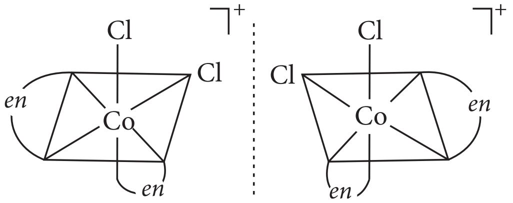


trans-form
(optically inactive)

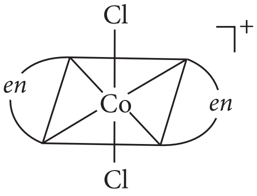


cis-form
(optically active)

19. (b) : Possible isomers of $[Co(en)_2Cl_2]Cl$:



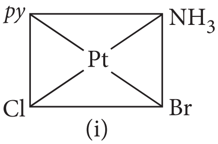
cis-isomer
(*d* and *l* forms)



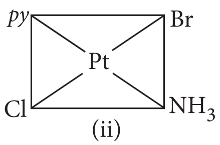
trans-isomer

20. (c) : Coordination isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in the complex. *e.g.*, $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

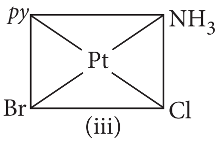
21. (a) : $[Pt(py)(NH_3)BrCl]$ can have three isomers.



(i)

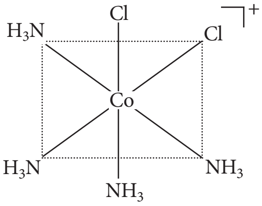


(ii)

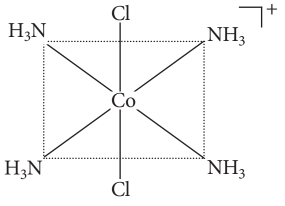


(iii)

22. (b) :



cis-form
(violet in colour)



trans-form
(green in colour)

23. (c) : Compounds having tetrahedral geometry does not exhibit isomerism due to presence of symmetry elements. Here, $[Ni(NH_3)_2Cl_2]$ has tetrahedral geometry.

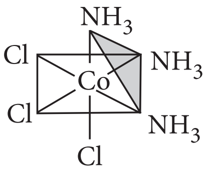
24. (a) : Optical isomerism is shown by :

(i) Complexes of the type $[M(AA)_2Y_2]$, containing one symmetrical bidentate ligand *i.e.*, $[Co(en)Cl_2(NH_3)_2]^+$.

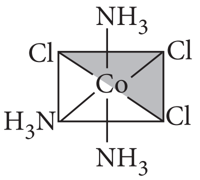
(ii) Complexes of the type $[M(AA)_3]$, containing a symmetrical bidentate ligand *i.e.*, $[Co(en)_3]^{3+}$.

(iii) Complexes of the type $[M(AA)_2X_2]$, *i.e.*, $[Co(en)_2Cl_2]^+$.
However complexes of the type $[MA_3B_3]$ show geometrical isomerism, known as *fac-mer* isomerism.

∴ $[Co(NH_3)_3Cl_3]$ exhibits *fac-mer* isomerism.

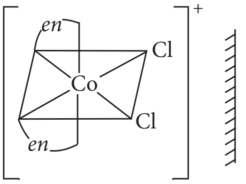


fac-isomer

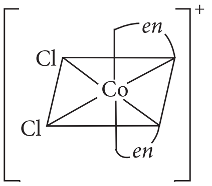


mer-isomer

25. (b) : Either a pair of crystals, molecules or compounds that are mirror images of each other but are not identical, and that rotate the plane of polarised light equally, but in opposite directions are called as enantiomorphs.



cis-*d*-isomer



cis-*l*-isomer

26. (c) : Ionization isomerism arises when the coordination compounds give different ions in solution.

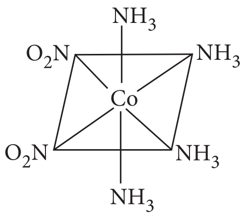
$[Co(NH_3)_4(NO_2)_2]Cl \rightleftharpoons [Co(NH_3)_4(NO_2)_2]^+ + Cl^-$

$[Co(NH_3)_4(NO_2)Cl]NO_2 \rightleftharpoons [Co(NH_3)_4(NO_2)Cl]^+ + NO_2^-$

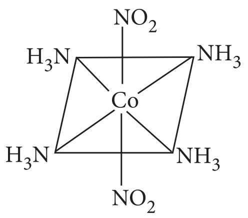
Linkage isomerism occurs in complex compounds which contain ambidentate ligands like NO_2^-, SCN^-, CN^-, $S_2O_3^{2-}$ and CO.

$[Co(NH_3)_4(NO_2)_2]Cl$ and $[Co(NH_3)_4(ONO)_2]Cl$ are linkage isomers as NO_2^- is linked through N or through O.

Octahedral complexes of the type Ma_4b_2 exhibit geometrical isomerism.



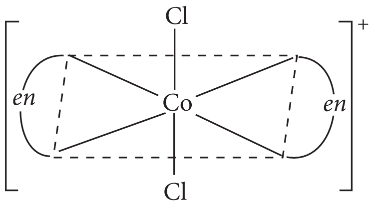
cis-form



trans-form

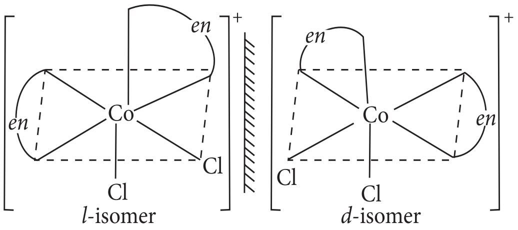
27. (c) : Optical isomerism is not shown by square planar complexes.

Octahedral complexes of general formulae, $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef]$, $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$ (where AA = symmetrical bidentate ligand), $[M(AA)_2ab]^{n\pm}$ and $[M(AB)_3]^{n\pm}$
(where AB = unsymmetrical ligands) show optical isomerism.



trans-$[Co(en)_2Cl_2]^+$

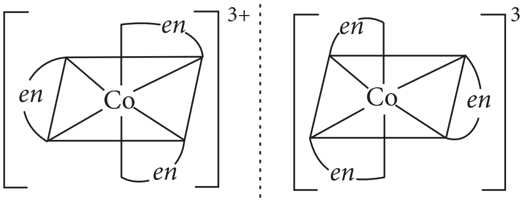
does not show optical isomerism (superimposable mirror image). But *cis*-form shows optical isomerism.



l-isomer *d*-isomer

cis-$[Co(en)_2Cl_2]^+$

28. (d) : $[Co(en)_3]^{3+}$:



d-form mirror *l*-form

29. (d) : $[Cr(SCN)_2(NH_3)_4]^+$ shows linkage, geometrical and optical isomerism.

30. (c) : $[Fe(PPh_3)_3NH_3ClBr]Cl$ can give two optical and two geometrical isomers. While other complexes do not form geometrical isomers.

31. (d) : The isomers of the complex compound $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ are :

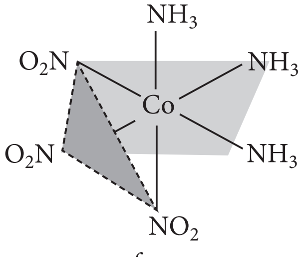
(i) $[Cu(NH_3)_3Cl]\ [Pt(NH_3)Cl_3]$

(ii) $[Pt(NH_3)_3Cl][Cu(NH_3)Cl_3]$

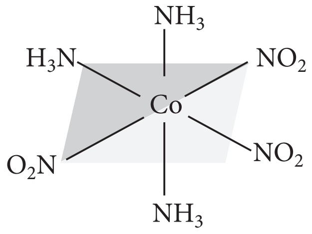
(iii) $[Pt(NH_3)_4][CuCl_4]$

So, the total no. of isomers are = 4

32. (c) : Possible geometrical isomers are :

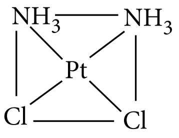


fac-



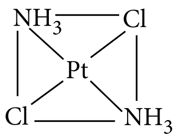
mer–

33. (d) :



cis-form

and



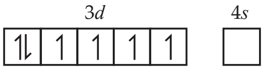
trans-form

34. (a) : According to spectrochemical series, order of increasing field strength is :

$SCN^- < F^- < C_2O_4^{2-} < CN^-$

35. (c) : In $K_4[Fe(CN)_6]$ complex, Fe is in +2 oxidation state.

Fe^{2+} :



As CN^- is a strong field ligand, it causes pairing of electrons therefore, electronic configuration of Fe^{2+} in $K_4[Fe(CN)_6]$ is $t_{2g}^6\, e_g^0$.

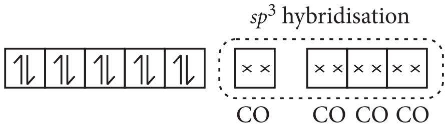
36. (a)

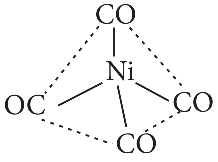
37. (d) : $\Delta_t = \frac{4}{9}\Delta_o \;=\; \frac{4}{9} \times 18000 = 8000\ \text{cm}^{-1}$

38. (b) : Ni(28) : $[Ar]3d^8 4s^2$

$\because$ CO is a strong field ligand, so, unpaired electrons get paired.

In $[Ni(CO)_4]$:





Thus, the complex is sp^3 hybridised with tetrahedral geometry and diamagnetic in nature.

39. (d) : Increasing order of crystal field splitting energy is : $H_2O < NH_3 < en$

Thus, increasing order of crystal field splitting energy for the given complexes is :

$[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(en)_3]^{3+}$

As, $E = \frac{hc}{\lambda}$

Thus, increasing order of wavelength of absorption is :

$[Co(en)_3]^{3+} < [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$

40. (b) : $[Mn(CN)_6]^{3-}$: Let oxidation state of Mn be x.

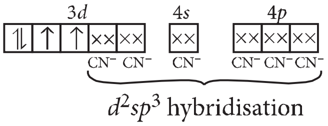
$x + 6 \times (-1) = -3 \Rightarrow x = +3$

Electronic configuration of Mn : $[Ar]4s^2\, 3d^5$

Electronic configuration of Mn^{3+} : $[Ar]3d^4$

CN^- is a strong field ligand thus, it causes pairing of electrons in 3*d*-orbital.

$[Mn(CN)_6]^{3-}$: [Ar]

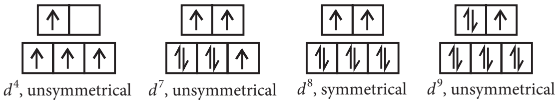


Thus, $[Mn(CN)_6]^{3-}$ has d^2sp^3 hybridisation and has octahedral geometry.

41. (b) : Jahn–Teller distortion is usually significant for asymmetrically occupied e_g orbitals since they are directed towards the ligands and the energy gain is considerably more.

In case of unevenly occupied t_{2g} orbitals, the Jahn–Teller distortion is very weak since the t_{2g} set does not point directly at the ligands and therefore, the energy gain is much less.

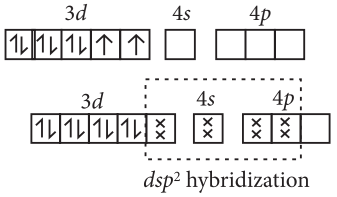
High spin complexes :



42. (d) : $[Ni(CN)_4]^{2-}$: Oxidation number of Ni = +2

Electronic configuration of Ni^{2+} : $3d^8 4s^0$

$[Ni(CN)_4]^{2-}$ =



Pairing of electrons in *d*-orbital takes place due to the presence of strong field ligand (CN^-).

43. (b) : H_2O is a weak field ligand, hence Δ_o < pairing energy.

$CFSE = (-0.4x + 0.6y)\Delta_o$

where, x and y are no. of electrons occupying t_{2g} and e_g orbitals respectively.

For $[Fe(H_2O)_6]^{3+}$ complex ion,

$Fe^{3+}\ (3d^5) = t^3_{2g}\, e_g^{\,2} = -0.4 \times 3 + 0.6 \times 2 = 0.0$ or $0\ \Delta_0$

44. (c) : Oxidation state of Cu in $[Cu(NH_3)_4]^{2+}$ is + 2

$Cu^{2+} = 3d^9$

It has one unpaired electron (n = 1).

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \text{BM}$$

45. (b) : $CFSE = (-0.4\, x + 0.6\, y)\, \Delta_o$

where, x = No. of electrons occupying t_{2g} orbitals

y = no. of electrons occupying e_g orbitals

$= (-0.4 \times 3 + 0.6 \times 1)\Delta_o \quad [\because \text{High spin } d^4 = t^3_{2g}\, e^1_g]$

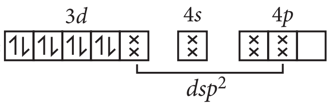
$= (-1.2 + 0.6)\Delta_o = -0.6\ \Delta_o$

46. (c) : Co^{2+} in $[CoBr_4]^{2-}$ has $3d^7 4s^0$ configuration and Br^- is a weak field ligand. Thus, it has 3 unpaired electrons and hence, paramagnetic.

47. (b) : In $[Ni(CN)_4]^{2-}$ all orbitals are doubly occupied, hence, it is diamagnetic.

$Ni^{2+} = 3d^8$

$[Ni(CN)_4]^{2-} =$



CN^- is a strong field ligand and causes pairing of $3d$-electrons of Ni^{2+}.

48. (a) : $[Ni(NH_3)_6]^{2+}$: sp^3d^2 (outer), octahedral, paramagnetic

$[Zn(NH_3)_6]^{2+}$: sp^3d^2 (outer), octahedral, diamagnetic

$[Cr(NH_3)_6]^{3+}$: d^2sp^3 (inner), octahedral, paramagnetic

$[Co(NH_3)_6]^{3+}$: d^2sp^3 (inner), octahedral, diamagnetic

49. (b) : CFSE = $(-0.4x + 0.6y)\Delta_o + zP$

where x = number of electrons occupying t_{2g} orbital

y = number of electrons occupying e_g orbital

z = number of pairs of electrons

For low spin d^6 complex electronic configuration

$= t_{2g}^6\ e_g^0$ or $t_{2g}^{2,2,2}\ e_g^0$

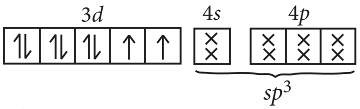
$\therefore\ x = 6, y = 0, z = 3$

CFSE = $(-0.4 \times 6 + 0 \times 0.6)\Delta_o + 3P$

$$= \frac{-12}{5}\Delta_o + 3P$$

50. (c) : $[Ni(dmg)_2]$ is square planar in structure not tetrahedral.

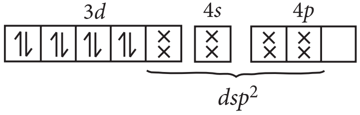
51. (b) : $[NiCl_4]^{2-}$:



Number of unpaired electrons = 2

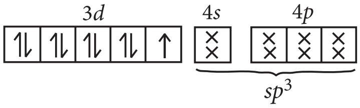
Hence, $[NiCl_4]^{2-}$ is paramagnetic.

$[Ni(CN)_4]^{2-}$:



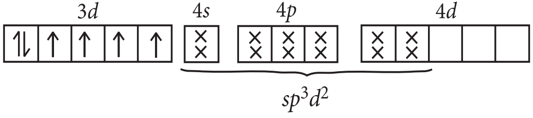
Number of unpaired electrons = 0, so it is diamagnetic in nature.

$[CuCl_4]^{2-}$:



No. of unpaired electron = 1, so it is paramagnetic.

$[CoF_6]^{3-}$:



No. of unpaired electrons = 4, so it is paramagnetic.

52. (c) : $[Mn(H_2O)_6]^{2+}$: $Mn^{2+} = 3d^5$

$\therefore$ Number of unpaired electrons = 5

$[Fe(H_2O)_6]^{2+}$: $Fe^{2+} = 3d^6$

$\therefore$ Number of unpaired electrons = 4

$[Co(H_2O)_6]^{2+}$: $Co^{2+} = 3d^7$

$\therefore$ Number of unpaired electrons = 3

$[Cr(H_2O)_6]^{2+}$: $Cr^{2+} = 3d^4$

$\therefore$ Number of unpaired electrons = 4

Minimum paramagnetic behaviour is shown by $[Co(H_2O)_6]^{2+}$.

53. (b) : Ti : [Ar] $3d^2\ 4s^2$, Ti^{3+} : [Ar] $3d^1\ 4s^0$

(1 unpaired electron)

Cr : [Ar] $3d^4\ 4s^2$, Cr^{3+} : [Ar] $3d^3\ 4s^0$

(3 unpaired electrons)

Co : [Ar] $3d^7\ 4s^2$, Co^{3+} : [Ar] $3d^6\ 4s^0$

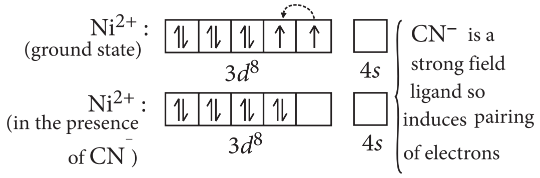
(No unpaired electrons because of pairing)

Zn : [Ar] $3d^{10}\ 4s^2$, Zn^{2+} : [Ar] $3d^{10}$

(No unpaired electrons)

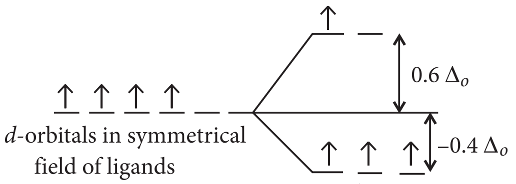
$[Cr(NH_3)_6]^{3+}$ exhibits highest paramagnetic behaviour as it contains 3 unpaired electrons.

54. (a) : A transition metal complex absorbs visible light only if it has unpaired electrons.



No unpaired electron so does not absorb visible light.

55. (d) :



high spin d^4 configuration in an octahedral field

CFSE = $3(-0.4)\Delta_o + 0.6\Delta_o = -1.2\Delta_o + 0.6\Delta_o = -0.6\Delta_o$

56. (b) : A species is coloured when it contains unpaired d-electrons which are capable of undergoing d-d transition on adsorption of light of a particular wavelength.

In TiF_6^{2-}, Ti^{4+} : $3d^0$, colourless

In CoF_6^{3-}, Co^{3+} : $3d^6$, coloured

In Cu_2Cl_2, Cu^+ : $3d^{10}$, colourless

In $NiCl_4^{2-}$, Ni^{2+} : $3d^8$, coloured

Thus, TiF_6^{2-} ($3d^0$) and Cu_2Cl_2 ($3d^{10}$) with empty and fully filled d-orbitals appear colourless as they are not capable of undergoing d-d transition.

57. (b) : $Ti^{4+} \rightarrow 3d^0$, $Cr^{3+} \rightarrow 3d^3$

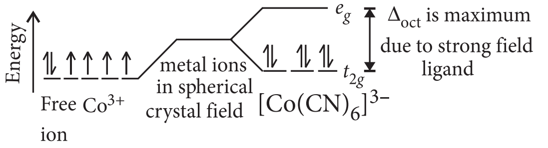
$Zn^{2+} \rightarrow 3d^{10}$, $Sc^{3+} \rightarrow 3d^0$

Transition metal ions containing completely filled d-orbitals or empty d-orbitals are colourless species.

Thus, only $[Cr(NH_3)_6]^{3+}$ having unpaired electron absorb visible light and is coloured.

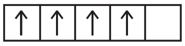
58. (a) : O.S. of Ti in the complex $[Ti(NH_3)_6]^{3+}$ is +3.
$Ti^{3+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$
No. of unpaired electrons in d orbital is one.
Let O.S. of V in complex $[V(gly)_2(OH)_2(NH_3)_2]^+$ is x.
$x + 2 \times 0 + 2 \times (-1) + 2 \times 0 = +1$
$\therefore\ x = +3$
$V^{3+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$
No. of unpaired electrons in d orbital is two.
O.S. of Fe in complex $[Fe(en)(bpy)(NH_3)_2]^{2+}$ is +2.
$\therefore\ Fe^{2+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
As all are strong ligands so, pairing of electrons takes place.
No. of unpaired electron in d orbital is zero.
Let O.S. of Co in the given complex $[Co(ox)_2(OH)_2]^-$ is x.
$x + 2 \times (-2) + 2 \times (-1) = -1 \Rightarrow x - 4 - 2 = -1$
$\therefore\ x = +5$
$Co^{5+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$
As ox and OH^- are weak field ligands so no pairing of electrons takes place, $t_{2g}^3\, e_g^1$ so, it has 4 unpaired electrons and has highest paramagnetic behaviour.

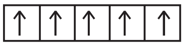
59. (a) : When the ligands are arranged in order of the magnitude of crystal field splitting, the arrangement, thus, obtained is called spectrochemical series.
Arranged in increasing field strength as
$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 < en < NO_2^- < CN^- < CO$
It has been observed that ligands before H_2O are weak field ligands while ligands after H_2O are strong field ligands.

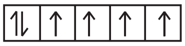


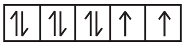
CFSE in octahedral field depends upon the nature of ligands. Stronger the ligands larger will be the value of Δ_{oct}.

60. (b) : 3d

$Cr^{2+} \Rightarrow$

4 unpaired electrons

$Mn^{2+} \Rightarrow$

5 unpaired electrons

$Fe^{2+} \Rightarrow$

4 unpaired electrons

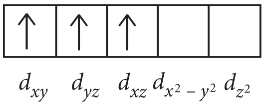
$Ni^{2+} \Rightarrow$

2 unpaired electrons

Greater the number of unpaired electrons, higher is the paramagnetism. Hence, $[Ni(H_2O)_6]^{2+}$ will exhibit the minimum paramagnetic behaviour.

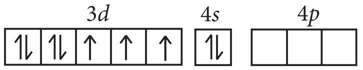
61. (d) : Magnetic moment $= \sqrt{n(n+2)}$

$3.83 = \sqrt{n(n+2)} \Rightarrow (3.83)^2 = n(n+2)$

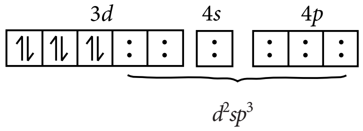
$\Rightarrow 14.6689 = n^2 + 2n$
On solving the equation, $n = 3$
$Cr^{3+} : [Ar]3d^3$



62. (c) : $[Co(NH_3)_6]^{3+}$; $Co(27) : [Ar]^{18}\ 3d^7\ 4s^2$

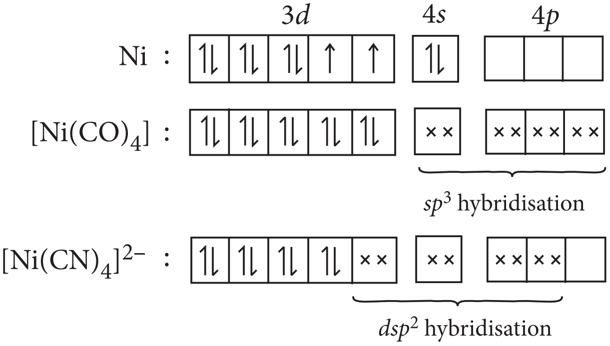


$Co^{3+} : [Ar]^{18}\ 3d^6$

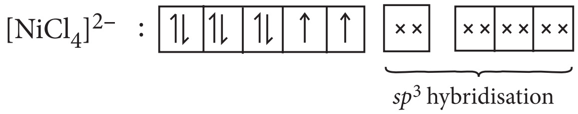


electron pair from six ligands(NH_3)
$d^2sp^3 \rightarrow$ inner octahedral complex and diamagnetic.
$[Zn(NH_3)_6]^{2+} \rightarrow sp^3d^2$(outer)and diamagnetic.
$[Cr(NH_3)_6]^{3+} \rightarrow d^2sp^3$(inner)and paramagnetic.
$[Ni(NH_3)_6]^{2+} \rightarrow sp^3d^2$(outer)and paramagnetic.

63. (b) :



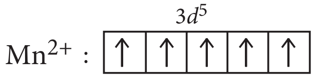
as CN^- is a strong field ligand.



as Cl^- is a weak field ligand.

64. (b) : Cyanide ion is strong field ligand because it is a pseudohalide ion. Pseudohalide ions are stronger coordinating ligands and they have the ability to form σ-bond (from the pseudohalide to the metal) and π bond (from the metal to pseudohalide).

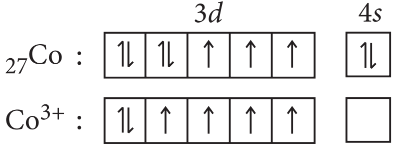
65. (b) : Mn (25) : $3d^5 4s^2$



In presence of weak field ligand, there will be no pairing of electrons. So, it will form a high spin complex, *i.e.*, the number of unpaired electrons = 5.

66. (a) : In the formation of d^2sp^3 hybrid orbitals, two $(n-1)d$ orbitals of e_g set [*i.e.* $(n-1)d_z^2$ and $(n-1)d_{x^2-y^2}$ orbitals)], one ns and three $np(np_x, np_y$ and $np_z)$ orbitals combine together and form six d^2sp^3 hybrid orbitals.

67. (c) : $[CoF_6]^{3-}$:



(weak field ligand F^-)

Thus, the number of unpaired electrons = 4.

68. (d) : Odd electrons, ions and molecules are paramagnetic.

In $Cr(CO)_6$ molecule 12 electrons are contributed by CO group and it contains no odd electron.

Cr : $3d^5\ 4s^1$

$Fe(CO)_5$ molecule also does not contain odd electron.

Fe : $3d^6\ 4s^2$

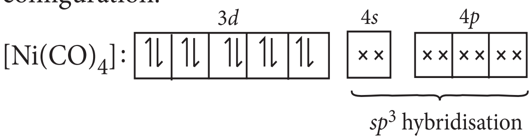
In $[Fe(CN)_6]^{4-}$ ion Fe(+2) : $3d^6\ 4s^0$

∴ No odd electrons.

In $[Cr(NH_3)_6]^{3+}$ ion Cr(+3) : $3d^3\ 4s^0$

This ion contains odd electron so it is paramagnetic.

69. (a) : In $Ni(CO)_4$ complex, Ni(0) will have $3d^{10}$ configuration.



Hence, $[Ni(CO)_4]$ will have tetrahedral geometry and diamagnetic as there are no unpaired electrons.

70. (b) : Based on the number of metal atoms present in a complex, they are classified as :

e.g., : $Fe(CO)_5$: mononuclear

$Co_2(CO)_8$: dinuclear ; $Fe_3(CO)_{12}$: trinuclear

71. (a) : In sigma bonded organometallic complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, *i.e.*, ligand contributes one electron and is therefore, called one electrons donor, *e.g.*, Grignard's reagent *R*-Mg-*X*.

72. (a) : The greater the negative charge on the carbonyl complex, the more easy it would be for the metal to permit its electrons to participate in the back bonding, the higher would be the *M*—C bond order and simultaneously there would be larger reduction in the C—O bond order. Thus, $[Fe(CO)_4]^{2-}$ has the lowest C—O bond order means the longest bond length.

73. (a) : The presence of positive charge on the metal carbonyl would resist the flow of the metal electron charge to π^* orbitals of CO. This would increase the CO bond order and hence, CO in a metal carbonyl cation would absorb at a higher frequency compared to its absorption in a neutral metal carbonyl.

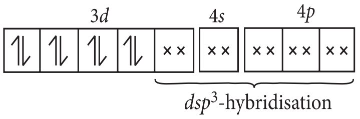
74. (a) : $Al(OC_2H_5)_3$ contains bonding through O and thus it does not have metal - carbon bond.

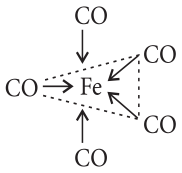
75. (d) : π-bonded organometallic compound includes organometallic compounds of alkenes, alkynes and some other carbon containing compounds having electrons in their *p*-orbitals.

76. (c) : $[Co(CO)_5NH_3]^{2+}$: In this complex, Co-atom is attached with NH_3 through σ bonding and with CO through dative π-bond.

77. (c) : In $Fe(CO)_5$, the 'Fe' atom is dsp^3 hybridised, therefore, shape of the molecule is trigonal bipyramidal.

Fe atom in $Fe(CO)_5$





78. (d) : In $M(CO)_4$, metal is bonded to the ligands via carbon atoms with both σ and π-bond character. Both metal to ligand and ligand to metal bonding are possible.

79. (b)

80. (c) : First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cyanide $[K_3Cu(CN)_4]$.

$$[CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4] \times 2$$

$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$$

$$Cu_2(CN)_2 + 6KCN \rightarrow 2K_3Cu(CN)_4$$

$$2CuSO_4 + 10KCN \rightarrow 2K_3Cu(CN)_4 + 2K_2SO_4 + (CN)_2$$

81. (c) : *cis-platin*, is *cis*-$[PtCl_2(NH_3)_2]$ is used as an anticancer agent.

82. (d) : Copper being more electropositive readily precipitate silver from their salt (Ag^+) solution.

$$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + Ag$$

In $K[Ag(CN)_2]$ solution, a complex anion $[Ag(CN)_2]^-$ is formed so Ag^+ ions are less available in the solution and Cu cannot displace Ag from this complex ion.

83. (b) : Copper sulphate reacts with potassium cyanide giving a white precipitate of cuprous cyanide and cyanogen gas. The cuprous cyanide dissolves in excess of KCN forming potassium cuprocyanide $K_3[Cu(CN)_4]$.

$$2CuSO_4 + 4KCN \rightarrow 2CuCN + (CN)_2 + 2K_2SO_4$$

$$CuCN + 3KCN \rightarrow K_3[Cu(CN)_4]$$

84. (c) : Undecomposed AgBr forms a soluble complex with hypo and the reaction is given as :

$$AgBr + 2Na_2S_2O_3 \rightarrow \underset{\text{Soluble complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

❖❖❖

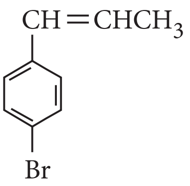
CHAPTER 10

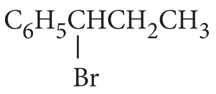
Haloalkanes and Haloarenes

10.4 Methods of Preparation of Haloalkanes

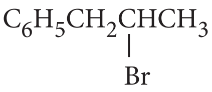
1. The reaction of $C_6H_5CH{=}CHCH_3$ with HBr produces

(a) $C_6H_5CH_2CH_2CH_2Br$

(b) 

(c) 

$C_6H_5\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

(d) 

$C_6H_5CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ *(2015, Cancelled)*

2. In the replacement reaction

$$\gt C{-}Cl + MF \longrightarrow \gt C{-}F + MI$$

The reaction will be most favourable if M happens to be

(a) Na (b) K

(c) Rb (d) Li *(Mains 2012)*

3. When chlorine is passed through propene at 400°C, which of the following is formed?

(a) PVC

(b) Allyl chloride

(c) Propyl chloride

(d) 1, 2-Dichloroethane *(1993)*

10.7 Chemical Reactions

4. Elimination reaction of 2-bromopentane to form pent-2-ene is

(A) β-Elimination reaction

(B) Follows Zaitsev rule

(C) Dehydrohalogenation reaction

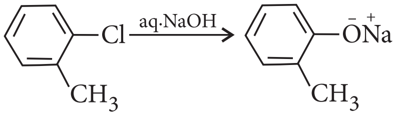
(D) Dehydration reaction

(a) (A), (B), (C) (b) (A), (C), (D)

(c) (B), (C), (D) (d) (A), (B), (D)

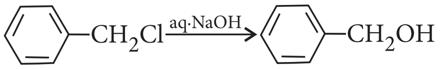
(NEET 2020)

5. The hydrolysis reaction that takes place at the slowest rate, among the following is

(a) 

(b) $H_3C{-}CH_2{-}Cl \xrightarrow{aq \cdot NaOH} H_3C{-}CH_2{-}OH$

(c) $H_2C{=}CH{-}CH_2Cl \xrightarrow{aq \cdot NaOH} H_2C{=}CH{-}CH_2OH$

(d) 

(Odisha NEET 2019)

6. The compound A on treatment with Na gives B, and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order

(a) C_2H_5OH, C_2H_6, C_2H_5Cl

(b) C_2H_5OH, C_2H_5Cl, C_2H_5ONa

(c) C_2H_5Cl, C_2H_6, C_2H_5OH

(d) C_2H_5OH, C_2H_5ONa, C_2H_5Cl *(NEET 2018)*

7. The compound C_7H_8 undergoes the following reactions :

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The product C is

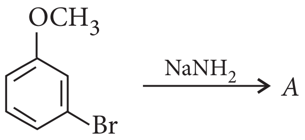
(a) m-bromotoluene

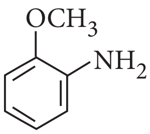
(b) o-bromotoluene

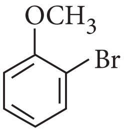
(c) 3-bromo-2,4,6-trichlorotoluene

(d) p-bromotoluene. *(NEET 2018)*

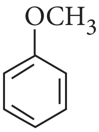
8. Identify A and predict the type of reaction.



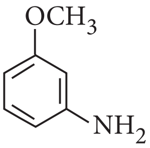
(a)  and elimination addition reaction

(b) 

and cine substitution reaction

(c) 

and cine substitution

(d) 

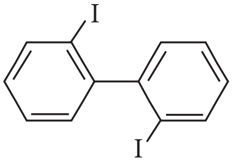
and substitution reaction *(NEET 2017)*

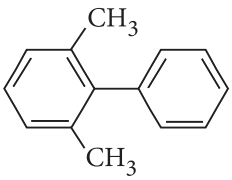
9. Consider the reaction,

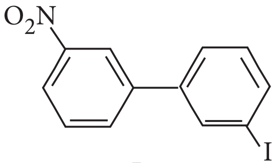
$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$

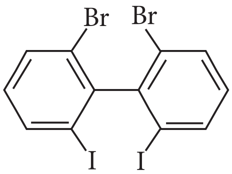
This reaction will be the fastest in
(a) ethanol
(b) methanol
(c) N, N'-dimethylformamide (DMF)
(d) water. *(NEET-II 2016)*

10. Which of the following biphenyls is optically active?

(a) 

(b) 

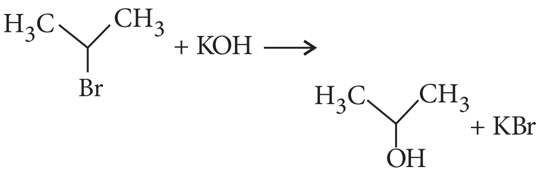
(c) 

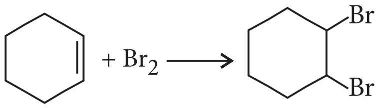
(d) 

(NEET-I 2016)

11. For the following reactions :

(A) $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH{=}CH_2 + KBr + H_2O$

(B) 

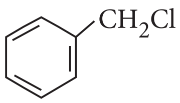
(C) 

Which of the following statements is correct?
(a) (A) is elimination, (B) and (C) are substitution reactions.
(b) (A) is substitution, (B) and (C) are addition reactions.
(c) (A) and (B) are elimination reactions and (C) is addition reaction.
(d) (A) is elimination, (B) is substitution and (C) is addition reaction. *(NEET-I 2016)*

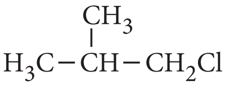
12. Two possible stereo-structures of $CH_3CHOHCOOH$, which are optically active, are called
(a) atropisomers
(b) enantiomers
(c) mesomers
(d) diastereomers. *(2015)*

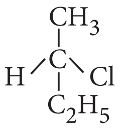
13. In an S_N1 reaction on chiral centres, there is
(a) inversion more than retention leading to partial racemisation
(b) 100% retention
(c) 100% inversion
(d) 100% racemisation. *(2015)*

14. Which of the following compounds will undergo racemisation when solution of KOH hydrolyses?

(i) 

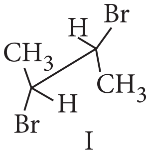
(ii) $CH_3CH_2CH_2Cl$

(iii) 
$H_3C-\overset{\overset{\large CH_3}{|}}{C}H-CH_2Cl$

(iv) 

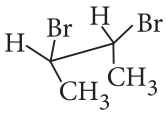
(a) (i) and (ii)
(b) (ii) and (iv)
(c) (iii) and (iv)
(d) (i) and (iv) *(2014)*

15. Given:



I

and



II

I and II are
(a) identical
(b) a pair of conformers
(c) a pair of geometrical isomers
(d) a pair of optical isomers. *(Karnataka NEET 2013)*

16. Which of the following acids does not exhibit optical isomerism?
(a) Maleic acid
(b) α-Amino acids
(c) Lactic acid
(d) Tartaric acid *(2012)*

17. Consider the reactions :

(i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5 + HBr$

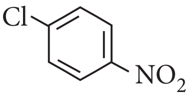
(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5 + Br^-$

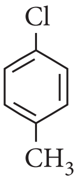
The mechanisms of reactions (i) and (ii) are respectively

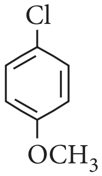
(a) S_N1 and S_N2 (b) S_N1 and S_N1
(c) S_N2 and S_N2 (d) S_N2 and S_N1

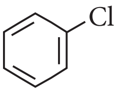
(Mains 2011)

18. Which of the following compounds undergoes nucleophilic substitution reaction most easily?

(a)


(b)


(c)


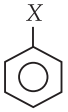
(d)


(Mains 2011)

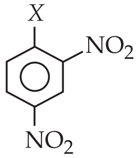
19. Which one is most reactive towards S_N1 reaction?

(a) $C_6H_5CH(C_6H_5)Br$
(b) $C_6H_5CH(CH_3)Br$
(c) $C_6H_5C(CH_3)(C_6H_5)Br$
(d) $C_6H_5CH_2Br$ *(2010)*

20. The correct order of increasing reactivity of C—*X* bond towards nucleophile in the following compounds is



I



II

$(CH_3)_3C-X$

III

$(CH_3)_2CH-X$

IV

(a) I < II < IV < III (b) II < III < I < IV
(c) IV < III < I < II (d) III < II < I < IV

(2010)

21. In the following reaction,

$$C_6H_5CH_2Br \xrightarrow[2.\ H_3O^+]{1.\ Mg,\ Ether} X,$$

the product '*X*' is

(a) $C_6H_5CH_2OCH_2C_6H_5$
(b) $C_6H_5CH_2OH$
(c) $C_6H_5CH_3$
(d) $C_6H_5CH_2CH_2C_6H_5$ *(Mains 2010)*

22. Which of the following reactions is an example of nucleophilic substitution reaction?

(a) $2RX + 2Na \longrightarrow R-R + 2NaX$
(b) $RX + H_2 \longrightarrow RH + HX$
(c) $RX + Mg \longrightarrow RMgX$
(d) $RX + KOH \longrightarrow ROH + KX$ *(2009)*

23. How many stereoisomers does this molecule have?

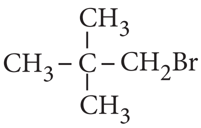
$CH_3CH=CHCH_2CHBrCH_3$

(a) 8 (b) 2
(c) 4 (d) 6 *(2008)*

24. In a S_N2 substitution reaction of the type

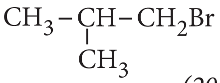
$$R—Br + Cl^- \xrightarrow{DMF} R—Cl + Br^-$$

which one of the following has the highest relative rate?

(a)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br$

(b) CH_3CH_2Br

(c) $CH_3CH_2CH_2Br$

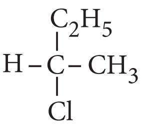
(d)

$CH_3-\underset{CH_3}{CH}-CH_2Br$

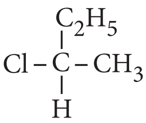
(2008)

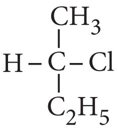
25. If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that

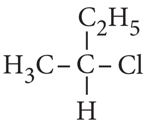
(a) the compound is certainly meso
(b) there is no compound in the solvent
(c) the compound may be a racemic mixture
(d) the compound is certainly a chiral. *(2007)*

26. $CH_3-CHCl-CH_2-CH_3$ has a chiral centre. Which one of the following represents its *R*-configuration?

(a)

$H-\overset{C_2H_5}{\underset{Cl}{C}}-CH_3$

(b)

$Cl-\overset{C_2H_5}{\underset{H}{C}}-CH_3$

(c)

$H-\overset{CH_3}{\underset{C_2H_5}{C}}-Cl$

(d)

$H_3C-\overset{C_2H_5}{\underset{H}{C}}-Cl$

(2007)

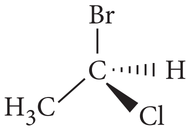
27. Which of the following is not chiral?

(a) 2-Hydroxypropanoic acid
(b) 2-Butanol
(c) 2,3-Dibromopentane
(d) 3-Bromopentane *(2006)*

28. Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism?

(a) Ethyl chloride
(b) Isopropyl chloride
(c) Chlorobenzene
(d) Benzyl chloride *(2005)*

29. The chirality of the compound

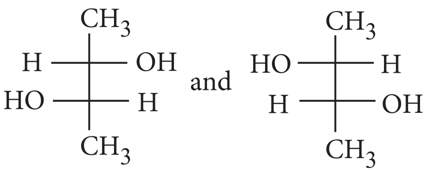


is

(a) *R* (b) *S*
(c) *E* (d) *Z* *(2005)*

30. Which of the following is least reactive in a nucleophilic substitution reaction?
(a) $(CH_3)_3C-Cl$
(b) $CH_2{=}CHCl$
(c) CH_3CH_2Cl
(d) $CH_2{=}CHCH_2Cl$ *(2004)*

31. Which of the following pairs of compounds are enantiomers?

(a)


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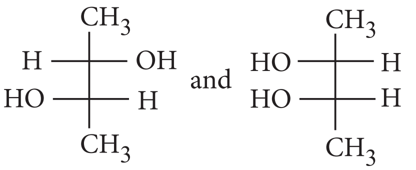

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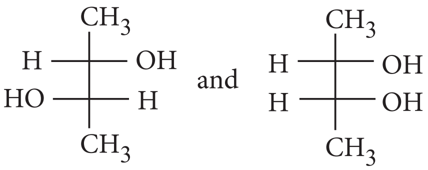
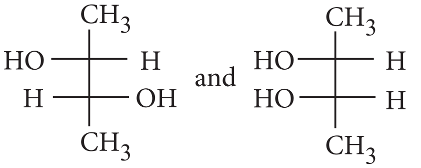


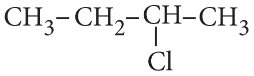
(d)


(2003)

32. Reactivity order of halides for dehydrohalogenation is
(a) $R-F > R-Cl > R-Br > R-I$
(b) $R-I > R-Br > R-Cl > R-F$
(c) $R-I > R-Cl > R-Br > R-F$
(d) $R-F > R-I > R-Br > R-Cl$ *(2002)*

33. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow{\text{acetic anhydride}} Z$

Z in the above reaction sequence is
(a) $CH_3CH_2CH_2NHCOCH_3$
(b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CH_2CONHCH_3$
(d) $CH_3CH_2CH_2CONHCOCH_3$ *(2002)*

34.

$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_3$ obtained by chlorination of *n*-butane will be
(a) meso form (b) racemic mixture
(c) *d*-form (d) *l*-form. *(2001)*

35. An organic compound $A(C_4H_9Cl)$ on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then, *A* is
(a) *t*-butyl chloride (b) *s*-butyl chloride
(c) *iso*-butyl chloride (d) *n*-butyl chloride. *(2001)*

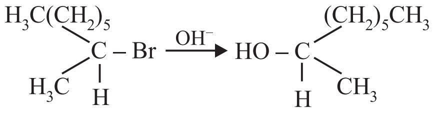
36. A compound of molecular formula C_7H_{16} shows optical isomerism, compound will be
(a) 2,3-dimethylpentane
(b) 2,2-dimethylbutane
(c) 2-methylhexane
(d) none of these. *(2001)*

37. Which of the following compounds is not chiral?
(a) CH_3CHDCH_2Cl (b) CH_3CH_2CHDCl
(c) $DCH_2CH_2CH_2Cl$ (d) $CH_3CHClCH_2D$ *(1998)*

38. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions. But chlorine of 2,4-dinitrochlorobenzene is readily replaced because
(a) NO_2 donates e^- at *meta* position
(b) NO_2 withdraws e^- from *ortho*/*para* positions
(c) NO_2 makes ring electron rich at *ortho* and *para*
(d) NO_2 withdraws e^- from meta position. *(1997)*

39. The alkyl halide is converted into an alcohol by
(a) elimination
(b) dehydrohalogenation
(c) addition
(d) substitution. *(1997)*

40. The following reaction is described as



(a) S_N2 (b) S_N0
(c) S_E2 (d) S_N1 *(1997)*

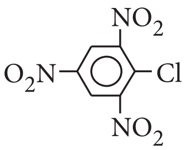
41. Reaction of *t*-butyl bromide with sodium methoxide produces
(a) sodium *t*-butoxide
(b) *t*-butyl methyl ether
(c) isobutane
(d) isobutylene. *(1994)*

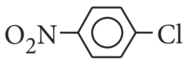
42. Grignard reagent is prepared by the reaction between
(a) magnesium and alkane
(b) magnesium and aromatic hydrocarbon
(c) zinc and alkyl halide
(d) magnesium and alkyl halide. *(1994)*

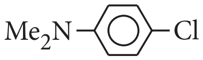
43. Chlorobenzene reacts with Mg in dry ether to give a compound (*A*) which further reacts with ethanol to yield
(a) phenol (b) benzene
(c) ethyl benzene (d) phenyl ether. *(1993)*

44. Benzene reacts with *n*-propyl chloride in the presence of anhydrous $AlCl_3$ to give
(a) 3-propyl-1-chlorobenzene
(b) *n*-propylbenzene
(c) no reaction
(d) isopropylbenzene. *(1993)*

45. Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a)


(b)


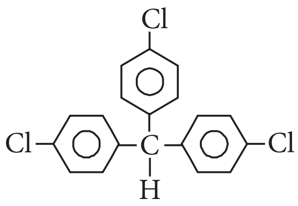
(c)


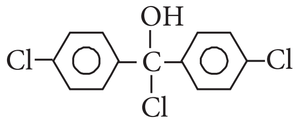
(d) C_6H_5Cl *(1989)*

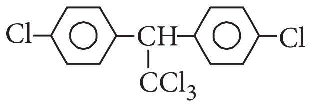
46. Which of the following is an optically active compound?
(a) 1-Butanol (b) 1-Propanol
(c) 2-Chlorobutane (d) 4-Hydroxyheptane
(1989)

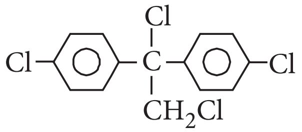
10.8 Polyhalogen Compounds

47. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces

(a)


(b)


(c)


(d)


(2009)

48. Industrial preparation of chloroform employs acetone and
(a) phosgene
(b) calcium hypochlorite
(c) chlorine gas
(d) sodium chloride. *(1993)*

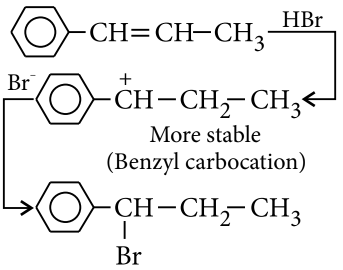
49. Phosgene is a common name for
(a) phosphoryl chloride
(b) thionyl chloride
(c) carbon dioxide and phosphine
(d) carbonyl chloride. *(1988)*

ANSWER KEY

1.	(c)	**2.**	(c)	**3.**	(b)	**4.**	(a)	**5.**	(a)	**6.**	(d)	**7.**	(a)	**8.**	(d)	**9.**	(c)	**10.**	(d)
11.	(d)	**12.**	(b)	**13.**	(a)	**14.**	(None)	**15.**	(b)	**16.**	(a)	**17.**	(c)	**18.**	(a)	**19.**	(c)	**20.**	(a)
21.	(c)	**22.**	(d)	**23.**	(c)	**24.**	(b)	**25.**	(a)	**26.**	(b)	**27.**	(d)	**28.**	(d)	**29.**	(a)	**30.**	(b)
31.	(a)	**32.**	(b)	**33.**	(a)	**34.**	(b)	**35.**	(a)	**36.**	(a)	**37.**	(c)	**38.**	(b)	**39.**	(d)	**40.**	(a)
41.	(d)	**42.**	(d)	**43.**	(b)	**44.**	(d)	**45.**	(a)	**46.**	(c)	**47.**	(c)	**48.**	(b)	**49.**	(d)		

Hints & Explanations

1. (c) :

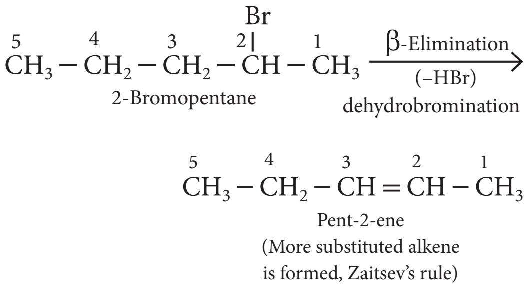


2. (c) : Tertiary halide shows S_N1 mechanism *i.e.*, ionic mechanism. In the given reaction negative ion will attack on carbocation. Thus greater the tendency of ionisation (greater ionic character in $M-F$ bond) more favourable will be reaction. The most ionic bond is Rb – F in the given examples thus most favourable reaction will be with Rb–F.

3. (b) : $CH_3CH{=}CH_2 \xrightarrow[-\,HCl]{Cl_2,\ 400°C} ClCH_2CH{=}CH_2$

At 400°C temperature, substitution occurs instead of addition.

4. (a) :



$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{\overset{Br}{|}}{\overset{2}{CH}}-\overset{1}{CH_3} \xrightarrow[(-HBr)]{\beta\text{-Elimination}}$$

2-Bromopentane dehydrobromination

$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_3}$$

Pent-2-ene
(More substituted alkene
is formed, Zaitsev's rule)

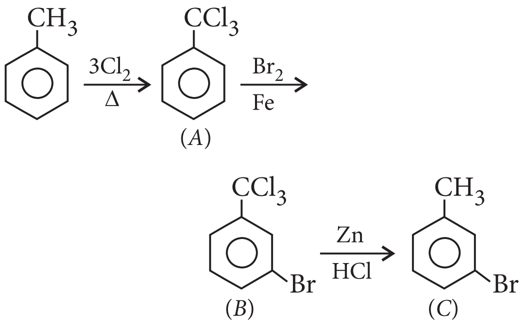
5. (a) : Aryl halides are less reactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles such as OH^-, NH_2^-, etc. In chlorobenzene, the electron pair of chlorine atom is in conjugation with π-electrons of benzene ring. Thus C—Cl bond acquires double bond character and is difficult to break.

6. (d) :

$$\begin{tikzcd} \underset{(A)}{C_2H_5OH} \arrow[r, "Na"] \arrow[d, "PCl_5"] & \underset{(B)}{C_2H_5O^-Na^+} \\ \underset{(C)}{C_2H_5Cl} & \end{tikzcd}$$

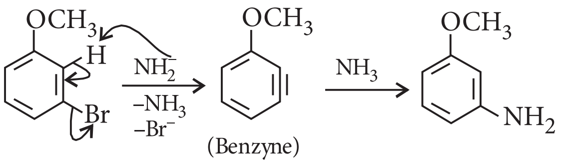
$$\underset{(B)}{C_2H_5O^-Na^+} + \underset{(C)}{C_2H_5Cl} \xrightarrow[\text{Williamson's synthesis}]{S_N2} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5}$$

7. (a) :



m-bromotoluene

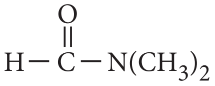
8. (d) : *m*-Bromoanisole gives only the respective *meta* substituted aniline. This is a substitution reaction which goes by an elimination-addition pathway.



9. (c) : The reaction,

$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$

follows S_N2 mechanism which is favoured by polar aprotic solvent *i.e.*, *N*, *N′* dimethylformamide (DMF),

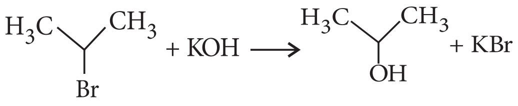


$$H-\overset{\overset{O}{\|}}{C}-N(CH_3)_2$$

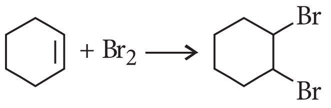
10. (d) : *o*-Substituted biphenyls are optically active as both the rings are not in one plane and their mirror images are non-superimposable.

11. (d) : $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH{=}CH_2 + KBr + H_2O$

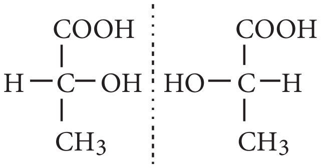
Saturated compound is converted into unsaturated compound by removal of group of atoms hence, it is an elimination reaction.



—Br group is replaced by — OH group hence, it is a substitution reaction.



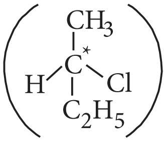
Addition of Br_2 converts an unsaturated compound into a saturated compound hence, it is an addition reaction.

12. (b) : 

Enantiomers

13. (a) : In case of optically active alkyl halides, S_N1 reaction is accompanied by racemisation. The carbocation formed in the slow step being sp^2 hybridised is planar and attack of nucleophile may take place from either side resulting in a mixture of products, one having the same configuration and other having inverted configuration.

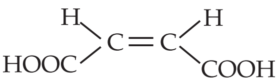
The isomer corresponding to inversion is present in slight excess because S_N1 also depends upon the degree of shielding of the front side of the reacting carbon.

14. (None) : Due to chirality , only compound (iv) will undergo racemisation.

Hence, all the given options are incorrect.

15. (b) : I and II are staggered and eclipsed conformers.

16. (a) : Maleic acid shows geometrical isomerism and not optical isomerism.



Maleic acid

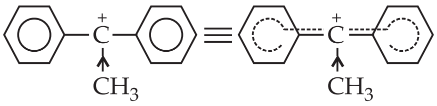
17. (c) : If reaction is S_N1, there will be the formation of carbocation and the rearrangement takes place. In these reactions there is no rearrangement hence both are S_N2 mechanism.

18. (a) : Electron withdrawing groups like $-NO_2$ facilitates nucleophilic substitution reaction in chlorobenzene.

19. (c) : S_N1 reactions proceed *via* the formation of a carbocation intermediate.

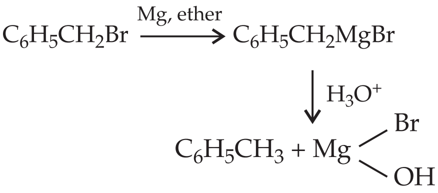
More stable is the carbocation more reactive is the alkyl/aryl halide towards S_N1.

In $C_6H_5C^+(CH_3)(C_6H_5)$ carbocation, the two phenyl rings by their $+R$ effect and $-CH_3$ by its $+I$ effect diminish the positive charge and make it stable.



20. (a) : I < II < IV < III

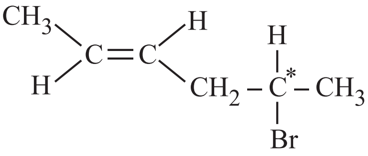
The order of reactivity is dependent on the stability of the intermediate carbocation formed by cleavage of C—X bond. The 3° carbocation (formed from III) will be more stable than its 2° counter part (formed from IV) which in turn will be more stable than the arenium ion (formed from I). Also, the aryl halide has a double bond character in the C—X bond which makes the cleavage more difficult. However, inspite of all the stated factors, II will be more reactive than I due to the presence of the electron withdrawing $-NO_2$ group. C—X bond becomes weak and undergoes nucleophilic substitution reaction.

21. (c) : 

$$C_6H_5CH_2Br \xrightarrow{\text{Mg, ether}} C_6H_5CH_2MgBr \xrightarrow{H_3O^+} C_6H_5CH_3 + Mg\begin{matrix}Br\\OH\end{matrix}$$

22. (d)

23. (c) : The given compound may be written as



Both geometrical isomerism (*cis-trans* form) and optical isomerism is possible in the given compound.

No. of optical isomer $= 2^n = 2^1 = 2$

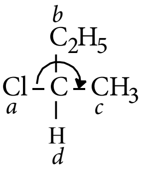
(where n = no. of asymmetric carbon)

Hence total no. of stereoisomers = 2 + 2 = 4

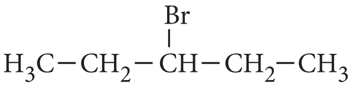
24. (b) : S_N2 mechanism is followed in case of primary and secondary alkyl halides *i.e.* S_N2 reaction is favoured by small groups on the carbon atoms attached to halogen so, $CH_3-X > R-CH_2-X > R_2CH-X > R_3C-X$.

Primary is more reactive than secondary and tertiary alkyl halides.

25. (a) : Meso compound does not rotate plane polarised light. Compound which contains tetrahedral atoms with four different groups but the whole molecule is achiral, is known as meso compound. It possesses a plane of symmetry and is optically inactive. One of the asymmetric carbon atoms turns the plane of polarised light to the right and other to the left and to the same extent so that the rotation due to upper half is compensated by the lower half, *i.e.*, internally compensated, and finally there is no rotation of plane polarised light.

26. (b) : 

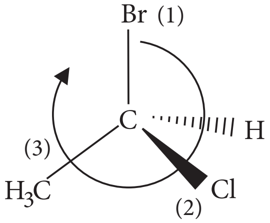
R-configuration

27. (d) : 
$H_3C-CH_2-\overset{\overset{\large Br}{|}}{C}H-CH_2-CH_3$

Due to absence of asymmetric carbon atom.

28. (d) : S_N1 reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens and nature of carbonium ion in substrate is

Benzyl > Allyl > Tertiary > Secondary > Primary > Methyl halides.

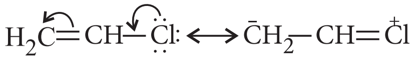
29. (a) : 

Lowest priority atom is always away from the viewer. Priority is seen on the basis of atomic no. and if atomic no. are same then on the basis of atomic mass.

If clockwise then it is *R*, if anticlockwise then it is *S*.

Name of the molecule is, (*R*) 1-bromo-1-chloroethane.

30. (b) : The non-reactivity of the chlorine atom in vinyl chloride can be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridisation, the C – Cl bond will be a σ-bond and the two lone pairs of electrons would occupy the other two sp^2 orbitals. This would leave a *p* orbital containing a lone pair, and this orbital could now conjugate with the π-bond of the ethylenic link. Thus two M.O's will be required to accommodate these four π-electrons. Furthermore, since chlorine is more electronegative than carbon, the electrons will tend to be found in the vicinity of the chlorine atom. Nevertheless, the chlorine atom has now lost full control of the lone pair and so, is less negative than it would have been had there been no conjugation. Since two carbon atoms have acquired a share in the lone pair, each carbon atom acquires a small negative charge. Hence, owing to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group, the lone pair must be localised again on the chlorine atom. This requires energy, and so the chlorine is more firmly bound.


$$H_2C=CH-\ddot{\underset{..}{Cl}}: \longleftrightarrow \bar{C}H_2-CH=\overset{+}{\ddot{Cl}}$$

31. (a) : These two are non-superimposable mirror images of each other, so they are enantiomers.

32. (b) : I > Br > Cl > F ⟶ atomic radii

F, Cl, Br, I belong to the same group orderly. Atomic radii go on increasing as the nuclear charge increases in preceding downwards in a group. The decreasing order of bond length C – I > C – Br > C – Cl > C – F. The order of bond dissociation energy *R* – F > *R* – Cl > *R* – Br > *R* – I. During dehydrohalogenation C – I bond breaks more easily than C – F bond. So reactivity order of halides is,

R – I > *R* – Br > *R* – Cl > *R* – F.

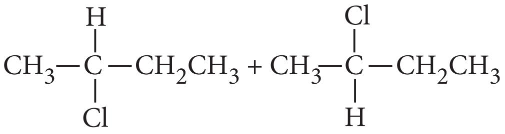
33. (a) : $CH_3CH_2Cl \xrightarrow{NaCN} \underset{(X)}{CH_3CH_2CN} \xrightarrow{Ni/H_2} \underset{(Y)}{CH_3CH_2CH_2NH_2} \xrightarrow[\text{anhydride}]{\text{acetic}} \underset{(Z)}{CH_3CH_2CH_2NHCOCH_3}$

34. (b) : Chlorination of *n*-butane takes place *via* free radical formation. *i.e.* $Cl_2 \longrightarrow \dot{C}l + \dot{C}l$

$CH_3CH_2CH_2CH_3 \xrightarrow{\dot{C}l} CH_3\dot{C}HCH_2CH_3 + HCl$

sp^2- hybrid planar shape intermediate and $\dot{C}l$ may attack from either side to give

$CH_3\dot{C}HCH_2CH_3 + \dot{C}l \longrightarrow$


$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-CH_2CH_3 + CH_3-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2CH_3$$

Racemic mixture

(Mixture of 50% *d*-form and 50% *l*-form)

35. (a) : Wurtz reaction : It involves the reaction of alkyl halides with Na in ether to form higher alkanes.

$2R-X + 2Na \longrightarrow R-R + 2NaX$

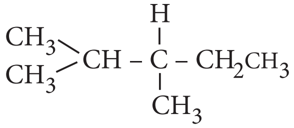
In the given problem,

$\underset{(A)}{2C_4H_9Cl} + 2Na \xrightarrow{\text{Ether}} C_4H_9 \cdot C_4H_9 + 2NaCl$

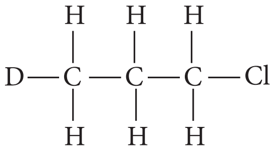
Compound *A* is *t*-butyl chloride, in this compound all $-CH_3$ groups have primary hydrogen only and able to give only, one chloro derivative.

$(CH_3)_3CC(CH_3)_3 \xrightarrow{Cl_2} CH_2Cl(CH_3)_2C-C(CH_3)_3$

36. (a) : Organic compounds exhibit the property of enantiomerism (optical isomerism) only when their molecules are chiral. Most chiral compounds have a chiral centre, which is an atom bonded to four different atoms or groups.

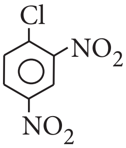


2,3-Dimethylpentane has one chiral C-atom and does not have any symmetric element.

37. (c) : 
$$D-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-Cl$$

The above compound has no chiral 'C'-atom. All the 'C' atoms are attached to two identical 'H' atoms, so they are not asymmetrical.

38. (b) :

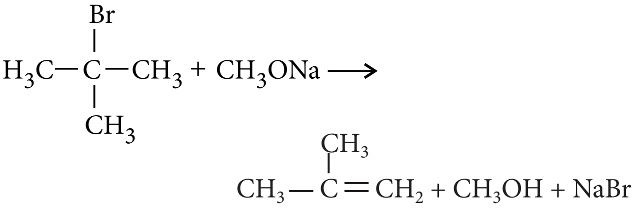


Withdrawal of electrons by $-NO_2$ groups from *ortho*/*para* positions cause easier removal of $-Cl$ atom due to the development of positive charge on *o*- and *p*- positions.

39. (d) : $\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{(aqueous)}}{KOH} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KBr$

40. (a) : S_N2 reaction are bimolecular reactions where rate of reaction depends on the concentration of both substrate and nucleophile. When OH^- attacks the substrate from the opposite side of the leaving group *i.e.*, Br^- a transition state results, to which both OH and Br are partially bonded to carbon atom.

41. (d) : Isobutylene is obtained.



$$H_3C-\underset{CH_3}{\overset{Br}{C}}-CH_3 + CH_3ONa \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + CH_3OH + NaBr$$

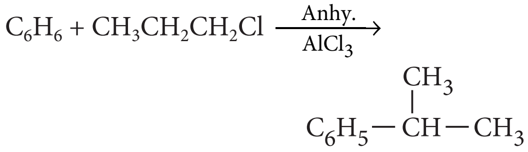
Thus, the reaction produces isobutylene.

42. (d) : Grignard reagent is prepared by heating an alkyl halide with dry magnesium powder in dry ether.

$$R-X + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

43. (b) : $C_6H_5Cl \xrightarrow{Mg} \underset{(A)}{C_6H_5MgCl} \xrightarrow{CH_3CH_2OH} C_6H_6 + CH_3CH_2OMgCl$

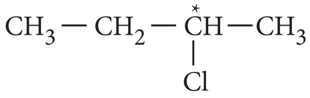
44. (d) :



$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[AlCl_3]{\text{Anhy.}} \underset{\text{Isopropylbenzene}}{C_6H_5-\overset{CH_3}{CH}-CH_3}$$

45. (a) : Cl in 2, 4, 6-trinitrochlorobenzene is activated by three $-NO_2$ groups at *o*-and *p*-positions and hence undergoes hydrolysis most readily.

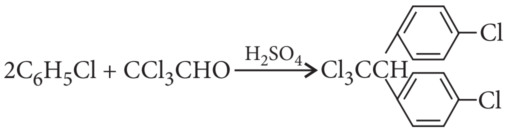
46. (c) :



$$CH_3-CH_2-\underset{Cl}{\overset{*}{C}H}-CH_3$$

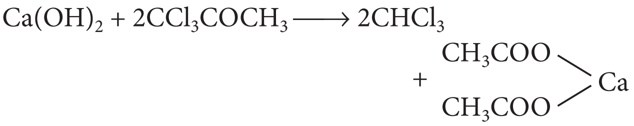
2-Chlorobutane contains a chiral carbon atom and hence it is optically active compound.

47. (c) : It gives D.D.T
(*p,p*- dichlorodiphenyltrichloroethane)



48. (b) : $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

$CH_3COCH_3 + 3Cl_2 \longrightarrow CCl_3COCH_3 + 3HCl$



$$Ca(OH)_2 + 2CCl_3COCH_3 \longrightarrow 2CHCl_3 + \begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\!\!>Ca$$

49. (d)

❖❖❖

CHAPTER
11

Alcohols, Phenols and Ethers

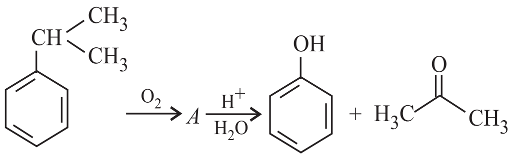
11.1 Classification

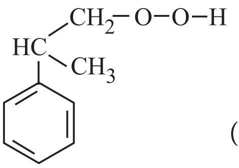
1. The general molecular formula, which represents the homologous series of alkanols is
(a) $C_nH_{2n+2}O$ (b) $C_nH_{2n}O_2$
(c) $C_nH_{2n}O$ (d) $C_nH_{2n+1}O$ *(2006)*

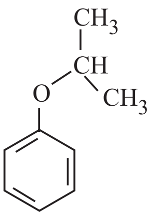
11.4 Alcohols and Phenols

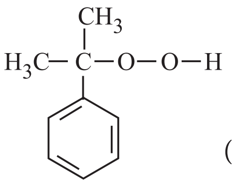
2. Reaction between acetone and methyl magnesium chloride followed by hydrolysis will give
(a) *iso*-propyl alcohol (b) *sec*-butyl alcohol
(c) *tert*-butyl alcohol (d) *iso*-butyl alcohol.
(NEET 2020)

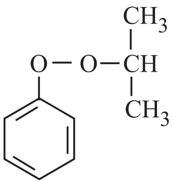
3. The structure of intermediate *A* in the following reaction is



(a) 

(b) 

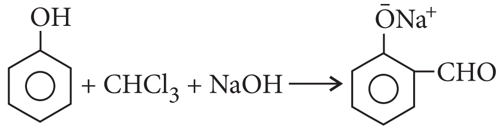
(c) 

(d) 

(NEET 2019)

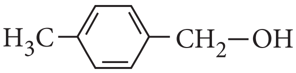
4. When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is
(a) a carboxylic acid (b) an aldehyde
(c) a ketone (d) an alkene.
(Odisha NEET 2019)

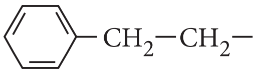
5. In the reaction,

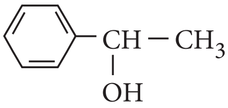


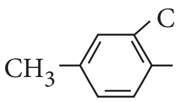
the electrophile involved is
(a) dichloromethyl cation $(\overset{+}{C}HCl_2)$
(b) formyl cation $(\overset{+}{C}HO)$
(c) dichloromethyl anion $(\overset{-}{C}HCl_2)$
(d) dichlorocarbene $(:CCl_2)$ *(NEET 2018)*

6. Compound *A*, $C_8H_{10}O$, is found to react with NaOI (produced by reacting *Y* with NaOH) and yields a yellow precipitate with characteristic smell. *A* and *Y* are respectively

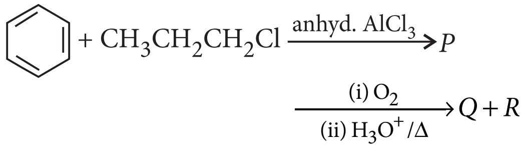
(a)  and I_2

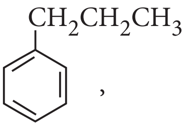
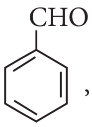
(b)  and I_2

(c)  and I_2

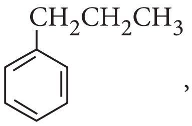
(d)  and I_2 *(NEET 2018)*

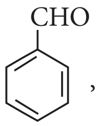
7. Identify the major products *P*, *Q* and *R* in the following sequence of reactions :



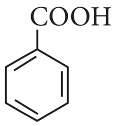
(a) *P* =  , *Q* =  ,

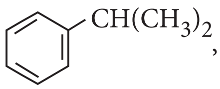
$R = CH_3CH_2-OH$

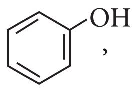
(b) $P =$ 

, $Q =$ 

,

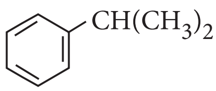
$R =$ 

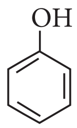
(c) $P =$ 

, $Q =$ 

,

$R = CH_3CH(OH)CH_3$

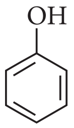
(d) $P =$ 

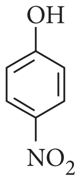
, $Q =$ 

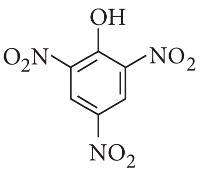
,

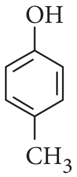
$R = CH_3-CO-CH_3$ *(NEET 2018)*

8. Which one is the most acidic compound?

(a) 

(b) 

(c) 

(d) 

(NEET 2017)

9. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group?

(a) $-COOH$ (b) $-CHCl_2$

(c) $-CHO$ (d) $-CH_2Cl$ *(2015)*

10. Which of the following reaction(s) can be used for the preparation of alkyl halides?

(I) $CH_3CH_2OH + HCl \xrightarrow{\text{Anh.}ZnCl_2}$

(II) $CH_3CH_2OH + HCl \longrightarrow$

(III) $(CH_3)_3COH + HCl \longrightarrow$

(IV) $(CH_3)_2CHOH + HCl \xrightarrow{\text{Anh.}ZnCl_2}$

(a) (I) and (II) only (b) (IV) only

(c) (III) and (IV) only

(d) (I), (III) and (IV) only *(2015)*

11. Which of the following will not be soluble in sodium hydrogen carbonate?

(a) 2,4,6-Trinitrophenol

(b) Benzoic acid

(c) *o*-Nitrophenol

(d) Benzenesulphonic acid *(2014)*

12. Number of isomeric alcohols of molecular formula $C_6H_{14}O$ which give positive iodoform test is

(a) three (b) four (c) five (d) two.

(Karnataka NEET 2013)

13. In the following sequence of reactions,

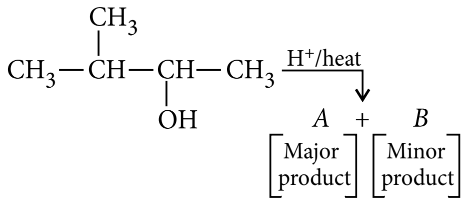
$$CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{ether}]{LiAlH_4} C$$

the end product (C) is

(a) acetone (b) methane

(c) acetaldehyde (d) ethyl alcohol. *(2012)*

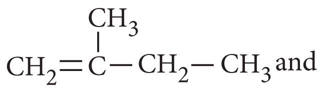
14. In the following reactions,

(i) 

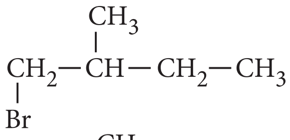
$$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{H^+/\text{heat}} \underset{\left[\begin{smallmatrix}\text{Major}\\\text{product}\end{smallmatrix}\right]}{A} + \underset{\left[\begin{smallmatrix}\text{Minor}\\\text{product}\end{smallmatrix}\right]}{B}$$

(ii) $$A \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\left[\begin{smallmatrix}\text{Major}\\\text{product}\end{smallmatrix}\right]}{C} + \underset{\left[\begin{smallmatrix}\text{Minor}\\\text{product}\end{smallmatrix}\right]}{D}$$

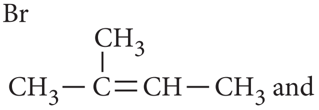
the major products (A) and (C) are respectively

(a) 

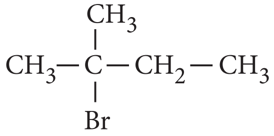
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and



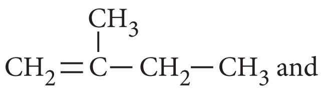
$\underset{Br}{CH_2}-\overset{CH_3}{CH}-CH_2-CH_3$

(b) 

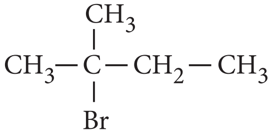
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and



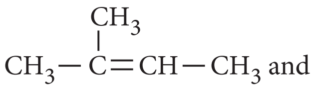
$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2-CH_3$

(c) 

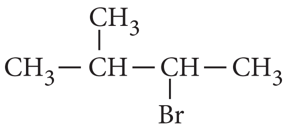
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and



$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2-CH_3$

(d) 

$CH_3-\overset{CH_3}{C}=CH-CH_3$ and



$CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3$ *(2011)*

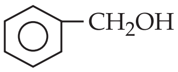
15. Given are cyclohexanol (I), acetic acid (II), 2,4,6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be

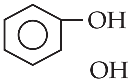
(a) III > II > IV > I (b) II > III > I > IV

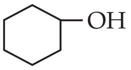
(c) II > III > IV > I (d) III > IV > II > I

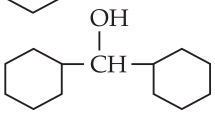
(2010)

16. Which of the following compounds has the most acidic nature?

(a) 

(b) 

(c) 

(d) 

(2010)

17. Among the following four compounds

(i) Phenol (ii) Methyl phenol

(iii) *Meta*-nitrophenol (iv) *Para*-nitrophenol

The acidity order is

(a) (iv) > (iii) > (i) > (ii) (b) (iii) > (iv) > (i) > (ii)

(c) (i) > (iv) > (iii) > (ii) (d) (ii) > (i) > (iii) > (iv)

(2010)

18. When glycerol is treated with excess of HI, it produces

(a) 2-iodopropane (b) allyl iodide

(c) propene (d) glycerol triiodide.

(Mains 2010)

19. Consider the following reaction :

$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{alc.KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4\text{, room temperature}} Z$$

the product *Z* is

(a) $CH_3CH_2-O-CH_2-CH_3$

(b) $CH_3-CH_2-O-SO_3H$

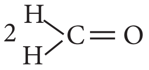
(c) CH_3CH_2OH

(d) $CH_2=CH_2$ *(2009)*

20. $HOCH_2CH_2OH$ on heating with periodic acid gives

(a) 2HCOOH

(b) 
$\begin{array}{c} CHO \\ | \\ CHO \end{array}$

(c) 
$2\,H_2C=O$

(d) $2CO_2$ *(2009)*

21. Consider the following reaction :

$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alkaline } KMnO_4} Z$$

the product *Z* is

(a) benzaldehyde (b) benzoic acid

(c) benzene (d) toluene. *(2009)*

22. Ethylene oxide when treated with Grignard reagent yields

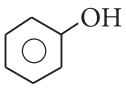
(a) primary alcohol (b) secondary alcohol

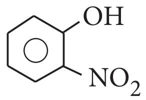
(c) tertiary alcohol (d) cyclopropyl alcohol.

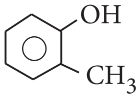
(2006)

23. Which one of the following compounds is most acidic?

(a) $Cl-CH_2-CH_2-OH$

(b) 

(c) 

(d) 

(2005)

24. Which one of the following will not form a yellow precipitate on heating with an alkaline solution of iodine?

(a) $CH_3CH(OH)CH_3$ (b) $CH_3CH_2CH(OH)CH_3$

(c) CH_3OH (d) CH_3CH_2OH *(2004)*

25. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?

(a) PCl_5 (b) Reduction

(c) Oxidation with potassium dichromate

(d) Ozonolysis *(2002)*

26. When phenol is treated with $CHCl_3$ and NaOH, the product formed is

(a) benzaldehyde (b) salicylaldehyde

(c) salicylic acid (d) benzoic acid. *(2002)*

27. Which of the following is correct?

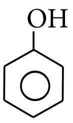
(a) On reduction, any aldehyde gives secondary alcohol.

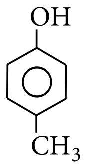
(b) Reaction of vegetable oil with H_2SO_4 gives glycerine.

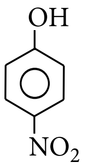
(c) Alcoholic iodine with NaOH gives iodoform.

(d) Sucrose on reaction with NaCl gives invert sugar. *(2001)*

28. The correct acidic order of the following is

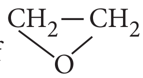
I. 

II. 

III. 

(a) I > II > III (b) III > I > II

(c) II > III > I (d) I > III > II *(2001)*

29. Reaction of  CH_2-CH_2 (with O bridging) with *RMgX* leads to the formation of

(a) RCH_2CH_2OH (b) $RCHOHCH_3$

(c) $RCHOHR$ (d) 
R_2CHCH_2OH

(1998)

30. When 3,3-dimethyl-2-butanol is heated with H_2SO_4, the major product obtained is

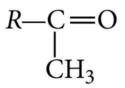
(a) 2,3-dimethyl-2-butene

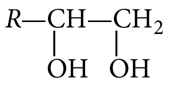
(b) *cis* and *trans* isomers of 2,3-dimethyl-2-butene

(c) 2,3-dimethyl-1-butene

(d) 3,3-dimethyl-1-butene. *(1995)*

31. The alkene $R-CH{=}CH_2$ reacts readily with B_2H_6 and the product on oxidation with alkaline hydrogen peroxides produces

(a) 
$R-\underset{\substack{|\\CH_3}}{C}{=}O$

(b) 
$R-\underset{\substack{|\\OH}}{CH}-\underset{\substack{|\\OH}}{CH_2}$

(c) $R-CH_2-CHO$
(d) $R-CH_2-CH_2-OH$ *(1995)*

32. On heating glycerol with conc. H_2SO_4, a compound is obtained which has bad odour. The compound is
(a) acrolein (b) formic acid
(c) allyl alcohol (d) glycerol sulphate. *(1994)*

33. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of
(a) H-bonding in ethanol
(b) H-bonding in dimethyl ether
(c) CH_3 group in ethanol
(d) CH_3 group in dimethyl ether. *(1993)*

34. Increasing order of acid strength among *p*-methoxyphenol, *p*-methylphenol and *p*-nitrophenol is
(a) *p*-nitrophenol, *p*-methoxyphenol, *p*-methylphenol
(b) *p*-methylphenol, *p*-methoxyphenol, *p*-nitrophenol
(c) *p*-nitrophenol, *p*-methylphenol, *p*-methoxyphenol
(d) *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol. *(1993)*

35. Which one of the following on oxidation gives a ketone?
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) All of these *(1993)*

36. What is formed when a primary alcohol undergoes catalytic dehydrogenation?
(a) Aldehyde (b) Ketone
(c) Alkene (d) Acid *(1993)*

37. How many isomers of $C_5H_{11}OH$ will be primary alcohols?
(a) 5 (b) 4 (c) 2 (d) 3 *(1992)*

38. HBr reacts fastest with
(a) 2-methylpropan-1-ol
(b) methylpropan-2-ol
(c) propan-2-ol
(d) propan-1-ol. *(1992)*

39. When phenol is treated with excess bromine water. It gives
(a) *m*-bromophenol
(b) *o*- and *p*-bromophenols
(c) 2,4-dibromophenol
(d) 2,4,6-tribromophenol. *(1992)*

40. The compound which reacts fastest with Lucas reagent at room temperature is
(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-1-ol
(d) 2-methylpropan-2-ol. *(1989)*

41. Which one of the following compounds will be most readily attacked by an electrophile?
(a) Chlorobenzene (b) Benzene
(c) Phenol (d) Toluene *(1989)*

42. Propene, $CH_3CH{=}CH_2$ can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal for the above conversion?
(a) $KMnO_4$ (alkaline)
(b) Osmium tetroxide (OsO_4/CH_2Cl_2)
(c) B_6H_6 and alk. H_2O_2 (d) O_3/Zn *(1989)*

43. Phenol is heated with $CHCl_3$ and aqueous KOH when salicylaldehyde is produced. This reaction is known as
(a) Rosenmund's reaction
(b) Reimer-Tiemann reaction
(c) Friedel-Crafts reaction
(d) Sommelet reaction. *(1989,1988)*

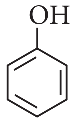
44. Lucas reagent is
(a) conc. HCl and anhydrous $ZnCl_2$
(b) conc. HNO_3 and hydrous $ZnCl_2$
(c) conc. HCl and hydrous $ZnCl_2$
(d) conc. HNO_3 and anhydrous $ZnCl_2$. *(1988)*

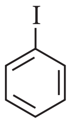
11.5 Some Commercially Important Alcohols

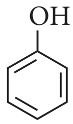
45. Methanol is industrially prepared by
(a) oxidation of CH_4 by steam at 900°C
(b) reduction of HCHO using $LiAIH_4$
(c) reaction of HCHO with a solution of NaOH
(d) reduction of CO using H_2 and $ZnO-Cr_2O_3$. *(1992)*

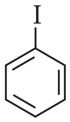
11.6 Ethers

46. Anisole on cleavage with HI gives

(a)  + CH_3I

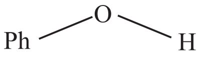
(b)  + CH_3OH

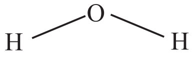
(c)  + C_2H_5I

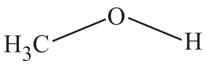
(d)  + C_2H_5OH

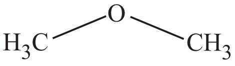
(NEET 2020)

47. The compound that is most difficult to protonate is

(a) 

(b) 

(c) 

(d) 

(NEET 2019)

48. The major products *C* and *D* formed in the following reactions respectively are

$H_3C–CH_2–CH_2–O–C(CH_3)_3 \xrightarrow{\text{excess HI}} C + D$

(a) $H_3C–CH_2–CH_2–I$ and $I–C(CH_3)_3$

(b) $H_3C–CH_2–CH_2–OH$ and $I–C(CH_3)_3$

(c) $H_3C–CH_2–CH_2–I$ and $HO–C(CH_3)_3$

(d) $H_3C–CH_2–CH_2–OH$ and $HO–C(CH_3)_3$

(Odisha NEET 2019)

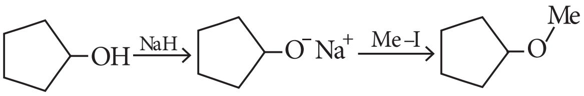
49. The heating of phenyl methyl ether with HI produces

(a) iodobenzene (b) phenol

(c) benzene (d) ethyl chloride.

(NEET 2017)

50. The reaction



can be classified as

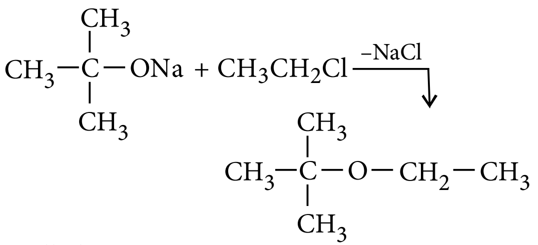
(a) dehydration reaction

(b) Williamson alcohol synthesis reaction

(c) Williamson ether synthesis reaction

(d) alcohol formation reaction. *(NEET-I 2016)*

51. The reaction,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa + CH_3CH_2Cl \xrightarrow{-NaCl} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2-CH_3$$

is called

(a) Etard reaction

(b) Gattermann-Koch reaction

(c) Williamson synthesis

(d) Williamson continuous etherification process.

(2015, Cancelled)

52. Among the following sets of reactants which one produces anisole?

(a) CH_3CHO ; *RMgX*

(b) C_6H_5OH ; NaOH ; CH_3I

(c) C_6H_5OH ; neutral $FeCl_3$

(d) $C_6H_5CH_3$; CH_3COCl ; $AlCl_3$ *(2014)*

53. Identify *Z* in the sequence of reactions :

$$CH_3CH_2CH=CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

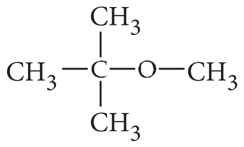
(a) $CH_3—(CH_2)_3—O—CH_2CH_3$

(b) $(CH_3)_2CH—O—CH_2CH_3$

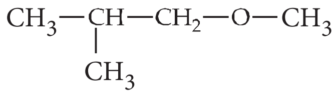
(c) $CH_3(CH_2)_4—O—CH_3$

(d) $CH_3CH_2—CH(CH_3)—O—CH_2CH_3$ *(2014)*

54. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

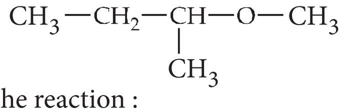
(a) 

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3$

(b) 

$CH_3-\underset{CH_3}{CH}-CH_2-O-CH_3$

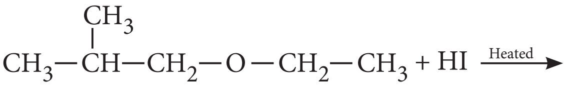
(c) $CH_3—CH_2—CH_2—O—CH_3$

(d) 

$CH_3-CH_2-\underset{CH_3}{CH}-O-CH_3$

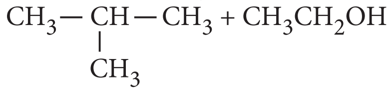
(NEET 2013)

55. In the reaction :

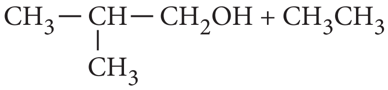


$$CH_3-\overset{CH_3}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{\text{Heated}}$$

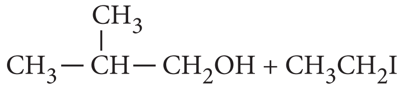
which of the following compounds will be formed?

(a) 

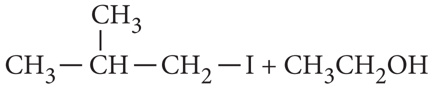
$CH_3-\underset{CH_3}{CH}-CH_3 + CH_3CH_2OH$

(b) 

$CH_3-\underset{CH_3}{CH}-CH_2OH + CH_3CH_3$

(c) 

$CH_3-\overset{CH_3}{CH}-CH_2OH + CH_3CH_2I$

(d) 

$CH_3-\overset{CH_3}{CH}-CH_2-I + CH_3CH_2OH$ *(2007)*

56. The major organic product in the reaction is

$CH_3 – O – CH(CH_3)_2 + HI \longrightarrow$ products

(a) $CH_3I + (CH_3)_2CHOH$

(b) $CH_3OH + (CH_3)_2CHI$

(c) $ICH_2OCH(CH_3)_2$

(d) 

$\underset{I}{CH_2}OC(CH_3)_2$ *(2006)*

57. Ethyl chloride is converted into diethyl ether by

(a) Perkins reaction (b) Grignard reaction

(c) Wurtz synthesis

(d) Williamson's synthesis. *(1999)*

58. Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions?

(a) Diethyl ether (b) Acetonitrile

(c) Acetamide (d) Methyl acetate *(1998)*

59. The compound which does not react with sodium is
(a) CH_3COOH (b) $CH_3CHOHCH_3$
(c) C_2H_5OH (d) CH_3OCH_3
(1994)

60. Which one is formed when sodium phenoxide is heated with ethyl iodide?
(a) Phenetole (b) Ethyl phenyl alcohol
(c) Phenol (d) None of these *(1988)*

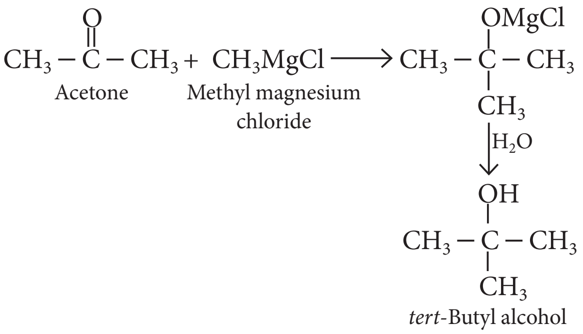
ANSWER KEY

1.	(a)	**2.**	(c)	**3.**	(c)	**4.**	(c)	**5.**	(d)	**6.**	(c)	**7.**	(d)	**8.**	(c)	**9.**	(c)	**10.**	(d)
11.	(c)	**12.**	(b)	**13.**	(d)	**14.**	(b)	**15.**	(a)	**16.**	(b)	**17.**	(a)	**18.**	(a)	**19.**	(c)	**20.**	(c)
21.	(b)	**22.**	(a)	**23.**	(c)	**24.**	(c)	**25.**	(c)	**26.**	(b)	**27.**	(c)	**28.**	(b)	**29.**	(a)	**30.**	(a)
31.	(d)	**32.**	(a)	**33.**	(a)	**34.**	(d)	**35.**	(b)	**36.**	(a)	**37.**	(b)	**38.**	(b)	**39.**	(d)	**40.**	(d)
41.	(c)	**42.**	(c)	**43.**	(b)	**44.**	(a)	**45.**	(d)	**46.**	(a)	**47.**	(a)	**48.**	(a)	**49.**	(b)	**50.**	(c)
51.	(c)	**52.**	(b)	**53.**	(a)	**54.**	(a)	**55.**	(c)	**56.**	(a)	**57.**	(d)	**58.**	(a)	**59.**	(d)	**60.**	(a)

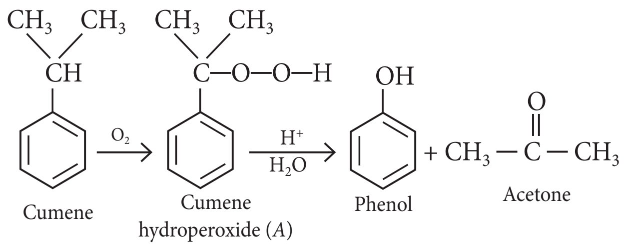
Hints & Explanations

1. (a) : All alcohols follow the general formula $C_nH_{2n+2}O$.
$CH_3OH\ [CH_{2+2}O]$; $C_2H_5OH[C_2H_{(2\times 2)+2}O]$
$n = 1,\qquad n = 2$

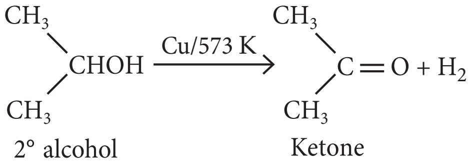
2. (c) :



3. (c) :



4. (c) :

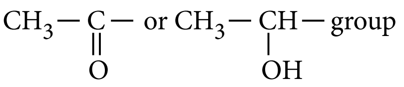


5. (d) : It is Reimer–Tiemann reaction. The electrophile formed is dichlorocarbene (:CCl_2) which is formed according to the following mechanism :

$$CHCl_3 + OH^- \rightleftharpoons \ddot{C}Cl_3 + H_2O$$
$$\downarrow -Cl^-\ (\alpha\text{-Elimination})$$
$$:CCl_2$$

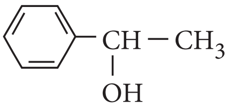
Dichlorocarbene
(electrophile)

6. (c) : As the compound is giving yellow precipitate with NaOI that shows it is undergoing haloform reaction. Haloform reaction is shown by the compounds having

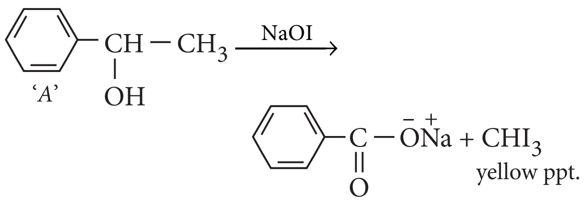


$CH_3-\underset{\underset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group

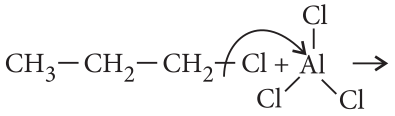
Hence, the compound *A* is



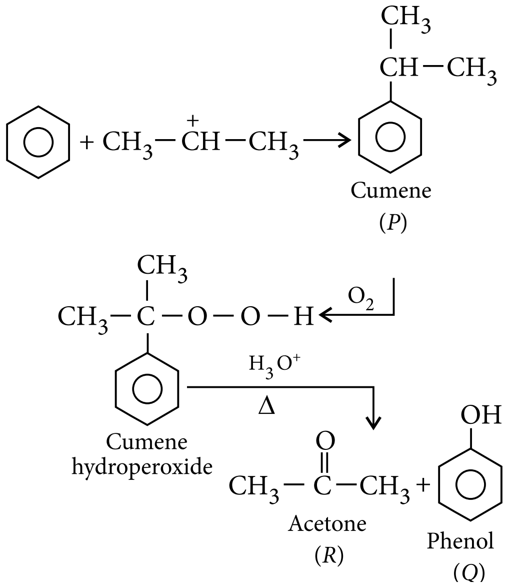
$$2NaOH + \underset{\text{'Y'}}{I_2} \longrightarrow NaOI + NaI + H_2$$



7. (d) :

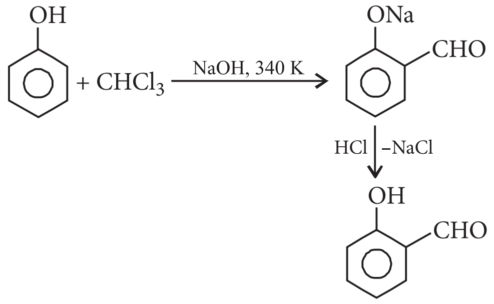


$$\underset{\text{(1° Carbocation)}}{CH_3-CH_2-\overset{+}{C}H_2} + AlCl_4^- \xrightarrow{1,\,2\ H^-\ \text{shift}} \underset{\text{(2° Carbocation)}}{CH_3-\overset{+}{C}H-CH_3}$$



8. (c) : Electron withdrawing groups increase the acidity while electron donating groups decrease the acidity of phenol.

9. (c) : This is Reimer–Tiemann reaction.



Salicylaldehyde

10. (d) : 1° and 2° alcohols react with HCl in presence of anhydrous $ZnCl_2$ as catalyst while in case of 3° alcohols $ZnCl_2$ is not required.

11. (c) : The reaction is as follows :

$$\text{Acid} + NaHCO_3 \rightarrow \underset{\text{(soluble)}}{\text{Sodium salt of acid}} + H_2CO_3$$

Among all the given compounds, *o*-nitrophenol is weaker acid than HCO_3^-. Hence, it does not react with $NaHCO_3$.

12. (b) : The iodoform test is positive for alcohols with formula $R - CHOH - CH_3$. Among $C_6H_{14}O$ isomers, the ones with positive iodoform test are:

I. $CH_3 - CH_2 - CH_2 - CH_2 - CHOH - CH_3$
2-Hexanol

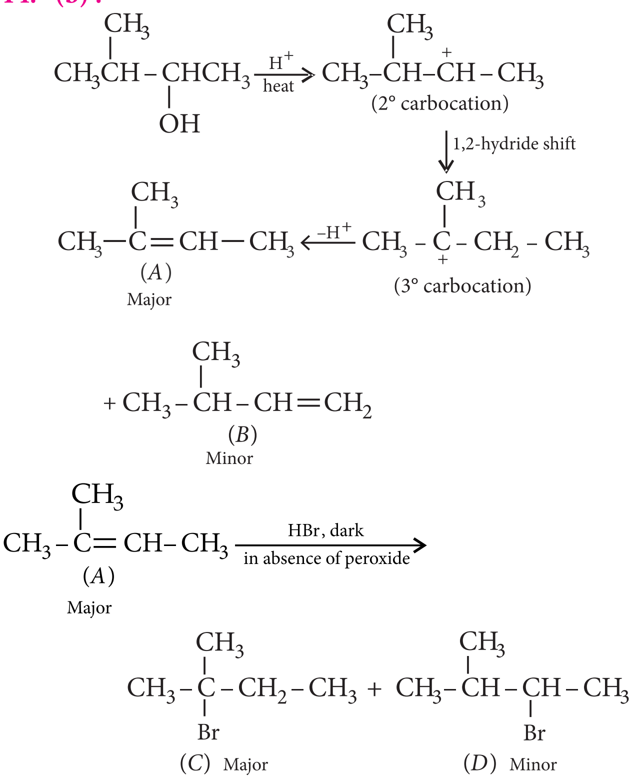
II. $CH_3 - CH_2 - CH(CH_3) - CHOH - CH_3$
3- Methyl-2-pentanol

III. $(CH_3)_2CH - CH_2 - CHOH - CH_3$
4- Methyl-2-pentanol

IV. $(CH_3)_3C - CHOH - CH_3$
3, 3- Dimethyl-2-butanol

13. (d) : $$CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{H_3O^+} \underset{(B)}{CH_3COOH} \xrightarrow[\text{ether}]{LiAlH_4} \underset{(C)}{CH_3CH_2OH}$$

14. (b) :



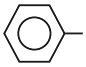
15. (a) : Since, phenols and carboxylic acids are more acidic than aliphatic alcohols, we find that cyclohexanol (I) is least acidic. Out of the two given phenols, III is more acidic than IV. This is because of the presence of three highly electron withdrawing $-NO_2$ groups on the benzene ring which makes the O—H bond extremely polarized. This facilitates the release of H as H^+. Thus, III > IV.

In acetic acid, the electron withdrawing $-\overset{O}{\overset{\|}{C}}-$ in the —COOH group polarises the O—H bond and increases the acidic strength. Acetic acid is therefore more acidic than phenol or cyclohexanol.

∴ The order of acidic character is III > II > IV > I.

16. (b) : Phenol is most acidic of all the given compounds.

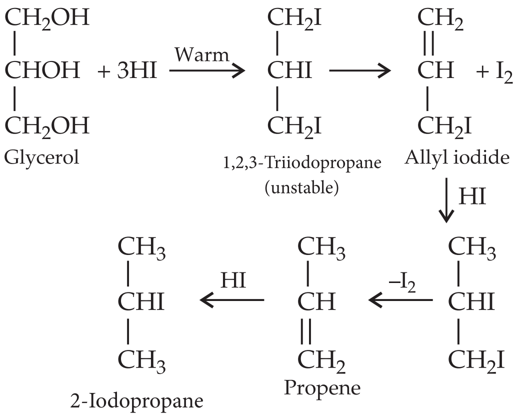
In phenol, the electron withdrawing phenyl ring polarizes the O—H bond, thereby facilitating the release of H as H^+ and hence, phenol is most acidic.

In —CH_2OH, the electron withdrawing effect of phenyl ring is somewhat diminished by the —CH_2 group and it is therefore, less acidic than phenol. In (c) and (d), —OH group is attached to alkyl groups which, due to their +*I* effect reduce the polarity of —OH bond and so, the acidic strength is low.

17. (a) : In phenols, the presence of electron releasing groups decrease the acidity, whereas presence of electron withdrawing groups increase the acidity, compared to phenol. Among the *meta* and *para*-nitrophenols, the later is more acidic as the presence of —NO_2 group at *para* position stabilises the phenoxide ion to a greater extent than when it is present at *meta* position. Thus, correct order of acidity is :

$$\underset{\text{(iv)}}{para\text{-nitrophenol}} > \underset{\text{(iii)}}{meta\text{-nitrophenol}} > \underset{\text{(i)}}{\text{phenol}} > \underset{\text{(ii)}}{\text{methyl phenol}}$$

18. (a) :



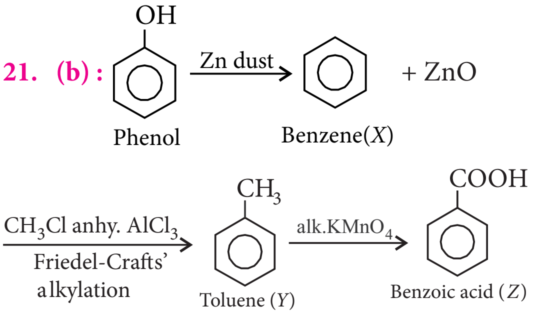
19. (c) : $$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{PBr_3} \underset{(X)}{C_2H_5Br} \xrightarrow[\text{dehydro-halogenation}]{\text{alc.KOH}}$$

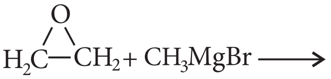
$$\underset{\substack{\text{Ethene}\\(Y)}}{CH_2=CH_2} \xrightarrow{H_2SO_4} CH_3CH_2-HSO_4 \xrightarrow{H_2O} \underset{(Z)}{C_2H_5-OH}$$

20. (c) : When 1,2-diol like ethylene glycol is treated with HIO_4, each alcoholic group is oxidised to a carbonyl group by HIO_4. Since in glycol, both the –OH groups are terminal, so oxidation would yield two formaldehyde molecules.

i.e., $$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} \xrightarrow{HIO_4} 2HCHO$$

21. (b) :

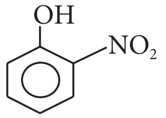


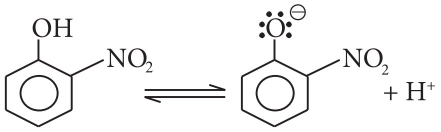
22. (a) : 

$$H_2C\overset{O}{—}CH_2 + CH_3MgBr \longrightarrow$$

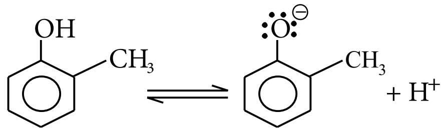
$$CH_3CH_2CH_2OMgBr \xrightarrow{H^+} \underset{\text{primary alcohol}}{CH_3CH_2CH_2OH}$$

23. (c) : Phenols are much more acidic than alcohols, due to the stabilisation of phenoxide ion by resonance.





—NO_2 is the electron withdrawing group and helps in stabilizing the negative charge on the oxygen hence equilibrium shifts in forward direction and more H^+ ions remove easily. Hence, it is most acidic.



—CH_3 is the electron donating group. Hence, electron density increases on the oxygen and destabilizes the product. Thus, equilibrium shifts in backward direction.

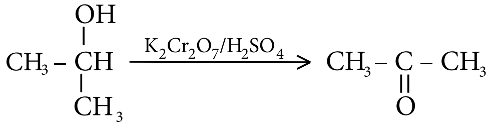
24. (c) : Formation of a yellow precipitate on heating a compound with an alkaline solution of iodine is known as iodoform reaction. Methyl alcohol does not respond to this test. Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketones and those alcohols which possess $CH_3CH(OH)$– group.

25. (c) : *n*-Propyl alcohol on oxidation with potassium dichromate gives an aldehyde which on further oxidation gives an acid. Both aldehyde and acid contain the same number of C atoms as the original alcohol.

$$CH_3CH_2CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{25^\circ C} CH_3CH_2CHO$$

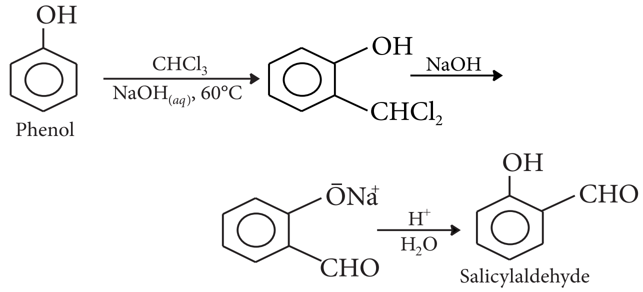
$$\xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3CH_2COOH$$

Isopropyl alcohol on oxidation gives a ketone with the same number of C atoms as the original alcohol.



$$CH_3-\underset{CH_3}{\overset{OH}{CH}} \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3$$

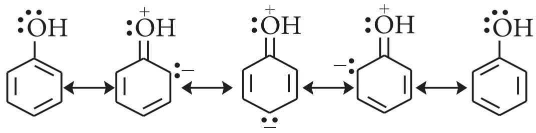
26. (b) : This reaction is called Reimer—Tiemann reaction.



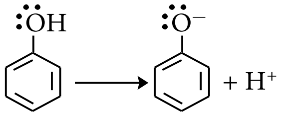
27. (c) : $C_2H_5OH + 4I_2 + NaOH \longrightarrow CHI_3 + NaI + HCOONa + H_2O$

Iodoform is a pale yellow solid which crystallises in hexagonal plates.

28. (b) : Phenol exists as a resonance hybrid of the following structures.

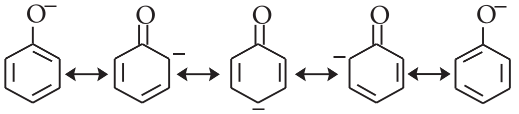


Thus, due to resonance the oxygen atom of the —OH group acquires a positive charge and hence attracts electron pair of the O – H bond leading to the release of hydrogen atom as proton.



Phenoxide ion

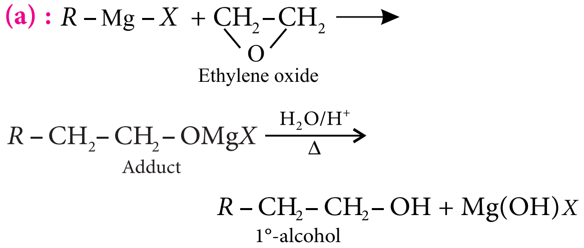
Once the phenoxide ion is formed it stabilises itself by resonance which is more stable than the parent phenol as there is no charge separation.



Effect of substituent : Presence of electron withdrawing groups ($—NO_2$, $—X$, —CN) increase the acidity of phenols while the presence of electron releasing groups ($—NH_2$, $—CH_3$)decrease the acidity of phenols. This explains the following order of acidity :

p-nitrophenol > phenol > *p*-cresol.

29. (a) :

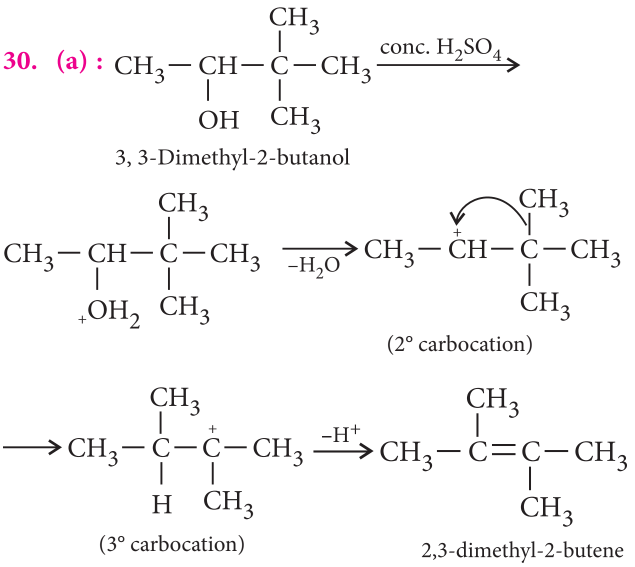


$$R-Mg-X + CH_2-CH_2 \longrightarrow$$

Ethylene oxide

$$\underset{\text{Adduct}}{R-CH_2-CH_2-OMgX} \xrightarrow[\Delta]{H_2O/H^+} \underset{\text{1°-alcohol}}{R-CH_2-CH_2-OH} + Mg(OH)X$$

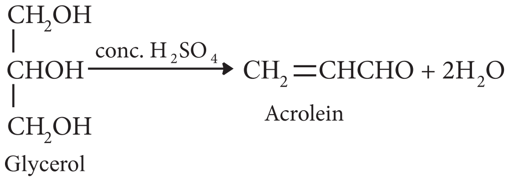
30. (a) :



31. (d) : $\underset{\text{Alkene}}{6(R-CH=CH_2)} \xrightarrow[\text{Ether, 0°C}]{B_2H_6} 2(RCH_2CH_2)_3B$

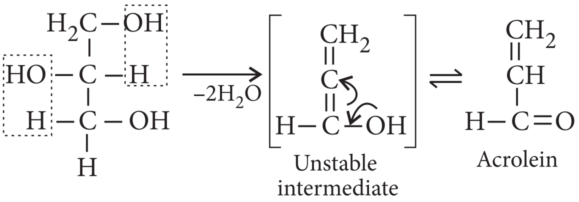
$$\xrightarrow[NaOH]{H_2O_2} 3RCH_2CH_2OH + 2H_3BO_3$$

32. (a) :



$$\underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{Acrolein}}{CH_2{=}CHCHO} + 2H_2O$$

Mechanism:



33. (a)

34. (d) : $—OCH_3$, $—CH_3$ are electron donating groups and decrease the acidic character of phenols. $—NO_2$, is electron withdrawing group and tends to increase the acidic character. Electron donating effect of $—OCH_3$ group (+*R* effect) is more than that of $—CH_3$ group (+*I* effect). Thus, the order is

p-methoxyphenol < *p*-methylphenol < *p*-nitrophenol.

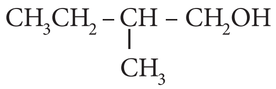
35. (b) : 2° alcohols on oxidation give ketones, 1° alcohols form aldehydes.

36. (a) : Primary alcohol undergoes catalytic dehydrogenation to give aldehyde.

37. (b) : 4-isomers are possible for $C_5H_{11}OH$.

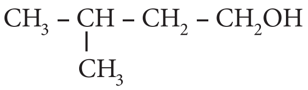
(i) $CH_3CH_2CH_2CH_2CH_2OH$

(ii)



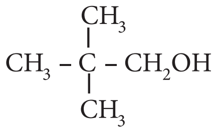
$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(iii)



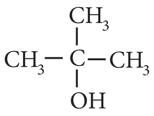
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2OH$

(iv)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2OH$

38. (b) :



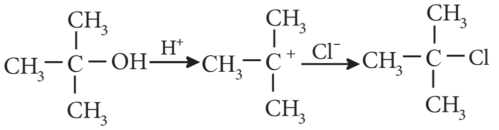
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3$

(methylpropan-2-ol)

, generates 3° carbocation which is very stable intermediate, thus it will react more rapidly with HBr.

39. (d) : Phenol on reaction with excess bromine water gives 2,4,6-tribromophenol.

40. (d) : 2-Methylpropan-2-ol reacts rapidly with Lucas reagent at room temperature.



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH \xrightarrow{H^+} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C^+}}}} \xrightarrow{Cl^-} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Cl$$

2-Methyl-2-propanol

41. (c) : –OH group being electron donor increases the electron density in phenol. Thus, the electron density in phenol is higher than that of toluene, benzene and chlorobenzene.

42. (c) :

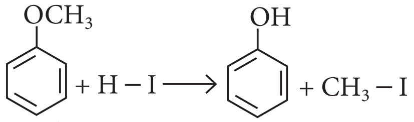
$$\underset{}{CH_3-CH=CH_2} \xrightarrow[\text{Hydroboration}]{BH_3,\ THF} \underset{\text{Tripropylborane}}{(CH_3CH_2CH_2)_3B} \xrightarrow[OH^-]{H_2O_2} \underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH}$$

43. (b) : Treatment of phenol with $CHCl_3$ and aqueous hydroxide introduces — CHO group, onto the aromatic ring generally *ortho* to the — OH group. This reaction is known as Reimer—Tiemann reaction.

44. (a)

45. (d) : $CO + 2H_2 \xrightarrow{ZnO\text{-}Cr_2O_3} CH_3OH$

46. (a) :



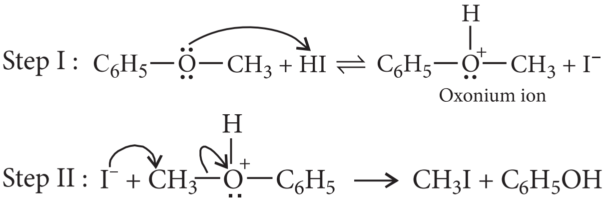
Anisole Phenol

47. (a) : In Ph — $\ddot{O}$ — H, the lone pair of oxygen is in conjugation with phenyl group so, it is least basic among the given compounds and is most difficult to protonate.

48. (a) : Ethers are readily attacked by HI to give an alkyl halide and alcohol. But when heated with excess of HI, the product alcohol first formed reacts further with HI to form the corresponding alkyl iodide.

$$R\text{–}O\text{–}R' + \underset{\text{(excess)}}{2HI} \xrightarrow{\text{Heat}} RI + R'I + H_2O$$

49. (b) : In case of phenyl methyl ether, methyl phenyl oxonium ion $\left(C_6H_5-\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}-CH_3\right)$ is formed by protonation of ether. The O—CH_3 bond is weaker than O—C_6H_5 bond as O—C_6H_5 has partial double bond character. Therefore, the attack by I^- ion breaks O—CH_3 bond to form CH_3I.



Step I : $C_6H_5-\ddot{O}-CH_3 + HI \rightleftharpoons C_6H_5-\overset{\displaystyle H}{\overset{|}{\overset{+}{\underset{\cdot\cdot}{O}}}}-CH_3 + I^-$

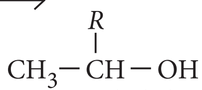
Oxonium ion

Step II : $I^- + CH_3-\overset{\displaystyle H}{\overset{|}{\overset{+}{\underset{\cdot\cdot}{O}}}}-C_6H_5 \longrightarrow CH_3I + C_6H_5OH$

50. (c) : Williamson's ether synthesis reaction involves the treatment of sodium alkoxide with a suitable alkyl halide to form an ether.

51. (c) : Williamson synthesis is the best method for the preparation of ethers.

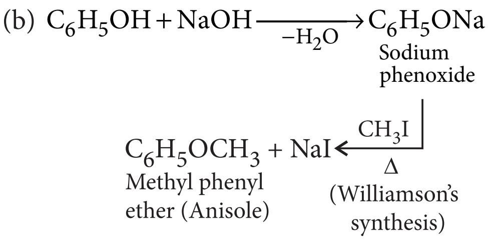
52. (b) : (a) $CH_3CHO + RMgX \xrightarrow{\text{ether}}$



$CH_3-\overset{\displaystyle R}{\overset{|}{CH}}-OH$

2°alcohol

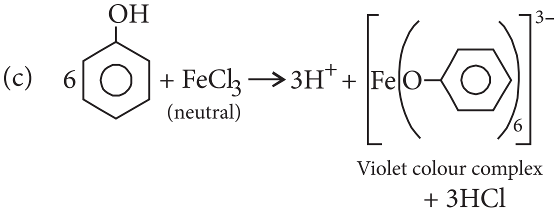
(b)



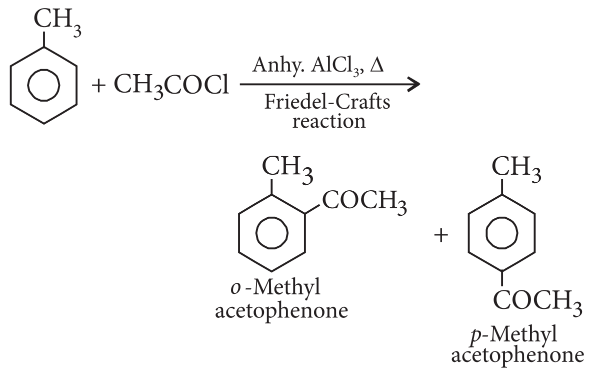
$$C_6H_5OH + NaOH \xrightarrow[-H_2O]{} \underset{\text{Sodium phenoxide}}{C_6H_5ONa} \xrightarrow[\Delta]{CH_3I} \underset{\text{Methyl phenyl ether (Anisole)}}{C_6H_5OCH_3} + NaI$$

(Williamson's synthesis)

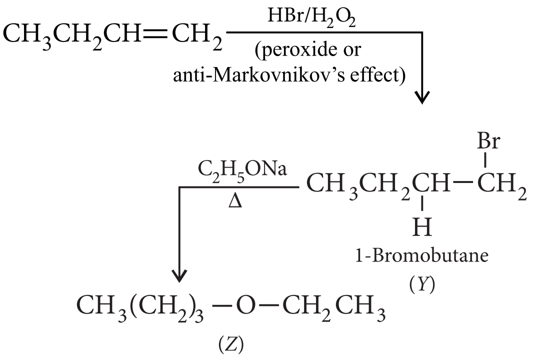
(c)



(d)

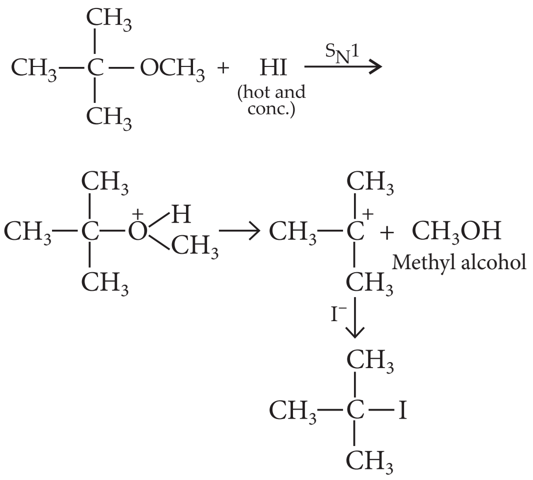


53. (a) :



$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(peroxide or anti-Markovnikov's effect)}]{HBr/H_2O_2} \underset{\underset{(Y)}{\text{1-Bromobutane}}}{CH_3CH_2\underset{H}{CH}-\overset{Br}{CH_2}} \xrightarrow[\Delta]{C_2H_5ONa} \underset{(Z)}{CH_3(CH_2)_3-O-CH_2CH_3}$$

54. (a) :



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OCH_3 + \underset{\text{(hot and conc.)}}{HI} \xrightarrow{S_N1}$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{O}{<}^{H}_{CH_3} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{\overset{+}{C}}} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$\xrightarrow{I^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I$$

55. (c) : The alkyl iodide produced depends on the nature of the alkyl groups. If one group is Me and the other a primary or secondary alkyl group, it is methyl iodide which is produced. This can be explained on the assumption that the mechanism is S_N2, and because of the steric effect of the larger group, I^- attacks the smaller methyl group.

When the substrate is a methyl *t*-alkyl ether, the products are *t*-*R*I and MeOH. This can be explained by S_N1 mechanism, the carbonium ion produced being the *t*-alkyl since tertiary carbonium ion is more stable than a primary or secondary carbonium ion.

56. (a) : With cold HI, a mixture of alkyl iodide and alcohol is formed. In the case of mixed ethers, the halogen atom attaches to a smaller and less complex alkyl group.

$$CH_3OCH(CH_3)_2 + HI \rightarrow CH_3I + (CH_3)_2CHOH$$

57. (d) : $C_2H_5-Cl + Na-O-C_2H_5 \longrightarrow C_2H_5-O-C_2H_5 + NaCl$

The above reaction is called as Williamson's synthesis.

58. (a) : Diethyl ether is a saturated compound, so it is resistant to nucleophilic attack by a hydroxyl ion (OH^-). Other compounds have unsaturation and the unsaturated 'C' atom bears partial +ve charge, therefore they undergo easy nucleophilic attack by OH^- ion.

59. (d) : Ethers are very inert. The chemical inertness of ethers is due to absence of active group in their molecules. Since $CH_3 - O - CH_3$ is inert and it does not contain active group, therefore it does not react with sodium.

60. (a) : Phenetole is formed when sodium phenoxide is heated with ethyl iodide.

$$C_6H_5ONa + C_2H_5I \xrightarrow{\Delta} \underset{\text{Phenetole}}{C_6H_5OC_2H_5}$$

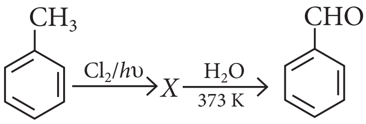
❖❖❖

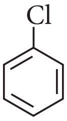
CHAPTER 12

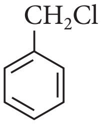
Aldehydes, Ketones and Carboxylic Acids

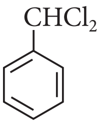
12.2 Preparation of Aldehydes and Ketones

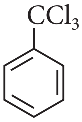
1. Identify compound X in the following sequence of reactions :



(a) 

(b) 

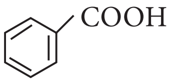
(c) 

(d) 

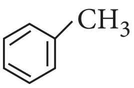
(NEET 2020)

2. Reaction by which benzaldehyde cannot be prepared

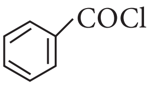
(a)  + CO + HCl in presence of anhydrous $AlCl_3$

(b) 

+ Zn/Hg and conc. HCl

(c) 

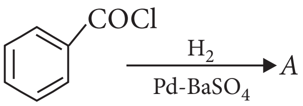
+ CrO_2Cl_2 in CS_2 followed by H_3O^+

(d) 

+ H_2 in presence of Pd-$BaSO_4$

(NEET 2013)

3. Consider the following reaction,



The product A is

(a) C_6H_5CHO (b) C_6H_5OH

(c) $C_6H_5COCH_3$ (d) C_6H_5Cl *(Mains 2012)*

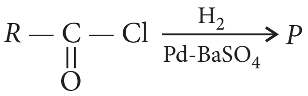
4. Which one of the following can be oxidised to the corresponding carbonyl compound?

(a) 2-Hydroxypropane (b) *ortho*-Nitrophenol

(c) Phenol

(d) 2-Methyl-2-hydroxypropane *(2004)*

5. In the following reaction, product P is

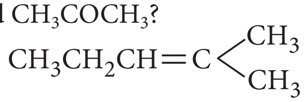


$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\text{Pd-BaSO}_4]{H_2} P$$

(a) RCH_2OH (b) $RCOOH$

(c) $RCHO$ (d) RCH_3 *(2002)*

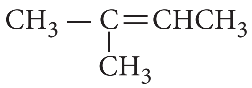
6. Which alkene on ozonolysis gives CH_3CH_2CHO and CH_3COCH_3?

(a) 

$$CH_3CH_2CH{=}C\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

(b) $CH_3CH_2CH{=}CHCH_2CH_3$

(c) $CH_3CH_2CH{=}CHCH_3$

(d) 

$$CH_3-\underset{\underset{CH_3}{|}}{C}{=}CHCH_3$$

(2001)

7. In the reaction, $CH_3CN + 2H \xrightarrow[\text{Ether}]{\text{HCl}} X \xrightarrow{\text{Boiling } H_2O} Y$; the term Y is

(a) acetaldehyde (b) ethanamine

(c) acetone (d) dimethylamine.

(1999)

8. Ketones $[RCOR_1]$ where $R = R_1$ = alkyl group. It can be obtained in one step by

(a) oxidation of tertiary alcohol

(b) reaction of acid halide with alcohols

(c) hydrolysis of esters

(d) oxidation of primary alcohol. *(1997)*

9. The oxidation of toluene to benzaldehyde by chromyl chloride is called

(a) Etard reaction

(b) Riemer–Tiemann reaction

(c) Wurtz reaction

(d) Cannizzaro's reaction. *(1996)*

12.4 Chemical Reactions

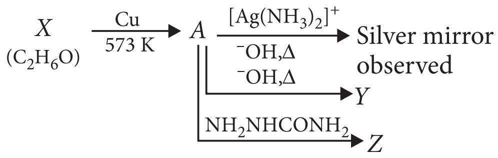
10. Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as

(a) Aldol condensation

(b) Cannizzaro's reaction

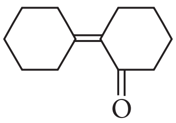
(c) Cross Cannizzaro's reaction
(d) Cross Aldol condensation. *(NEET 2020)*

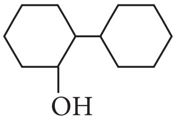
11. Consider the reactions,

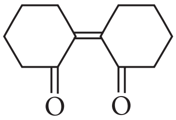


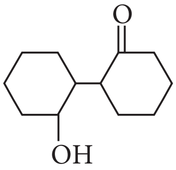
Identify *A*, *X*, *Y* and *Z*.
(a) *A*-Methoxymethane, *X*-Ethanol, *Y*-Ethanoic acid, *Z*-Semicarbazide.
(b) *A*-Ethanal, *X*-Ethanol, *Y*-But-2-enal, *Z*-Semicarbazone.
(c) *A*-Ethanol, *X*-Acetaldehyde, *Y*-Butanone, *Z*-Hydrazone.
(d) *A*-Methoxymethane, *X*-Ethanoic acid, *Y*-Acetate ion, *Z*-Hydrazine. *(NEET 2017)*

12. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?

(a) 

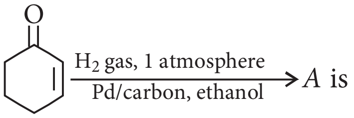
(b) 

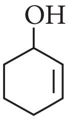
(c) 

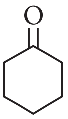
(d) 

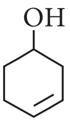
(NEET 2017)

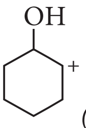
13. The correct structure of the product '*A*' formed in the reaction



(a) 

(b) 

(c) 

(d) 

(NEET-II 2016)

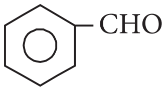
14. Which of the following reagents would distinguish *cis*-cyclopenta-1,2-diol from the *trans*-isomer?
(a) MnO_2
(b) Aluminium isopropoxide
(c) Acetone
(d) Ozone *(NEET-I 2016)*

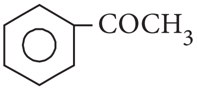
15. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is
(a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
(b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
(c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
(d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration. *(NEET-I 2016)*

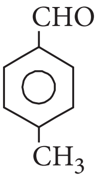
16. The product formed by the reaction of an aldehyde with a primary amine is
(a) carboxylic acid
(b) aromatic acid
(c) Schiff's base
(d) ketone. *(NEET-I 2016)*

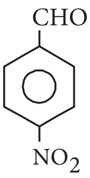
17. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is
(a) hydrazine in presence of feebly acidic solution
(b) hydrocyanic acid
(c) sodium hydrogen sulphite
(d) a Grignard reagent. *(2015)*

18. Which one is most reactive towards nucleophilic addition reaction?

(a) 

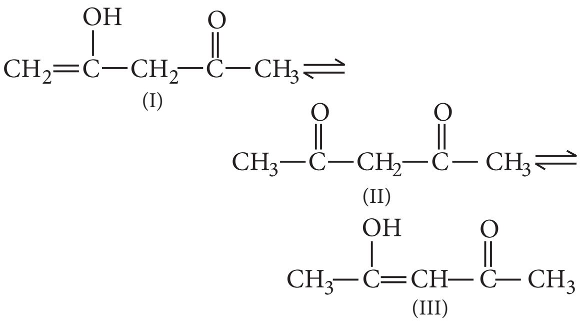
(b) 

(c) 

(d) 

(2014)

19. The order of stability of the following tautomeric compounds is

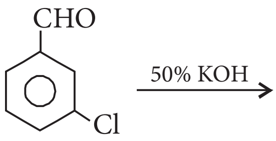


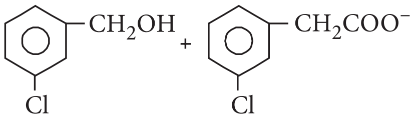
$$\underset{\text{(I)}}{CH_2{=}\overset{OH}{\overset{|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \rightleftharpoons \underset{\text{(II)}}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \rightleftharpoons \underset{\text{(III)}}{CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

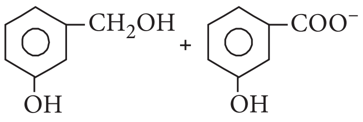
(a) II > I > III (b) II > III > I
(c) I > II > III (d) III > II > I

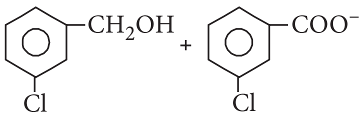
(NEET 2013)

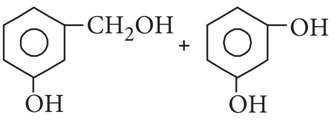
20. Predict the products in the given reaction.



(a)


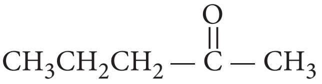
(b)


(c)


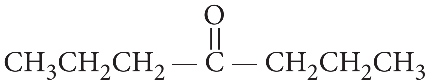
(d)


(2012)

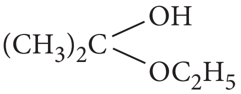
21. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is

(a)


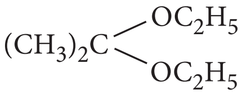
$CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-CH_3$

(b)


$CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-CH_2CH_2CH_3$

(c)


$(CH_3)_2C(OH)(OC_2H_5)$

(d)


$(CH_3)_2C(OC_2H_5)(OC_2H_5)$

(2012)

22. CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by
(a) Benedict's test
(b) iodoform test
(c) Tollens' reagent test
(d) Fehling's solution test. *(2012)*

23. Consider the reaction :

$$RCHO + NH_2NH_2 \rightarrow RCH{=}N-NH_2$$

What sort of reaction is it?
(a) Electrophilic addition-elimination reaction
(b) Free radical addition-elimination reaction
(c) Electrophilic substitution-elimination reaction
(d) Nucleophilic addition-elimination reaction

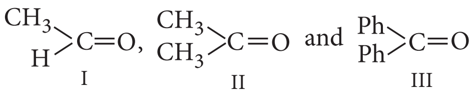
(Mains 2012)

24. Which of the following compounds will give a yellow precipitate with iodine and alkali?
(a) Acetophenone (b) Methyl acetate
(c) Acetamide (d) 2-Hydroxypropane

(Mains 2012)

25. Clemmensen reduction of a ketone is carried out in the presence of which of the following?
(a) Glycol with KOH
(b) Zn-Hg with HCl
(c) $LiAlH_4$
(d) H_2 and Pt as catalyst *(2011)*

26. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds :

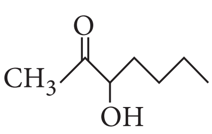


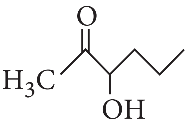
(a) III > II > I (b) II > I > III
(c) I > III > II (d) I > II > III

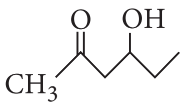
(Mains 2011)

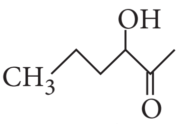
27. Which of the following reactions will not result in the formation of carbon-carbon bonds?
(a) Reimer–Tiemann reaction
(b) Cannizzaro reaction
(c) Wurtz reaction
(d) Friedel–Crafts acylation *(2010)*

28. Which one of the following compounds will be most readily dehydrated?

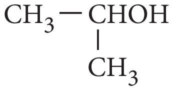
(a)


(b)


(c)


(d)


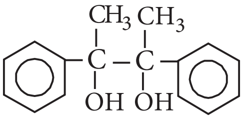
(Mains 2010)

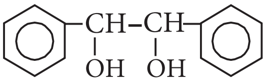
29. Following compounds are given,
(i) CH_3CH_2OH (ii) CH_3COCH_3
(iii)

$CH_3-\underset{\underset{CH_3}{|}}{CH}OH$
(iv) CH_3OH

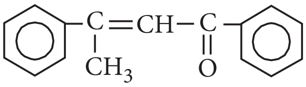
Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?
(a) (i), (iii) and (iv) (b) Only (ii)
(c) (i), (ii) and (iii) (d) (i) and (ii)

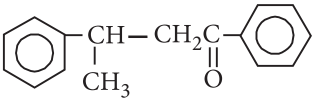
(Mains 2010)

30. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure

(a) 

(b) 

(c) 

(d)  *(2008)*

31. A strong base can abstract an α-hydrogen from
(a) ketone (b) alkane
(c) alkene (d) amine. *(2008)*

32. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
(a) Cope reduction (b) Dow reduction
(c) Wolff–Kishner reduction
(d) Clemmensen reduction. *(2007)*

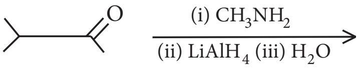
33. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?
(a) C_6H_5CHO (b) $CH_3CH_2CH_2CHO$
(c) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (d) $C_6H_5CH_2CHO$
(2007)

34. The product formed in aldol condensation is
(a) a beta-hydroxy aldehyde or a beta-hydroxy ketone
(b) an alpha-hydroxy aldehyde or ketone
(c) an alpha, beta unsaturated ester
(d) a beta-hydroxy acid. *(2007)*

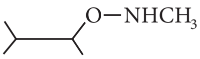
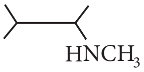
35. Nucleophilic addition reaction will be most favoured in
(a) CH_3CHO
(b) $CH_3-CH_2-CH_2\overset{\overset{O}{\|}}{C}-CH_3$
(c) $(CH_3)_2C=O$ (d) CH_3CH_2CHO *(2006)*

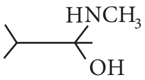
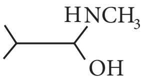
36. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is
(a) formaldehyde (b) acetaldehyde
(c) acetone (d) diethyl ketone. *(2006)*

37. The major organic product formed from the following reaction :



is

(a) 
(b) 

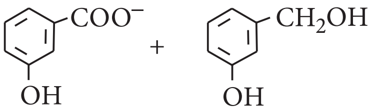
(c) 
(d)  *(2005)*

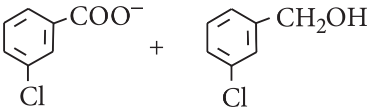
38. In this reaction :

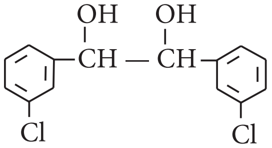
$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN \xrightarrow{HOH} CH_3CH(OH)COOH$$

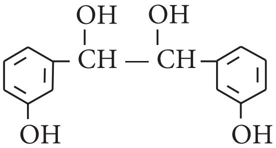
an asymmetric centre is generated. The acid obtained would be
(a) *D*-isomer
(b) *L*-isomer
(c) 50% *D* + 50% *L*-isomer
(d) 20% *D* + 80% *L*-isomer. *(2003)*

39. When *m*-chlorobenzaldehyde is treated with 50% KOH solution, the product(s) obtained is (are)

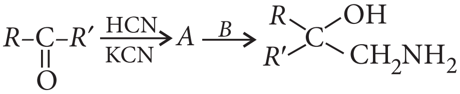
(a) 

(b) 

(c) 

(d)  *(2003)*

40. *A* and *B* in the following reactions are :

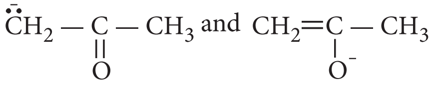


(a) $A = RR'C\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.$, $B = NH_3$

(b) $A = RR'C\left\langle\begin{matrix}CN\\OH\end{matrix}\right.$, $B = H_3O^+$

(c) $A = RR'CHCN$, $B = NaOH$

(d) $A = RR'C\left\langle\begin{matrix}CN\\OH\end{matrix}\right.$, $B = LiAlH_4$ *(2003)*

41. 
$\ddot{C}H_2-\underset{\underset{O}{\|}}{C}-CH_3$ and $CH_2=\underset{\underset{O^-}{|}}{C}-CH_3$

are
(a) resonating structures
(b) tautomers
(c) geometrical isomers
(d) optical isomers. *(2002)*

42. Which of the following is incorrect?
(a) $FeCl_3$ is used in detection of phenol.
(b) Fehling solution is used in detection of glucose.
(c) Tollens' reagent is used in detection of unsaturation.
(d) $NaHSO_3$ is used in detection of carbonyl compound. *(2001)*

43. Polarisation in acrolein can be described as
(a) $\overset{+\delta}{C}H_2=CH-\overset{+\delta}{C}HO$
(b) $\overset{-\delta}{C}H_2=CH-\overset{+\delta}{C}HO$
(c) $\overset{-\delta}{C}H_2=CH-CH\overset{+\delta}{O}$
(d) $\overset{+\delta}{C}H_2=CH-CH\overset{-\delta}{O}$ *(2000)*

44. First product of the reaction between $RCHO$ and NH_2NH_2 is
(a) $RCH=NNH_2$ (b) $RCH=NH$
(c) RCH_2NH_2 (d) $RCON_3$ *(2000)*

45. An ester (A) with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed, was treated with H_2SO_4 to give an olefin (B). Ozonolysis of (B) gave a ketone with molecular formula C_8H_8O which shows +ve iodoform test. The structure of (A) is
(a) $H_3CCH_2COC_6H_5$ (b) $C_2H_5COOC_6H_5$
(c) $C_6H_5COOC_2H_5$
(d) p-$H_3CO-C_6H_4-COCH_3$ *(1998)*

46. Iodoform test is not given by
(a) ethanal (b) ethanol
(c) 2-pentanone (d) 3-pentanone. *(1998)*

47. Phenylmethanol can be prepared by reducing the benzaldehyde with
(a) CH_3Br and Na (b) CH_3I and Mg
(c) CH_3Br (d) Zn and HCl. *(1997)*

48. The oxidation of toluene with CrO_3 in the presence of $(CH_3CO)_2O$ gives a product A, which on treatment with aqueous NaOH produces
(a) C_6H_5COONa (b) 2, 4-diacetyl toluene
(c) C_6H_5CHO (d) $(C_6H_5CO)_2O$ *(1995)*

49. When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as
(a) Schiff's base (b) Benedict's reagent
(c) Millon's base (d) Schiff's reagent. *(1995)*

50. Compound A has a molecular formula C_2Cl_3OH. It reduces Fehling's solution and on oxidation, it gives a monocarboxylic acid B. If A is obtained by the action of chlorine on ethyl alcohol, then compound A is
(a) methyl chloride
(b) monochloroacetic acid
(c) chloral
(d) chloroform. *(1994)*

51. Which of the following compounds will undergo self aldol condensation in the presence of cold dilute alkali?
(a) $CH\equiv C-CHO$ (b) $CH_2=CHCHO$
(c) C_6H_5CHO (d) CH_3CH_2CHO *(1994)*

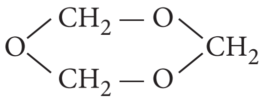
52. Which of the following compounds will give positive test with Tollens' reagent?
(a) Acetic acid (b) Acetone
(c) Acetamide (d) Acetaldehyde *(1994)*

53. $(CH_3)_2C=CHCOCH_3$ can be oxidised to $(CH_3)_2C=CHCOOH$ by
(a) chromic acid (b) NaOI
(c) Cu at 300°C (d) $KMnO_4$ *(1993)*

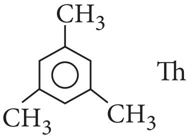
54. In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation?
(a) CH_3COCH_3 (b) CCl_3CH_2CHO
(c) $CH_3CH_2CH_2OH$ (d) CH_3CH_2CHO *(1992)*

55. Acetaldehyde reacts with
(a) electrophiles only (b) nucleophiles only
(c) free radicals only
(d) both electrophiles and nucleophiles. *(1991)*

56. The reagent which can be used to distinguish acetophenone from benzophenone is
(a) 2,4-dinitrophenylhydrazine
(b) aqueous solution of $NaHSO_3$
(c) Benedict reagent
(d) I_2 and NaOH. *(1990)*

57. 

The above shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is
(a) trioxane (b) formose
(c) paraformaldehyde (d) metaldehyde. *(1989)*

58.  The given compound describes a condensation polymer which can be obtained in two ways : either treating 3 molecules of acetone (CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($CH_3C \equiv CH$) through a red hot tube. The polymer is

(a) phorone (b) mesityl oxide
(c) deacetonyl alcohol (d) mesitylene. *(1989)*

59. $\underset{(A)}{3CH_3COCH_3} \xrightarrow[-3H_2O]{HCl}$

$\underset{(B)}{(CH_3)_2C{=}CH-CO-CH{=}C(CH_3)_2}$

This polymer (*B*) is obtained when acetone is saturated with hydrogen chloride gas, *B* can be

(a) phorone (b) formose
(c) diacetone alcohol (d) mesityl oxide. *(1989)*

60. If formaldehyde and KOH are heated, then we get

(a) methane (b) methyl alcohol
(c) ethyl formate (d) acetylene. *(1988)*

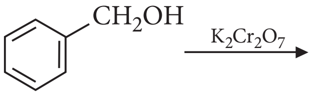
12.5 Uses of Aldehydes and Ketones

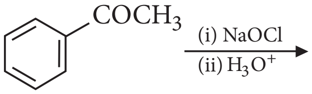
61. Formalin is an aqueous solution of

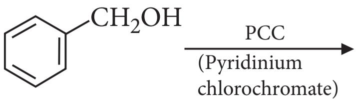
(a) fluorescein (b) formic acid
(c) formaldehyde (d) furfuraldehyde. *(1988)*

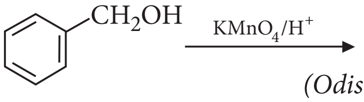
12.7 Methods of Preparation of Carboxylic Acids

62. The reaction that does not give benzoic acid as the major product is

(a) 

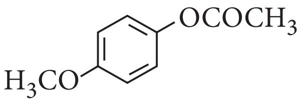
(b) 

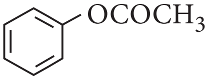
(c) 

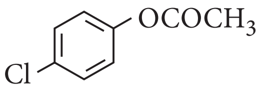
(d) 

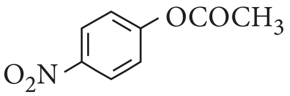
(Odisha NEET 2019)

63. Which one of the following esters gets hydrolysed most easily under alkaline conditions?

(a) 

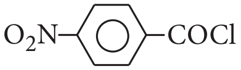
(b) 

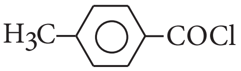
(c) 

(d)  *(2015)*

64. Consider the following compounds :

(i) C_6H_5COCl

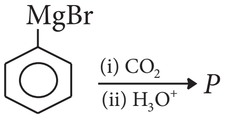
(ii) 

(iii) 

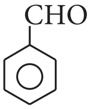
(iv) 

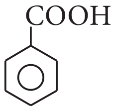
The correct decreasing order of their reactivity towards hydrolysis is

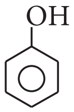
(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (ii) > (i) > (iii)
(c) (ii) > (iv) > (i) > (iii)
(d) (ii) > (iv) > (iii) > (i) *(2007)*

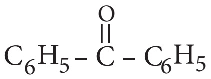
65. 

In the above reaction product *P* is

(a) 

(b) 

(c) 

(d) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$

(2002)

66. Which of the following compounds gives benzoic acid on hydrolysis?

(a) Chlorobenzene (b) Benzoyl chloride
(c) Chlorophenol (d) Chlorotoluene *(1996)*

12.8 Physical Properties

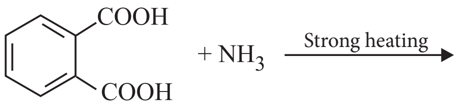
67. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

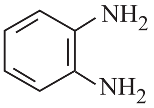
(a) formation of intramolecular H-bonding
(b) formation of carboxylate ion
(c) more extensive association of carboxylic acid *via* van der Waals' forces of attraction
(d) formation of intermolecular H-bonding.

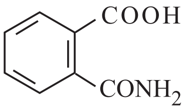
(NEET 2018)

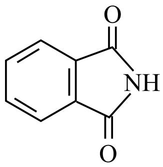
12.9 Chemical Reactions

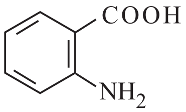
68. The major product of the following reaction is



(a) 

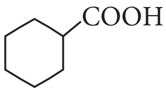
(b) 

(c) 

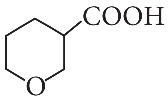
(d) 

(NEET 2019)

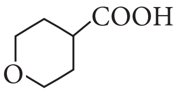
69. The correct order of strengths of the carboxylic acids



I



II



III

is

(a) I > II > III (b) II > III > I

(c) III > II > I (d) II > I > III

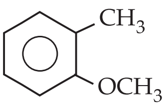
(NEET-II 2016)

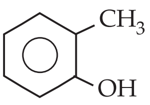
70. The correct order of decreasing acid strength of trichloroacetic acid (*A*), trifluoroacetic acid (*B*), acetic acid (*C*) and formic acid (*D*) is

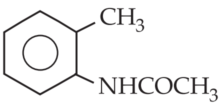
(a) $B > A > D > C$ (b) $B > D > C > A$

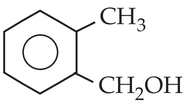
(c) $A > B > C > D$ (d) $A > C > B > D$ *(2012)*

71. Which one of the following is most reactive towards electrophilic reagent?

(a) 

(b) 

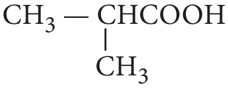
(c) 

(d) 

(2011, 2010)

72. An organic compound *A* on treatment with NH_3 gives *B*, which on heating gives *C*. *C* when treated with Br_2 in the presence of KOH produces ethyl amine. Compound *A* is

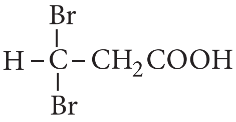
(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$

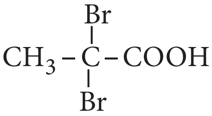
(d) CH_3CH_2COOH

(Mains 2011)

73. Propionic acid with Br_2/P yields a dibromo product. Its structure would be

(a) 
$H-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_2COOH$

(b) $CH_2(Br)-CH_2-COBr$

(c) 
$CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-COOH$

(d) $CH_2(Br)-CH(Br)-COOH$ *(2009)*

74. Which of the following represents the correct order of the acidity in the given compounds?

(a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$

(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

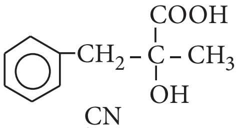
(d) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

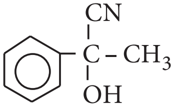
(2007)

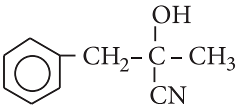
75. In a set of reactions acetic acid yielded a product *D*.

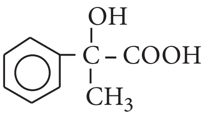
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{anhy. }AlCl_3]{\text{benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$$

The structure of *D* would be

(a) 

(b) 

(c) 

(d) 

(2005)

76. The –OH group of an alcohol or the –COOH group of a carboxylic acid can be replaced by –Cl using

(a) phosphorus pentachloride

(b) hypochlorous acid

(c) chlorine

(d) hydrochloric acid. *(2004)*

77. Which one of the following orders of acid strength is correct?

(a) $RCOOH > ROH > HOH > HC\equiv CH$

(b) $RCOOH > HOH > ROH > HC\equiv CH$

(c) $RCOOH > HOH > HC\equiv CH > ROH$

(d) $RCOOH > HC\equiv CH > HOH > ROH$ *(2003)*

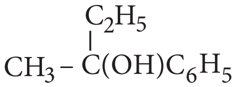
78. In a set of the given reactions, acetic acid yielded a product *C*.

$CH_3COOH + PCl_5 \rightarrow A \xrightarrow[\text{Anh. AlCl}_3]{C_6H_6} B \xrightarrow[\text{ether}]{C_2H_5MgBr} C$

Product *C* would be

(a) $CH_3CH(OH)C_2H_5$ (b) $CH_3COC_6H_5$

(c) $CH_3CH(OH)C_6H_5$

(d) 
$CH_3-\overset{C_2H_5}{\overset{|}{C}}(OH)C_6H_5$ *(2003)*

79. Ethyl benzoate can be prepared from benzoic acid by using

(a) ethyl alcohol

(b) ethyl alcohol and dry HCl

(c) ethyl chloride (d) sodium ethoxide. *(2000)*

80. Reduction by $LiAlH_4$ of hydrolysed product of an ester gives

(a) two alcohols (b) two aldehydes

(c) one acid and one alcohol

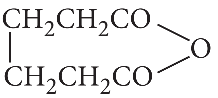
(d) two acids. *(2000)*

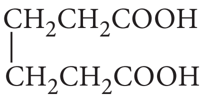
81. Which one of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide?

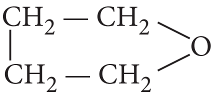
(a) Acetic acid (b) *n*-Hexanol

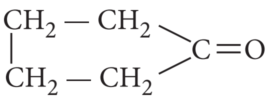
(c) Phenol (d) Both (b) and (c) *(1999)*

82. Which one of the following product is formed when adipic acid is heated?

(a) 

(b) 
$\begin{array}{l} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{array}$

(c) 

(d)  *(1995)*

83. An acyl halide is formed when PCl_5 reacts with an

(a) amide (b) ester

(c) acid (d) alcohol. *(1994)*

84. Benzoic acid gives benzene on being heated with *X* and phenol gives benzene on being heated with *Y*. Therefore, *X* and *Y* are respectively

(a) soda-lime and copper

(b) Zn dust and NaOH

(c) Zn dust and soda-lime

(d) soda-lime and zinc dust. *(1992)*

85. *A* is a lighter phenol and *B* is an aromatic carboxylic acid. Separation of a mixture of *A* and *B* can be carried out easily by using a solution of

(a) sodium hydroxide (b) sodium sulphate

(c) calcium chloride (d) sodium bicarbonate. *(1992)*

86. The compound formed when malonic acid is heated with urea is

(a) cinnamic acid (b) butyric acid

(c) barbituric acid (d) crotonic acid. *(1989)*

87. Among the following the strongest acid is

(a) CH_3COOH (b) CH_2ClCH_2COOH

(c) $CH_2ClCOOH$ (d) CH_3CH_2COOH *(1988)*

88. Which of the following is the correct decreasing order of acidic strength of

(i) methanoic acid (ii) ethanoic acid

(iii) propanoic acid (iv) butanoic acid

(a) (i) > (ii) > (iii) > (iv) (b) (ii) > (iii) > (iv) > (i)

(c) (i) > (iv) > (iii) > (ii) (d) (iv) > (i) > (iii) > (ii) *(1988)*

12.A Derivatives of Carboxylic Acids

89. Match the compounds given in List-I with List-II and select the suitable option using the codes given below.

List-I	**List-II**
(A) Benzaldehyde	(i) Phenolphthalein
(B) Phthalic anhydride	(ii) Benzoin condensation
(C) Phenyl benzoate	(iii) Oil of wintergreen
(D) Methyl salicylate	(iv) Fries rearrangement

(a) (A)-(iv), (B)-(i), (C)-(iii), (D)-(ii)

(b) (A)-(iv), (B)-(ii), (C)-(iii), (D)-(i)

(c) (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i)

(d) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii) *(Mains 2011)*

90. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is

(a) CH_3COOCH_3 (b) CH_3CONH_2

(c) $CH_3COOCOCH_3$ (d) CH_3COCl *(2010)*

91. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of

(a) acid anhydride > amide > ester > acyl chloride

(b) acyl chloride > ester > acid anhydride > amide

(c) acyl chloride > acid anhydride > ester > amide

(d) ester > acyl chloride > amide > acid anhydride. *(2008)*

92. Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields

(a) ethyl propionate (b) ethyl butyrate

(c) acetoacetic ester (d) methyl acetoacetate. *(2006)*

93. Which one of the following esters cannot undergo Claisen self-condensation?
(a) $C_6H_5CH_2COOC_2H_5$ (b) $C_6H_5COOC_2H_5$
(c) $CH_3CH_2CH_2CH_2COOC_2H_5$
(d) $C_6H_{11}CH_2COOC_2H_5$ *(1998)*

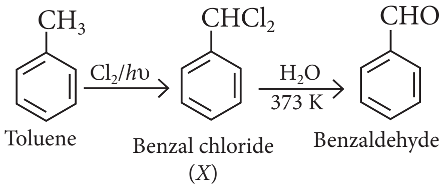
94. Sodium formate on heating yields
(a) oxalic acid and H_2
(b) sodium oxalate and H_2
(c) CO_2 and NaOH
(d) sodium oxalate. *(1993)*

ANSWER KEY

1.	(c)	**2.**	(b)	**3.**	(a)	**4.**	(a)	**5.**	(c)	**6.**	(a)	**7.**	(a)	**8.**	(a)	**9.**	(a)	**10.**	(d)
11.	(b)	**12.**	(a)	**13.**	(b)	**14.**	(c)	**15.**	(b)	**16.**	(c)	**17.**	(a)	**18.**	(d)	**19.**	(d)	**20.**	(c)
21.	(d)	**22.**	(b)	**23.**	(d)	**24.**	(a,d)	**25.**	(b)	**26.**	(d)	**27.**	(b)	**28.**	(c)	**29.**	(c)	**30.**	(c)
31.	(a)	**32.**	(d)	**33.**	(a)	**34.**	(a)	**35.**	(a)	**36.**	(b)	**37.**	(b)	**38.**	(c)	**39.**	(b)	**40.**	(d)
41.	(a)	**42.**	(c)	**43.**	(d)	**44.**	(a)	**45.**	(c)	**46.**	(d)	**47.**	(d)	**48.**	(a)	**49.**	(a)	**50.**	(c)
51.	(d)	**52.**	(d)	**53.**	(b)	**54.**	(a)	**55.**	(b)	**56.**	(d)	**57.**	(a)	**58.**	(d)	**59.**	(a)	**60.**	(b)
61.	(c)	**62.**	(c)	**63.**	(d)	**64.**	(c)	**65.**	(b)	**66.**	(b)	**67.**	(d)	**68.**	(c)	**69.**	(b)	**70.**	(a)
71.	(d)	**72.**	(d)	**73.**	(c)	**74.**	(c)	**75.**	(d)	**76.**	(a)	**77.**	(b)	**78.**	(d)	**79.**	(b)	**80.**	(a)
81.	(a)	**82.**	(a)	**83.**	(c)	**84.**	(d)	**85.**	(d)	**86.**	(c)	**87.**	(c)	**88.**	(a)	**89.**	(d)	**90.**	(d)
91.	(c)	**92.**	(c)	**93.**	(b)	**94.**	(b)												

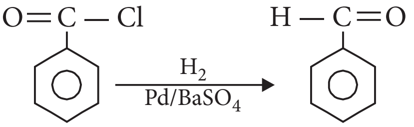
Hints & Explanations

1. (c) :



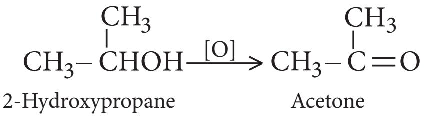
2. (b) : Clemmensen reduction in presence of Zn-Hg and conc. HCl reduces aldehydes and ketones to $—CH_2$ group but carboxylic acid group remains unaffected.

3. (a) :



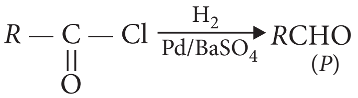
It is Rosenmund's reduction.

4. (a) : Secondary alcohol on oxidation gives a ketone containing the same number of carbon atoms.



$$CH_3-\underset{\text{2-Hydroxypropane}}{\overset{CH_3}{\overset{|}{C}HOH}} \xrightarrow{[O]} \underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O}$$

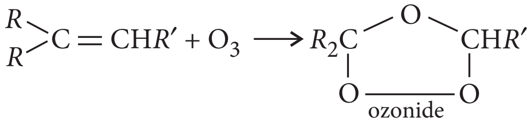
5. (c) : This is Rosenmund reduction.



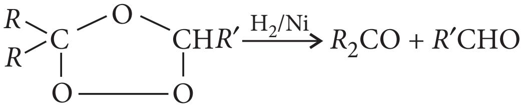
$$R-\underset{O}{\underset{\|}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} \underset{(P)}{RCHO}$$

$BaSO_4$ prevents the aldehyde from being reduced and acts as a poison to the palladium catalyst in this reaction.

6. (a) : On passing a steam of ozone through a solution of olefin in an organic solvent, an ozonide is obtained.



The ozonide on reduction with Zn and acid or H_2/Ni gives aldehydes and/or ketones.



The nature of these products helps in locating the position of the double bond in olefin.

7. (a) : $CH_3-C\equiv N + 2H \xrightarrow[\text{ether}]{HCl}$

$$\underset{(X)}{CH_3-CH=NH}$$

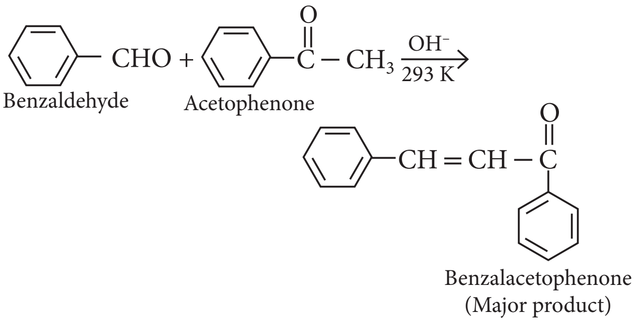
$$\underset{(X)}{CH_3-CH=NH} \xrightarrow[\Delta]{H_2O} \underset{(Y)}{CH_3-CHO} + NH_3$$

Y = Acetaldehyde

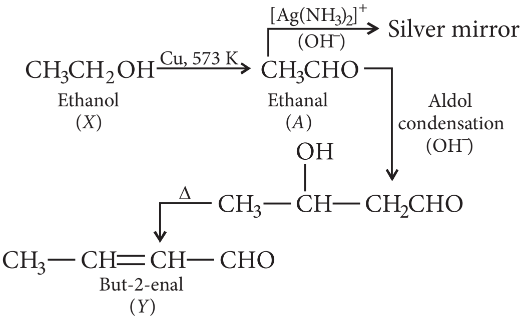
8. (a) : A tertiary alcohol is difficult to oxidise. But when it is treated with an acidic oxidising agent under some conditions, it is oxidised to ketone and then to acids. Both the ketone and acid contain the lesser number of carbon atoms than the starting alcohol.

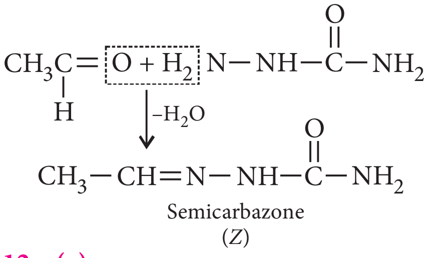
9. (a) : The oxidation of toluene ($C_6H_5CH_3$) with chromyl chloride (CrO_2Cl_2) in CCl_4 or CS_2 to give benzaldehyde is called Etard reaction. In this reaction, the chromyl chloride first forms a brown complex, which is separated and then decomposed with H_2O to give benzaldehyde (C_6H_5CHO).

10. (d) : Cross aldol condensation



11. (b) : Since, *A* gives silver mirror test, it must be an aldehyde and aldehydes are formed by oxidation of 1° alcohols. Thus, '*X*' is a 1° alcohol, *i.e.*, CH_3CH_2OH.

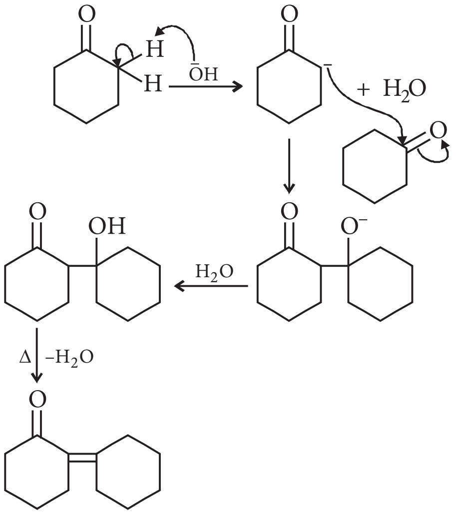




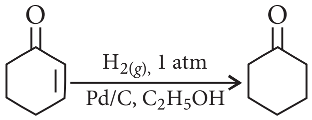
$$CH_3\underset{\displaystyle H}{\underset{|}{C}}=\boxed{O+H_2}N-NH-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{-H_2O} CH_3-CH=N-NH-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$$

Semicarbazone
(*Z*)

12. (a) :

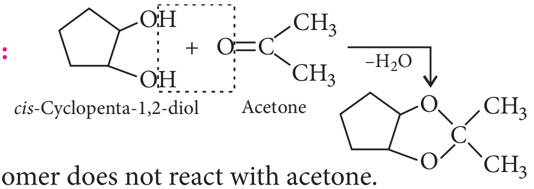


13. (b) :



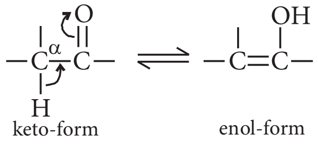
C = C bond is reduced faster than C = O bond with H_2(Pd—C).

14. (c) :

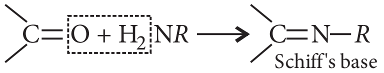


Trans-isomer does not react with acetone.

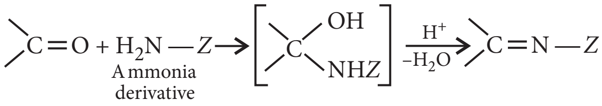
15. (b) : Keto-enol tautomerism :



16. (c) :

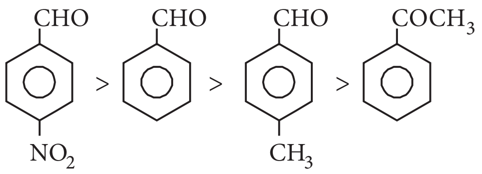


17. (a) : Carbonyl compounds react with ammonia derivatives in weakly acidic medium as follows :

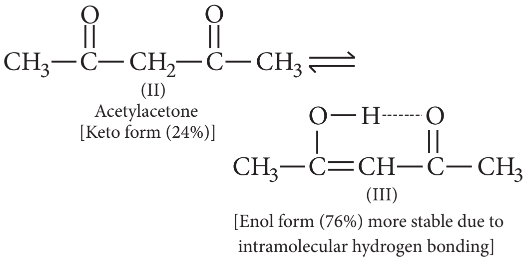


18. (d) : Aromatic aldehydes are more reactive than alkyl aryl ketones. Electron withdrawing group (—NO_2) increases the reactivity towards nucleophilic addition reactions whereas, electron donating group (—CH_3) decreases the reactivity towards nucleophilic addition reactions.

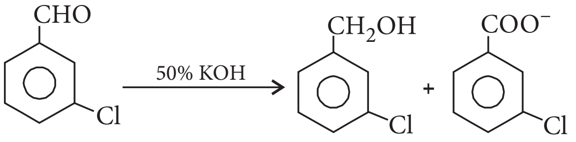
Therefore, the order is :



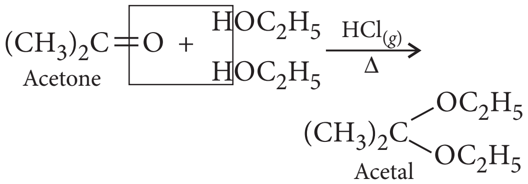
19. (d) :



20. (c) : Aldehyde having no α-hydrogen atoms on heating with concentrated alkali solution (50%) undergoes Cannizzaro's reaction.



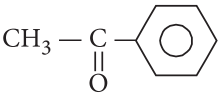
21. (d) :



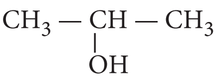
22. (b) : Acetaldehyde, acetone and methyl ketones having CH_3CO- group undergo haloform reaction. Thus, CH_3CHO will give yellow precipitate with I_2 and NaOH but $C_6H_5CH_2CHO$ will not.

23. (d)

24. (a, d) : This example shows iodoform reaction. The compound with $CH_3-\underset{\underset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group will give yellow precipitate of iodoform (CHI_3) when react with iodine and alkali.

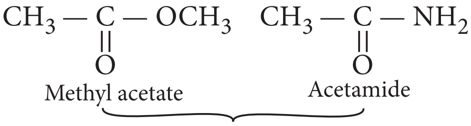


Acetophenone
(+ve iodoform)



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

2-Hydroxypropane
(+ve iodoform)



$$\underbrace{\underset{\text{Methyl acetate}}{CH_3-\underset{\underset{O}{\|}}{C}-OCH_3}\qquad \underset{\text{Acetamide}}{CH_3-\underset{\underset{O}{\|}}{C}-NH_2}}$$

−ve iodoform
(Acid derivatives do not give iodoform test.)

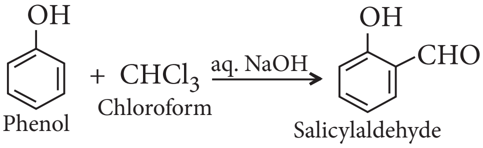
25. (b) : Carbonyl group is reduced to $-CH_2$ group, when treated with amalgamated zinc and conc. HCl. This process is called Clemmensen's reduction.

$$>C=O \xrightarrow{\text{Zn-Hg/HCl}} >CH_2$$

26. (d) : Greater the number of alkyl / phenyl groups attached to the carbonyl groups lower will be its reactivity I > II > III.

+*R*-effect is stronger than +*I*-effect.

27. (b) : (a) Reimer–Tiemann reaction :



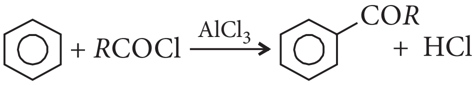
(b) Cannizzaro reaction :

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{50\%\ \text{NaOH}} \underset{\text{Sodium formate}}{HCOO^-\,Na^+} + \underset{\text{Methanol}}{CH_3OH}$$

(c) Wurtz reaction :

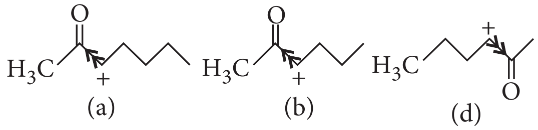
$$\underset{\text{Methyl iodide}}{H_3C-I} + 2Na + I-CH_3 \rightarrow \underset{\text{Ethane}}{CH_3-CH_3} + 2NaI$$

(d) Friedel–Crafts acylation :



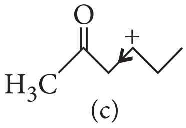
From the above examples it is evident that C—C bond formation does not take place in Cannizzaro reaction.

28. (c) : The ease of dehydration of the given compounds can be explained on the basis of the stability of the carbocation formed. In case of options (a), (b) and (d), a secondary carbocation is formed but the presence of an electron withdrawing $>C=O$ group adjacent to the positively charged carbon, intensifies the charge and hence, destabilises the species.



(a) (b) (d)

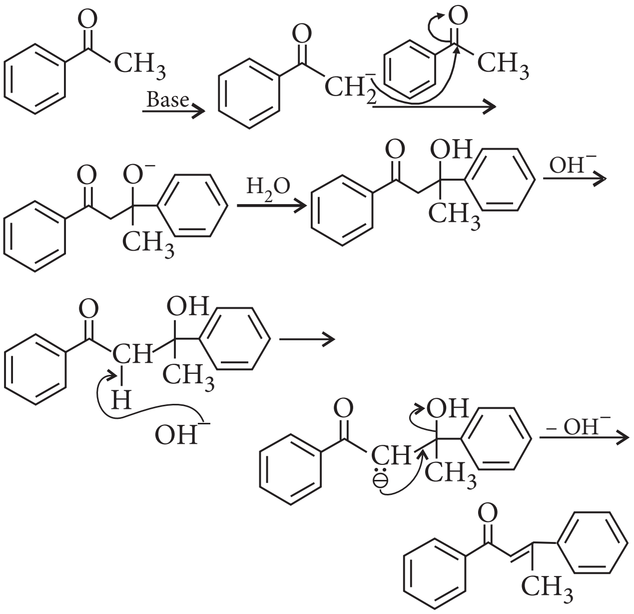
However, in case of option (c), a secondary carbocation is formed, but the electron withdrawing $>C=O$ group is present farther away, as a result, the effect of this group is diminished and hence, the carbocation is relatively more stable.



(c)
More stable

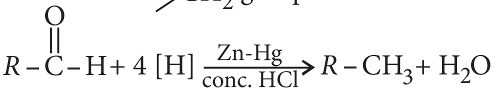
29. (c) : Compounds with $CH_3-\underset{\underset{OH}{|}}{CH}-$ or $CH_3-\underset{\underset{O}{\|}}{C}-$ give positive iodoform hence, (i), (ii) and (iii) will give positive iodoform not (iv).

30. (c) : The first step is a simple condensation reaction. The last step is an example of E1cB mechanism and the leaving group is hydroxide, which is unusual. Still this step manages to take place owing to the stability incorporated therein the product, which is a conjugated carbonyl compound.



31. (a) : The base (OH^-) ion removes one of the α-hydrogen atom (which is some what acidic) from aldehydes and ketones to form a carbanion or the enolate ion. The acidity of α-hydrogen is due to resonance stabilization of enolate anion.

32. (d) : Aldehydes and ketones are converted to alkanes when treated with zinc amalgam and conc. HCl. This is known as Clemmensen reduction. Here $>C=O$ group is reduced to $>CH_2$ group.



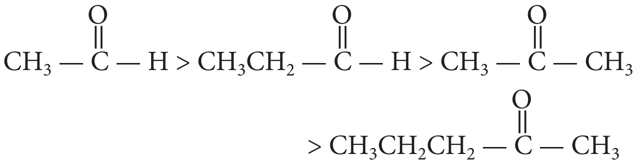
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 4\,[H] \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}} R-CH_3 + H_2O$$

33. (a) : Aldehydes which do not have α-H atom, in presence of 50% NaOH or 50% KOH undergo disproportionation reaction to produce alcohol and sodium salt of acid. This reaction is known as Cannizzaro reaction. C_6H_5CHO containing no α-H atom undergoes Cannizzaro reaction to produce benzyl alcohol and sodium benzoate.

$$C_6H_5CHO \xrightarrow{\text{50\% NaOH}} C_6H_5CH_2OH + C_6H_5COONa$$

34. (a) : The aldehydes or ketones containing α-H atom in presence of dilute alkali undergo self condensation reaction to form β-hydroxyaldehyde or β-hydroxyketone. This reaction is known as aldol condensation.

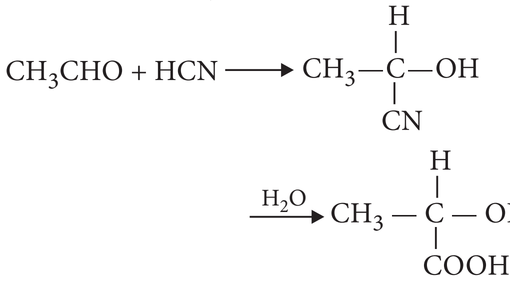
35. (a) : The reactivity of the carbonyl group towards the addition reactions depends upon the magnitude of the positive charge on the carbonyl carbon atom. The introduction of group with –*I* effect increases the reactivity while introduction of alkyl group (+*I* effect) decreases the reactivity.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H > CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H > CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 > CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

+*I*-effect increases, reactivity decreases.

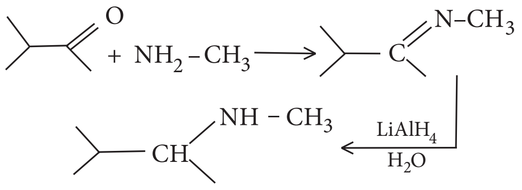
36. (b) :



$$CH_3CHO + HCN \longrightarrow CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-OH \xrightarrow{H_2O} CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}-OH$$

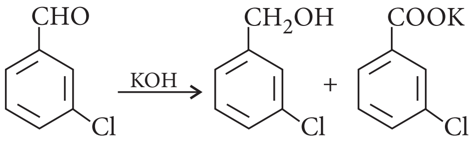
Lactic acid

37. (b) :



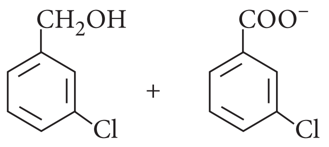
38. (c) : Lactic acid ($CH_3CH(OH)COOH$) is an optically active compound due to the presence of asymmetric carbon atom. It exists in *D*- and *L*-form, the ratio of which is found to be (1 : 1), *i.e.*, a racemic mixture is obtained.

39. (b) :



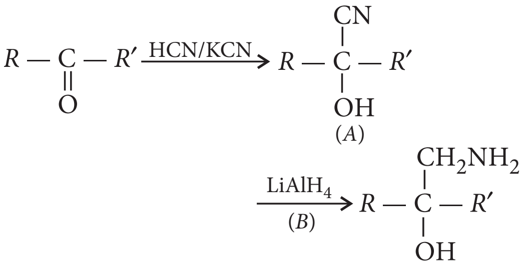
m-chlorobenzaldehyde

or



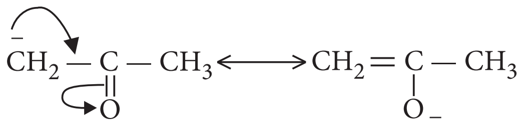
The above reaction is known as Cannizzaro's reaction.

40. (d) :



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-R' \xrightarrow{HCN/KCN} \underset{(A)}{R-\overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R'} \xrightarrow[(B)]{LiAlH_4} R-\overset{\overset{\displaystyle CH_2NH_2}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R'$$

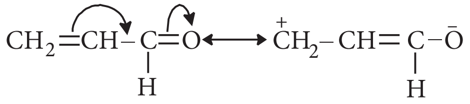
41. (a) : They are resonating forms because the position of the atomic nuclei remains the same and only electron redistribution has occurred.



42. (c) : Tollens' reagent is a solution of ammoniacal silver nitrate and used for the detection of —CHO group. Aldehydes reduce Tollens' reagent and itself gets oxidised to convert Ag^+ ions to Ag powder which forms the silver coloured mirror in the test tube. So, this test is also known as silver mirror test.

$$R-CHO + [Ag(NH_3)_2]^+ \rightarrow R-COO^- + \underset{\text{(Powder)}}{Ag}$$

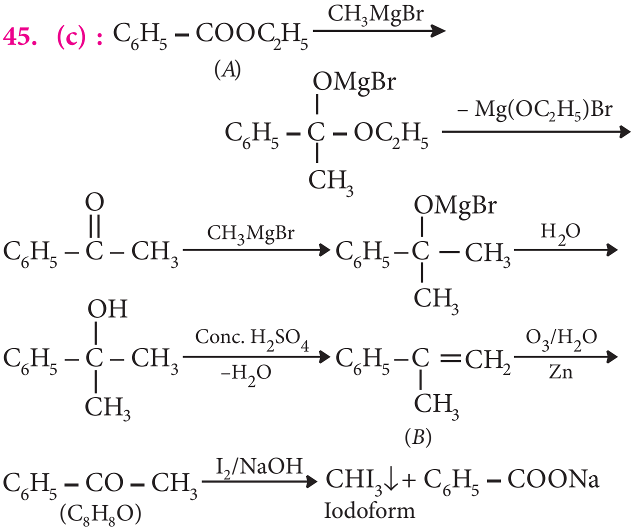
43. (d) : O-atom is more electronegative than C-atom, therefore O-atom bears partial –ve charge and C-atom to which it is attached bear partial +ve charge.



44. (a) : It is a simple condensation reaction which proceeds with elimination of water.

$$R-CH=\boxed{O + H_2}N-NH_2 \xrightarrow[-H_2O]{} RCH=N-NH_2$$

45. (c) :



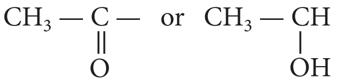
$$\underset{(A)}{C_6H_5-COOC_2H_5} \xrightarrow{CH_3MgBr} C_6H_5-\underset{CH_3}{\overset{OMgBr}{C}}-OC_2H_5 \xrightarrow{-Mg(OC_2H_5)Br}$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CH_3MgBr} C_6H_5-\underset{CH_3}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{H_2O}$$

$$C_6H_5-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow[-H_2O]{Conc.\ H_2SO_4} \underset{(B)}{C_6H_5-\underset{CH_3}{C}=CH_2} \xrightarrow[Zn]{O_3/H_2O}$$

$$\underset{(C_8H_8O)}{C_6H_5-CO-CH_3} \xrightarrow{I_2/NaOH} \underset{Iodoform}{CHI_3\downarrow} + C_6H_5-COONa$$

46. (d) : Compounds containing

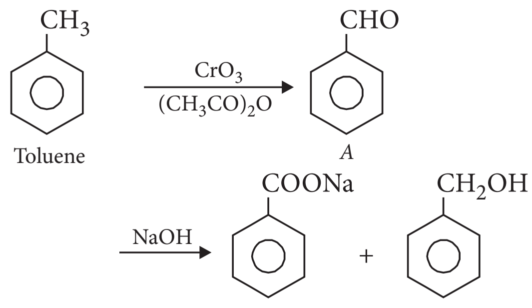


$CH_3-\underset{O}{\underset{\|}{C}}-$ or $CH_3-\underset{OH}{\underset{|}{CH}}-$ group show iodoform test. So iodoform test is not given by 3-pentanone.

47. (d) : $C_6H_5CHO + 2[H] \xrightarrow{Zn/HCl} C_6H_5CH_2OH$

Benzaldehyde Phenylmethanol (Benzyl alcohol)

48. (a) :



(Cannizzaro product)

49. (a) : Benzaldehyde reacts with primary aromatic amines to form Schiff's base (Benzylidene aniline).

$C_6H_5HC{=}O + C_6H_5NH_2 \rightarrow C_6H_5HC{=}NC_6H_5 + H_2O$

Benzaldehyde Aniline Benzylidene aniline

50. (c) : $\underset{\text{(Ethyl alcohol)}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\text{(Acetaldehyde)}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{(Chloral)}}{CCl_3CHO}$

(*A*)

$CCl_3CHO \xrightarrow{[O]} CCl_3COOH$

Monocarboxylic acid
(*B*)

The compound '*A*' reduces Fehling's solution thus, it must have free —CHO group.

Thus, the compound *A* is chloral.

51. (d) : Since CH_3CH_2CHO has α-hydrogen atom, therefore it will undergo aldol condensation in the presence of cold dilute alkali.

52. (d) : Acetaldehyde reduces Tollens' reagent to silver mirror.

$\underset{\text{(Acetaldehyde)}}{CH_3CHO} + \underset{\text{(Tollens' reagent)}}{2[Ag(NH_3)_2]^+} + 3OH^- \rightarrow CH_3COO^- + 2H_2O + \underset{\text{(Silver mirror)}}{2Ag} + 4NH_3$

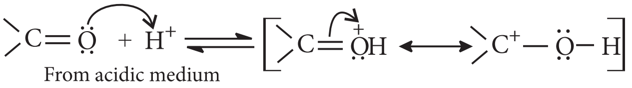
53. (b) : $(CH_3)_2C{=}CHCOCH_3 \xrightarrow{NaOI} (CH_3)_2C{=}CHCOOH + CHI_3$

$(NaOH + I_2)$/NaOI is the best suitable reagent for the given reaction.

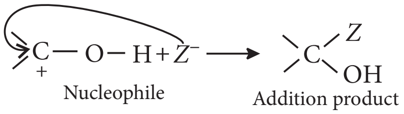
54. (a) : Ketones on oxidation give carboxylic acids with lesser number of carbon atoms *i.e*,

$CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$

55. (b) : Acetaldehyde reacts only with nucleophiles. Since the mobile π-electrons of carbon oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron deficient and carbonyl oxygen is electron rich. Thus, the electron deficient carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagent, *i.e.*, by base.



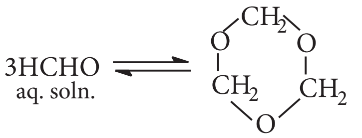
The nucleophile, then attacks the protonated carbonyl group to form addition product.



56. (d) : Acetophenone reacts with NaOH and I_2 to give yellow ppt. of CHI_3 but benzophenone $(C_6H_5COC_6H_5)$ does not. Hence, it can be used to distinguish between them.

$C_6H_5COCH_3 \xrightarrow{I_2,\ NaOH} \underset{\text{yellow ppt.}}{CHI_3\downarrow} + C_6H_5COONa$

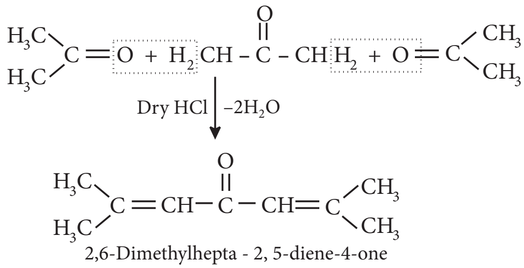
57. (a) :



Trioxane (metaformaldehyde)

58. (d) : Acetone forms mesitylene (1,3,5-trimethylbenzene) on distillation with conc. H_2SO_4.

59. (a) :



2,6-Dimethylhepta - 2, 5-diene-4-one
(phorone)

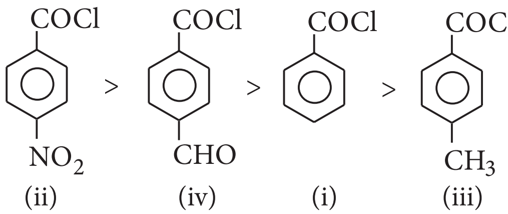
60. **(b) :** $HCHO + KOH \xrightarrow{50\%\ KOH} HCOOK + CH_3OH$
The above reaction is called as Cannizzaro's reaction.

61. **(c) :** Formula is an aqueous solution of 40% HCHO.

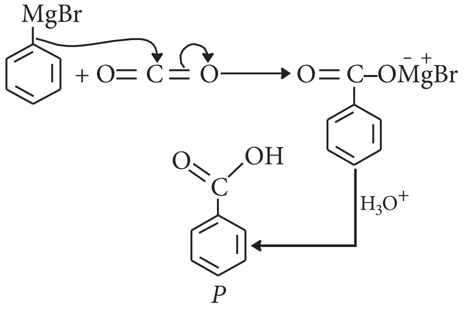
62. **(c) :** PCC (Pyridium chlorochromate) stops oxidation at the aldehyde stage, thereby preventing the further oxidation of aldehydes to carboxylic acids.

63. **(d) :** Electron withdrawing groups increase the reactivity towards nucleophilic substitution reaction and $-NO_2$ is a strong electron withdrawing group.

64. **(c) :** The ease of hydrolysis depends upon the magnitude of the +ve charge on the carbonyl group. Electron withdrawing groups increase the magnitude of positive charge and electron donating groups decrease the magnitude of positive charge. Hence, the decreasing order of reactivity towards hydrolysis is



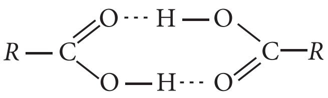
65. **(b) :**



The product (P) is benzoic acid.

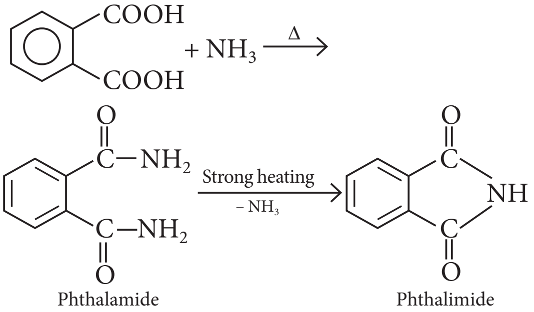
66. **(b) :** $\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl$

67. **(d) :** Due to the formation of intermolecular H-bonding, association occurs in carboxylic acids.



So, they have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass.

68. **(c) :**

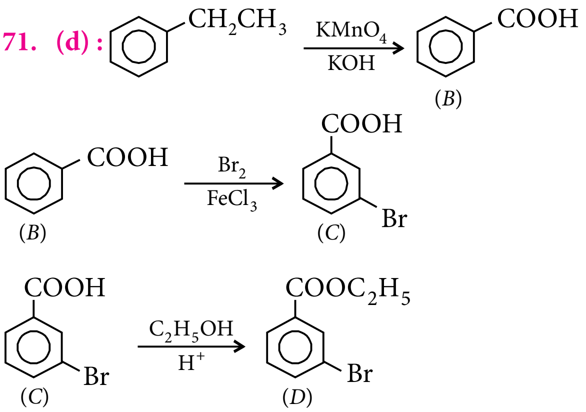


69. **(b) :** Acidic strength ∝ – I effect
As oxygen is more electron withdrawing (II) and (III) show greater – I effect than (I). Thus, (I) is least acidic. Out of (II) and (III), (II) is more acidic than (III) as distance of O increases from —COOH group and acidic strength decreases.

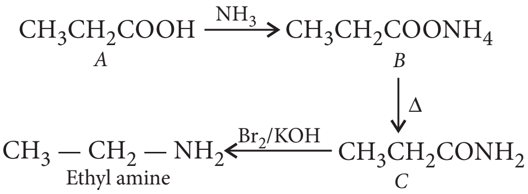
70. **(a) :** As $-I$ effect increases, —COOH group becomes more electron deficient and tendency to loose H^+ ions increases *i.e.*, acid strength increases. As $+I$ effect increases, acid strength decreases.
Thus, correct order of acid strength is

$$\underset{(B)}{CF_3COOH} > \underset{(A)}{CCl_3COOH} > \underset{(D)}{HCOOH} > \underset{(C)}{CH_3COOH}$$

71. **(d) :**

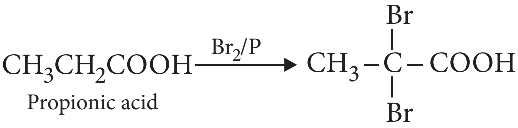


72. **(d) :** The compound will be CH_3CH_2COOH.



$$\begin{tikzcd}\underset{A}{CH_3CH_2COOH} \arrow[r, "NH_3"] & \underset{B}{CH_3CH_2COONH_4} \arrow[d, "\Delta"] \\ \underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2} & \underset{C}{CH_3CH_2CONH_2} \arrow[l, "Br_2/KOH"']\end{tikzcd}$$

73. **(c) :** This is Hell–Volhard–Zelinsky reaction. In this reaction, acids containing α-H react with X_2/red P giving product in which the α-hydrogens are substituted by X.

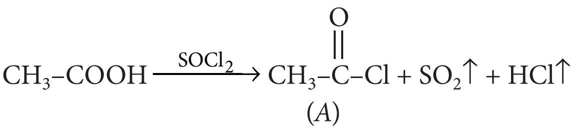


$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{Br_2/P} CH_3-\overset{Br}{\underset{Br}{C}}-COOH$$

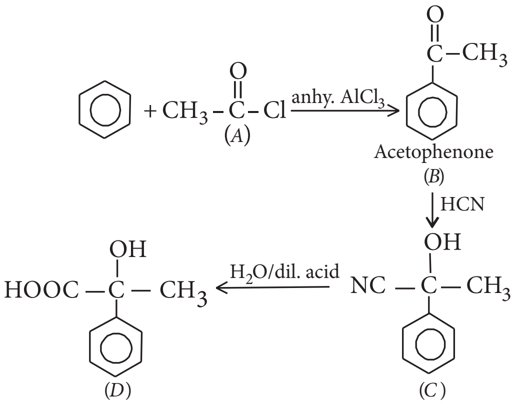
74. **(c) :** $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

Acidity decreases as the $-I$ effect of the group decreases, F is the most electronegative atom and hence it has highest $-I$ effect among the halogens.

75. **(d) :**



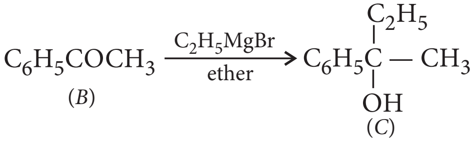
$$CH_3-COOH \xrightarrow{SOCl_2} \underset{(A)}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + SO_2\uparrow + HCl\uparrow$$



76. (a) : $ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$
$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

77. (b) : Carboxylic acid is much stronger than water and alcohol. Since the carboxylate ion after the removal of proton is stabilised by resonating structures. The —OH in alcohols is almost neutral. Acetylene is also weakest acid among the given examples.

78. (d) : $CH_3COOH + PCl_5 \longrightarrow \underset{(A)}{CH_3COCl} \xrightarrow[\text{anhy. AlCl}_3]{C_6H_6}$



$$\underset{(B)}{C_6H_5COCH_3} \xrightarrow[\text{ether}]{C_2H_5MgBr} \underset{(C)}{C_6H_5\overset{C_2H_5}{\underset{OH}{C}} - CH_3}$$

79. (b) : Ethyl benzoate can be prepared by heating benzoic acid with ethyl alcohol in presence of dry HCl or conc. H_2SO_4. The reaction is called as esterification reaction.

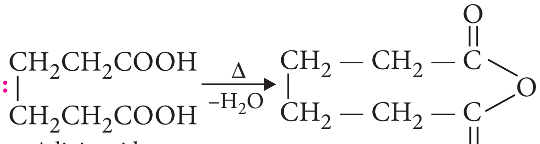
$$C_6H_5-COOH + C_2H_5-OH \xrightarrow[-H_2O]{\text{dry HCl}} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5}$$

80. (a) : Reduction of hydrolysed product of ester by $LiAlH_4$ produces two alcohols.

$$R-COOR' \xrightarrow{H_2O} R-COOH + R'OH$$
$$\xrightarrow[\text{ether}]{LiAlH_4} R-CH_2OH + R'OH$$

81. (a) : $NaHCO_3$ is weakly basic, so it can only react with the acid CH_3COOH. While phenol is weakly acidic and n-hexanol is neutral, they do not react with $NaHCO_3$.
$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$

82. (a) :



Adipic acid

Adipic anhydride

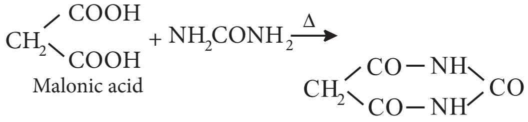
83. (c) : $\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$

84. (d) : $C_6H_5COOH \xrightarrow{\text{Soda-lime}(X)} C_6H_6 + Na_2CO_3$

$C_6H_5OH \xrightarrow{\text{Zn dust }(Y)} C_6H_6 + ZnO$

85. (d) : Carboxylic acids dissolve in $NaHCO_3$ but phenols do not.

86. (c) :



Malonic acid

Barbituric acid

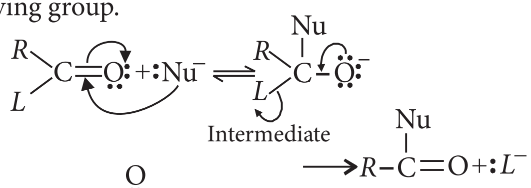
87. (c) : Strongest acid is $CH_2ClCOOH$ as $-I$ effect of Cl atom decreases with the increase in distance.

88. (a) : $+I$ effect of the alkyl group increases from CH_3 to CH_3CH_2 to $CH_3CH_2CH_2$ to $CH_3CH_2CH_2CH_2$, resulting in decrease of acid character. Therefore, the order is (i) > (ii) > (iii) > (iv).

89. (d)

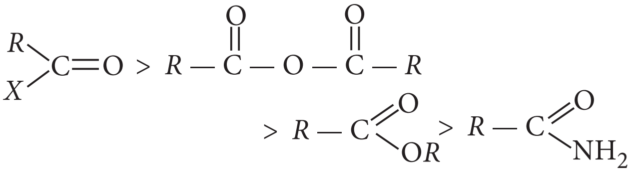
90. (d) : CH_3COCl is most susceptible to nucleophilic attack. The susceptibility of a substrate towards nucleophilic attack depends on how good a leaving group is attached to it. Cl^- is a weak base and therefore, a good leaving group.

91. (c) :



$(L = X^-, NH_2^-, O^- - \overset{O}{\overset{\|}{C}} - R \text{ or } O^-R)$

The relative reactivities of various compounds have been found to be in the following order :



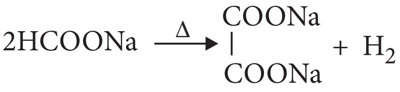
$$\begin{matrix}R\\X\end{matrix}\!>\!C{=}O > R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R > R-C\begin{matrix}{=}O\\ OR\end{matrix} > R-C\begin{matrix}{=}O\\ NH_2\end{matrix}$$

92. (c) : Ethyl acetate undergoes Claisen condensation in presence of sodium ethoxide involving α-hydrogen atom in which two molecules of ethyl acetate combine together to form acetoacetic ester.

$$CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa}$$
$$\underset{\text{Acetoacetic ester}}{CH_3COCH_2COOC_2H_5} + C_2H_5OH$$

93. (b) : The esters having active methylene group $(-\ CH_2\ -)$, show Claisen condensation reaction. As $C_6H_5-COOC_2H_5$ has no α-hydrogen atom or active methylene group, so it cannot undergo Claisen condensation reaction.

94. (b) :



$$2HCOONa \xrightarrow{\Delta} \begin{matrix}COONa\\|\\COONa\end{matrix} + H_2$$

Sodium oxalate

* * *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CHAPTER 13

Amines

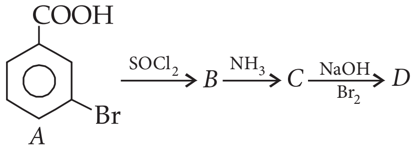
13.4 Preparation of Amines

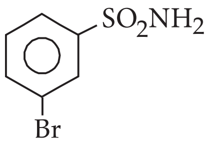
1. Which of the following reactions is appropriate for converting acetamide to methanamine?
(a) Hoffmann hypobromamide reaction
(b) Stephen's reaction
(c) Gabriel phthalimide synthesis
(d) Carbylamine reaction *(NEET 2017)*

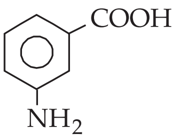
2. Method by which aniline cannot be prepared is
(a) degradation of benzamide with bromine in alkaline solution
(b) reduction of nitrobenzene with H_2/Pd in ethanol
(c) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
(d) hydrolysis of phenylisocyanide with acidic solution. *(2015)*

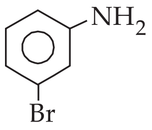
3. The electrolytic reduction of nitrobenzene in strongly acidic medium produces
(a) azobenzene (b) aniline
(c) *p*-aminophenol (d) azoxybenzene.
(2015, Cancelled)

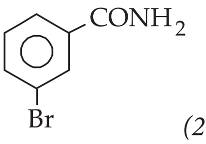
4. In a set of reactions *m*-bromobenzoic acid gave a product *D*. Identify the product *D*.



(a)


(b)


(c)


(d)


(2011)

5. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine?
(a) $NaOH-Br_2$ (b) Sodalime
(c) Hot conc.H_2SO_4 (d) PCl_5 *(2010)*

6. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?
(a) Methyl isocyanide (b) Acetamide
(c) Methyl cyanide (d) Nitroethane *(2007)*

7. In a set of reactions propionic acid yielded a compound *D*.

$$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow[Br_2]{KOH} D$$

The structure of *D* would be
(a) $CH_3CH_2NH_2$ (b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CONH_2$ (d) $CH_3CH_2NHCH_3$
(2006)

8. Electrolytic reduction of nitrobenzene in weakly acidic medium gives
(a) *N*-phenylhydroxylamine
(b) nitrosobenzene
(c) aniline
(d) *p*-hydroxyaniline. *(2005)*

9. Intermediates formed during reaction of $RCONH_2$ with Br_2 and KOH are
(a) *R*CONHBr and *R*NCO
(b) *R*NHCOBr and *R*NCO
(c) *R*NH – Br and *R*CONHBr
(d) $RCONBr_2$ *(2001)*

10. Amides may be converted into amines by a reaction named after
(a) Hoffmann (b) Claisen
(c) Perkin (d) Kekule. *(1999)*

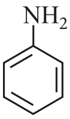
11. Indicate which nitrogen compound amongst the following would undergo Hoffmann reaction (*i.e.*, reaction with Br_2 and strong KOH) to furnish the primary amine ($R–NH_2$)?

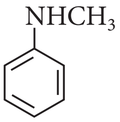
(a) $RCONHCH_3$ (b) $RCOONH_4$
(c) $RCONH_2$ (d) $R-CO-NHOH$

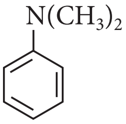
(1989)

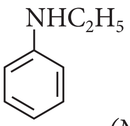
13.6 Chemical Reactions

12. Which of the following amines will give the carbylamine test?

(a) 

(b) 

(c) 

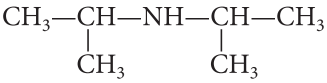
(d) 

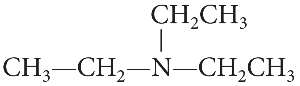
(NEET 2020)

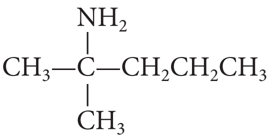
13. The correct order of the basic strength of methyl substituted amines in aqueous solution is

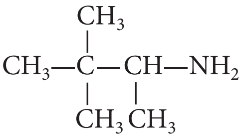
(a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
(b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
(c) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
(d) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$ *(NEET 2019)*

14. The amine that reacts with Hinsberg's reagent to give an alkali insoluble product is

(a) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-NH-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(b) 
$CH_3-CH_2-\overset{CH_2CH_3}{\overset{|}{N}}-CH_2CH_3$

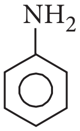
(c) 
$CH_3-\underset{CH_3}{\underset{|}{\overset{NH_2}{\overset{|}{C}}}}-CH_2CH_2CH_3$

(d) 
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{CH_3}{\underset{|}{CH}}-NH_2$ *(Odisha NEET 2019)*

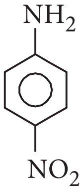
15. Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because

(a) inspite of substituents nitro group always goes to only *m*-position
(b) in electrophilic substitution reactions amino group is *meta* directive
(c) in absence of substituents nitro group always goes to *m*-position
(d) in acidic (strong) medium aniline is present as anilinium ion. *(NEET 2018)*

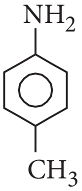
16. The correct increasing order of basic strength for the following compounds is



(I)



(II)



(III)

(a) III < I < II (b) III < II < I
(c) II < I < III (d) II < III < I

(NEET 2017)

17. The correct statement regarding the basicity of arylamines is

(a) arylamines are generally more basic than alkylamines because of aryl group
(b) arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridised
(c) arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system
(d) arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π-electron system.

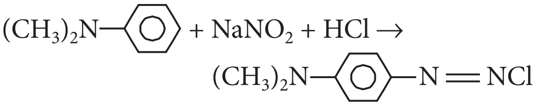
(NEET-I 2016)

18. On hydrolysis of a "compound", two compounds are obtained. One of which on treatment with sodium nitrite and hydrochloric acid gives a product which does not respond to iodoform test. The second one reduces Tollens' reagent and Fehling's solution. The "compound" is

(a) $CH_3CH_2CH_2NC$ (b) $CH_3CH_2CH_2CN$
(c) $CH_3CH_2CH_2ON{=}O$
(d) $CH_3CH_2CH_2CON(CH_3)_2$

(Karnataka NEET 2013)

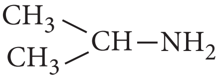
19. Some reactions of amines are given. Which one is not correct?

(a) 

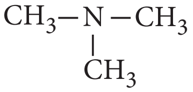
(b) $CH_3CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2OH + N_2$
(c) $CH_3NH_2 + C_6H_5SO_2Cl \rightarrow CH_3NHSO_2C_6H_5$
(d) $(CH_3)_2NH + NaNO_2 + HCl \rightarrow (CH_3)_2N-N{=}O$

(Karnataka NEET 2013)

20. An organic compound (C_3H_9N) (*A*), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (*A*) on warming with $CHCl_3$ and caustic potash gave (*C*) which on reduction gave isopropylmethylamine. Predict the structure of (*A*).

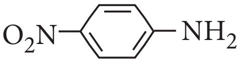
(a) 
$(CH_3)_2CH-NH_2$

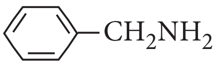
(b) $CH_3CH_2-NH-CH_3$

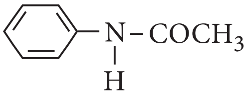
(c) 
$CH_3-N(CH_3)-CH_3$

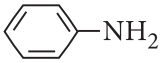
(d) $CH_3CH_2CH_2-NH_2$ *(2012)*

21. Which of the following compounds is most basic?

(a) 

(b) 

(c) 

(d) 

(Mains 2011)

22. Which of the following statements about primary amines is false?

(a) Alkyl amines are stronger bases than aryl amines.
(b) Alkyl amines react with nitrous acid to produce alcohols.
(c) Aryl amines react with nitrous acid to produce phenols.
(d) Alkyl amines are stronger bases than ammonia.

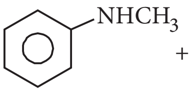
(2010)

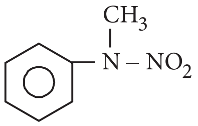
23. Match the compounds given in List I with their characteristic reactions given in List II. Select the correct option.

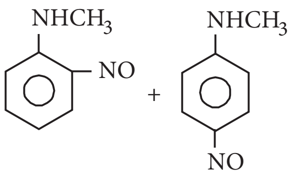
	List I (Compounds)		List II (Reactions)
A.	$CH_3(CH_2)_3NH_2$	(i)	Alkaline hydrolysis
B.	$CH_3C\equiv CH$	(ii)	With KOH (alcohol) and $CHCl_3$ produces bad smell
C.	$CH_3CH_2COOCH_3$	(iii)	Gives white ppt. with ammoniacal $AgNO_3$
D.	$CH_3CH(OH)CH_3$	(iv)	With Lucas reagent cloudiness appears after 5 minutes

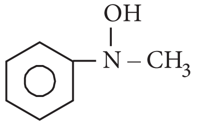
(a) A-(ii), B-(i), C-(iv), D-(iii)
(b) A-(iii), B-(ii), C-(i), D-(iv)
(c) A-(ii), B-(iii), C-(i), D-(iv)
(d) A-(iv), B-(ii), C-(iii), D-(i) *(Mains 2010)*

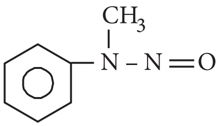
24. Predict the product.


+ $NaNO_2$ + HCl ⟶ Product

(a) 

(b) 

(c) 

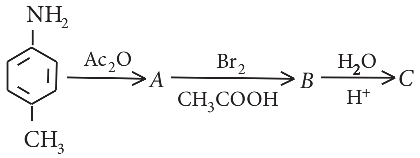
(d) 

(2009)

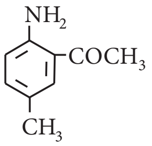
25. Which of the following is more basic than aniline?

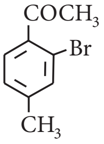
(a) Benzylamine
(b) Diphenylamine
(c) Triphenylamine
(d) *p*-Nitroaniline *(2006)*

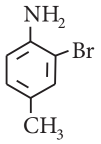
26. The final product *C*, obtained in this reaction,

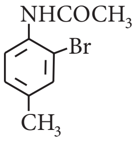


would be

(a) 

(b) 

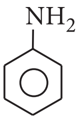
(c) 

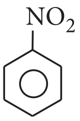
(d) 

(2003)

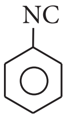
27. $A \xrightarrow{\text{reduction}} B \xrightarrow{CHCl_3/KOH} C \xrightarrow{\text{reduction}}$ *N*-methylaniline,

then *A* is

(a) 

(b) 

(c) CH_3NH_2

(d) 

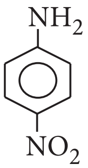
(2000)

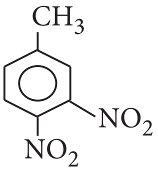
28. Phenyl isocyanides are prepared by which of the following reaction?

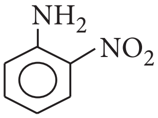
(a) Reimer–Tiemann reaction
(b) Carbylamine reaction
(c) Rosenmund's reaction
(d) Wurtz reaction *(1999)*

29. The compound obtained by heating a mixture of ethylamine and chloroform with ethanolic potassium hydroxide (KOH) is
(a) an amide
(b) an amide and nitro compound
(c) an ethyl isocyanide
(d) an alkyl halide. *(1997)*

30. An aniline on nitration gives

(a) 

(b) 

(c) 

(d) both (a) and (c). *(1996)*

31. The action of nitrous acid on an aliphatic primary amine gives
(a) secondary amine (b) nitro alkane
(c) alcohol (d) alkyl nitrite. *(1994)*

32. Which one of the following order is wrong, with respect to the property indicated?
(a) Benzoic acid > phenol > cyclohexanol (acid strength)
(b) Aniline > cyclohexylamine > benzamide (basic strength)
(c) Formic acid > acetic acid > propanoic acid (acid strength)
(d) Fluoroacetic acid > chloroacetic acid > bromoacetic acid (acid strength) *(1994)*

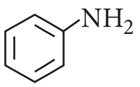
33. For carbylamine reaction, we need hot alcoholic KOH and
(a) any primary amine and chloroform
(b) chloroform and silver powder
(c) a primary amine and an alkyl halide
(d) a monoalkylamine and trichloromethane. *(1992)*

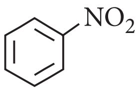
13.7 Methods of Preparation of Diazonium Salts

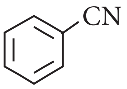
34. Which of the following will be most stable diazonium salt $RN_2^+X^-$?
(a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$
(c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$ *(2014)*

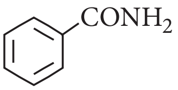
13.9 Chemical Reactions

35. A given nitrogen-containing aromatic compound '*A*' reacts with Sn/HCl, followed by HNO_2 to give an unstable compound '*B*'. '*B*', on treatment with phenol, forms a beautiful coloured compound '*C*' with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound '*A*' is

(a) 

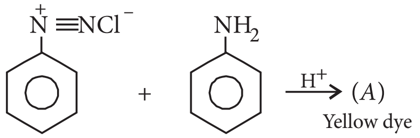
(b) 

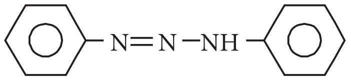
(c) 

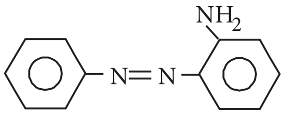
(d) 

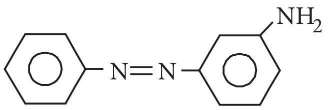
(NEET-II 2016)

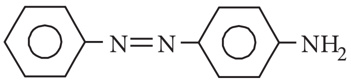
36. In the following reaction, the product (*A*) is



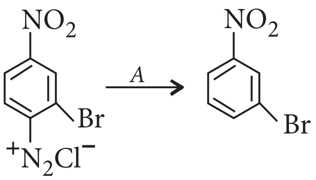
(a) 

(b) 

(c) 

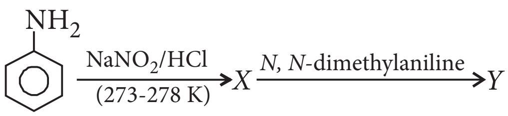
(d) 

(2014)

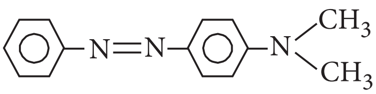
37. In the reaction 

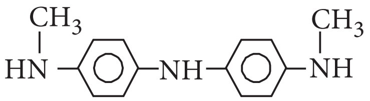
A is
(a) H_3PO_2 and H_2O (b) H^+/H_2O
(c) $HgSO_4/H_2SO_4$ (d) Cu_2Cl_2 *(NEET 2013)*

38. Aniline in a set of the following reactions yielded a coloured product *Y*.

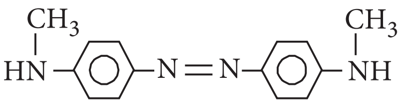


The structure of '*Y*' would be

(a) 

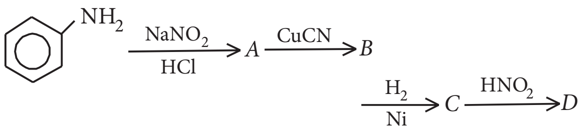
(b) 

(c) 

(d) 

(2010, 2008, 2004)

39. Aniline in a set of reactions yielded a product *D*.



The structure of the product *D* would be

(a) C_6H_5NHOH (b) $C_6H_5NHCH_2CH_3$

(c) $C_6H_5CH_2NH_2$ (d) $C_6H_5CH_2OH$ *(2005)*

40. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated to dry. The final product is

(a) *p*-bromoaniline

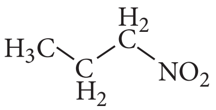
(b) *p*-bromofluorobenzene

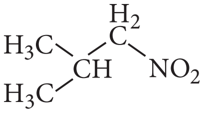
(c) 1, 3, 5-tribromobenzene

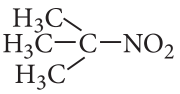
(d) 2, 4, 6-tribromofluorobenzene. *(1998)*

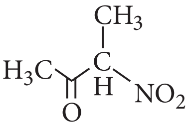
13.A Other Nitrogen Containing Compounds

41. Which one of the following nitro-compounds does not react with nitrous acid?

(a) 

(b) 

(c) 

(d) 

(NEET-II 2016)

42. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at 80–100°C forms which one of the following products?

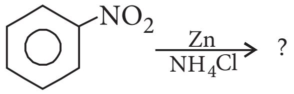
(a) 1, 4-Dinitrobenzene

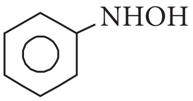
(b) 1, 2, 4-Trinitrobenzene

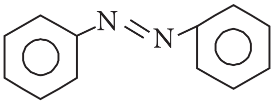
(c) 1, 2-Dinitrobenzene

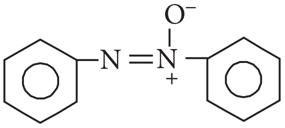
(d) 1, 3-Dinitrobenzene *(NEET 2013)*

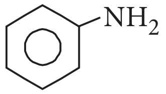
43. What is the product obtained in the following reaction?



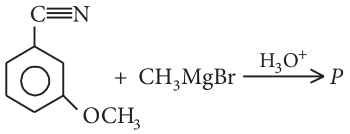
(a) 

(b) 

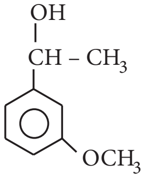
(c) 

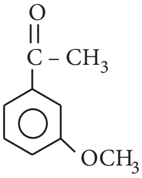
(d) 

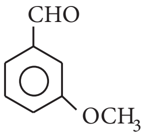
(2011)

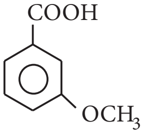
44. 

Product '*P*' in the above reaction is

(a) 

(b) 

(c) 

(d) 

(2002)

45. Which product is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl?

(a) Methyl cyanide (b) Acetic anhydride

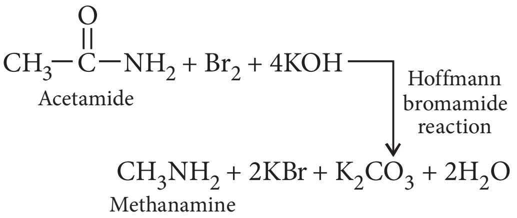
(c) Acetic acid (d) Acetamide *(1995)*

ANSWER KEY

1.	(a)	**2.**	(c)	**3.**	(c)	**4.**	(c)	**5.**	(a)	**6.**	(a)	**7.**	(a)	**8.**	(c)	**9.**	(a)	**10.**	(a)
11.	(c)	**12.**	(a)	**13.**	(b)	**14.**	(a)	**15.**	(d)	**16.**	(c)	**17.**	(c)	**18.**	(a)	**19.**	(a)	**20.**	(a)
21.	(b)	**22.**	(c)	**23.**	(c)	**24.**	(d)	**25.**	(a)	**26.**	(c)	**27.**	(b)	**28.**	(b)	**29.**	(c)	**30.**	(d)
31.	(c)	**32.**	(b)	**33.**	(a)	**34.**	(b)	**35.**	(b)	**36.**	(d)	**37.**	(a)	**38.**	(a)	**39.**	(d)	**40.**	(d)
41.	(c)	**42.**	(d)	**43.**	(a)	**44.**	(b)	**45.**	(d)										

Hints & Explanations

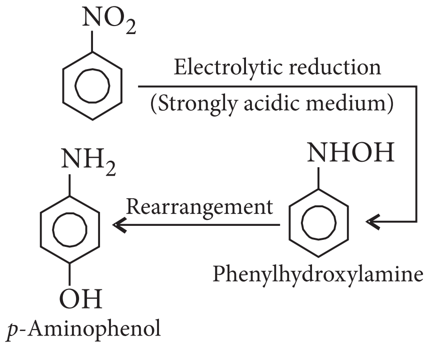
1. (a) :



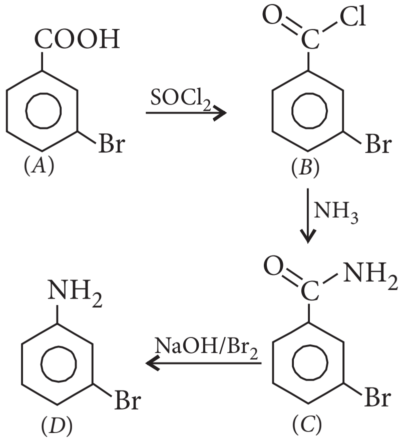
$$\underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{||}{C}}-NH_2} + Br_2 + 4KOH \xrightarrow{\text{Hoffmann bromamide reaction}} \underset{\text{Methanamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

2. (c) : Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

3. (c) :



4. (c) :



5. (a) : $\underset{\text{Acetamide}}{CH_3CONH_2} + 4NaOH + Br_2 \rightarrow$

$$\underset{1°\text{ Amine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

This reaction is called Hoffmann Bromamide degradation reaction.

6. (a) : Alkyl isocyanide on reduction with lithium aluminium hydride forms secondary amine containing methyl as one of the alkyl groups.

$$\underset{\text{Alkyl isocyanide}}{R-N\overset{\rightarrow}{\equiv}C} + [H] \xrightarrow{LiAlH_4} \underset{\text{Secondary amine}}{RNHCH_3}$$

$$\underset{\text{Methyl isocyanide}}{H_3C-N\overset{\rightarrow}{\equiv}C} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Dimethylamine}}{H_3C-NH-CH_3}$$

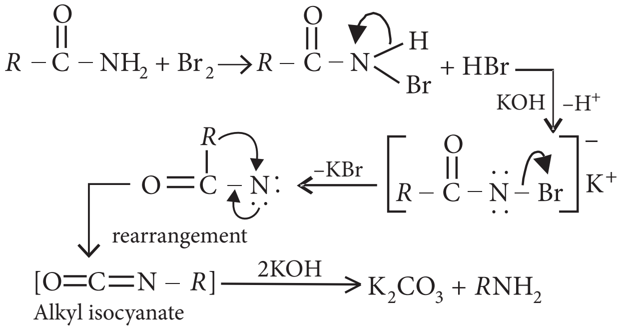
7. (a) : $CH_3CH_2COOH \xrightarrow{SOCl_2} \underset{(B)}{CH_3CH_2COCl}$

$$\xrightarrow{NH_3} \underset{(C)}{CH_3CH_2CONH_2} \xrightarrow[Br_2]{KOH} \underset{(D)}{CH_3CH_2NH_2}$$

8. (c) : Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline but in strongly acidic medium it gives *p*-aminophenol through the acid-catalysed rearrangement of the initially formed phenylhydroxylamine.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{(Weakly acidic medium)}]{\text{Electrolytic reduction}} \underset{\text{Aniline}}{C_6H_5NH_2}$$

9. (a) : The reaction, $RCONH_2 + Br_2 + KOH \rightarrow RNH_2$ is known as Hoffmann bromamide degradation reaction. The mechanism of the reaction is



This reaction is used to descent the series, *i.e.*, for preparing a lower homologue from a higher one.

10. (a) :

$$\underset{\text{Acid amide}}{R-\underset{O}{\underset{||}{C}}-NH_2} + Br_2 + 4KOH \longrightarrow \underset{1°\text{ amine}}{R-NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

This reaction is called Hoffmann bromamide degradation reaction.

11. (c) : The amide ($-CONH_2$) group is converted into primary amino group ($-NH_2$) by Hoffmann's bromamide degradation reaction.

$$RCONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} \underset{1°\text{amine}}{R-NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

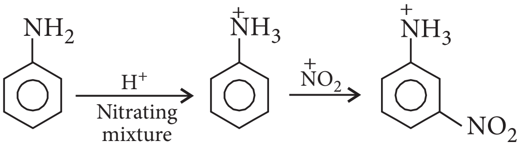
12. (a) : Aliphatic and aromatic primary amines give carbylamine test. Secondary and tertiary amines do not show this reaction.

13. (b) : The basicity of amines in aqueous solution depends on the stability of the ammonium cation or conjugate acid formed by accepting a proton from water which in turn depends on the + *I*-effect of alkyl group, extent of hydrogen bonding and steric factor. All these factors are favourable for 2° amines. Therefore, 2° amines are the strongest bases. If the alkyl group is small *i.e.*, CH_3 then there is no steric hindrance to H-bonding. Thus, the stability due to hydrogen bonding predominates over the stability due to + *I*-effect of $—CH_3$ group and hence primary amine is a stronger base than 3° amine. Hence, overall decreasing basic strength for methylamines in aqueous solution is

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

14. (a) : Secondary amines on reaction with Hinsberg's reagent gives *N*, *N*-dialkylbenzene sulphonamide which does not contain any hydrogen atom attached to N-atom, it is not acidic and hence, insoluble in alkali. Tertiary amines do not react with Hinsberg's reagent. Primary amines gives products which are soluble in alkali.

15. (d) :



The reason for formation of an unexpected amount of *m*-nitroaniline is that under strongly acidic condition of nitration, most of the aniline is converted into anilinium ion and since, $-\overset{+}{N}H_3$ is a *m*-directing group, therefore, a large amount of *m*-nitroaniline is also obtained.

16. (c) : +*I* effect of substituted group increases the basic strength while –*I* effect of substitutent decreases the basic strength of aniline.

17. (c) : In arylamines, lone pair of electrons on nitrogen atom is delocalised over the benzene ring, thus, not available for donation. So, arylamines are less basic than alkylamines .

18. (a) : $CH_3CH_2CH_2NC + 2H_2O \xrightarrow{H^+} \underset{\text{I}}{CH_3CH_2CH_2NH_2} + \underset{\text{II}}{HCOOH}$

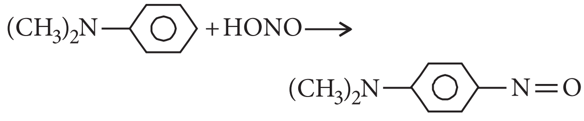
$$CH_3CH_2CH_2NH_2 \xrightarrow{NaNO_2\ +\ HCl} CH_3CH_2CH_2N_2^+Cl^- \xrightarrow{H_2O} CH_3CH_2CH_2OH$$

Does not respond to iodoform test

HCOOH reduces Tollens' reagent and Fehling's solution.

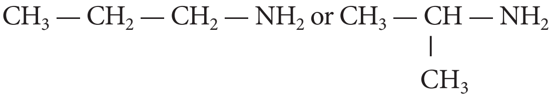
19. (a) : Aromatic tertiary amines undergo electrophilic substitution with nitrosonium ion at *p*-position of the phenyl ring to form green-coloured *p*-nitrosoamines.

$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$



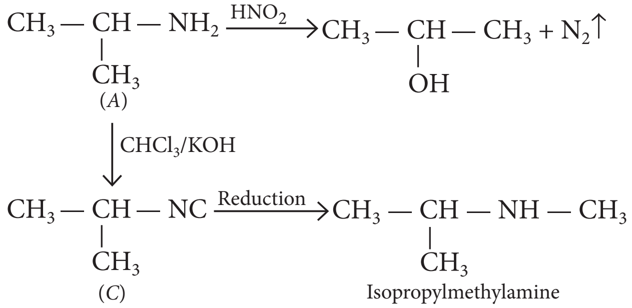
p-Nitro-*N*, *N*-dimethyl aniline (green)

20. (a) : As *A* gives alcohol on treatment with nitrous acid thus, it should be primary amine. C_3H_9N has two possible structures with $–NH_2$ group.



$CH_3—CH_2—CH_2—NH_2$ or $CH_3—\underset{\underset{CH_3}{|}}{CH}—NH_2$

As it gives isopropylmethylamine thus, it should be isopropyl amine not *n*-propyl amine.



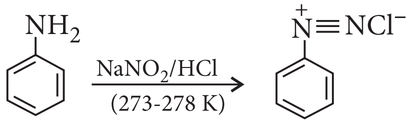
$$\underset{(A)}{CH_3—\underset{\underset{CH_3}{|}}{CH}—NH_2} \xrightarrow{HNO_2} CH_3—\underset{\underset{OH}{|}}{CH}—CH_3 + N_2\uparrow$$

$$\downarrow CHCl_3/KOH$$

$$\underset{(C)}{CH_3—\underset{\underset{CH_3}{|}}{CH}—NC} \xrightarrow{\text{Reduction}} \underset{\text{Isopropylmethylamine}}{CH_3—\underset{\underset{CH_3}{|}}{CH}—NH—CH_3}$$

21. (b) : In benzylamine the electron pair present on the nitrogen is not delocalised with the benzene ring.

22. (c) : Aryl amines react with nitrous acid to produce diazonium salts.



(Diazonium salt)

23. (c) : $\underset{1^\circ\ \text{Amine}}{CH_3CH_2CH_2CH_2NH_2} \xrightarrow[CHCl_3]{KOH(alc)}$

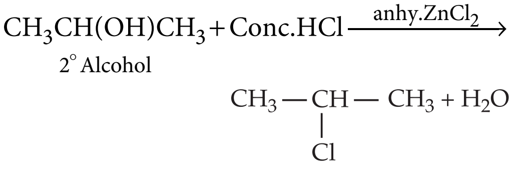
$\underset{\text{Bad smell (isocyanide)}}{CH_3CH_2CH_2CH_2NC} + 3KCl + 3H_2O$

$CH_3C\equiv CH + \text{Amm. } AgNO_3 \longrightarrow$

$\underset{\text{White ppt.}}{CH_3C\equiv\bar{C}Ag^+} + HNO_3$

$CH_3CH_2COOCH_3 + NaOH \xrightarrow{\text{Heat}}$

$CH_3CH_2COONa + CH_3OH$

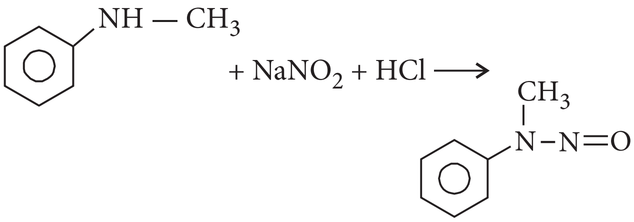


$\underset{2^\circ\ \text{Alcohol}}{CH_3CH(OH)CH_3} + \text{Conc.}HCl \xrightarrow{\text{anhy.}ZnCl_2}$

$CH_3—\underset{\underset{Cl}{|}}{CH}—CH_3 + H_2O$

cloudiness appears in 5 minutes

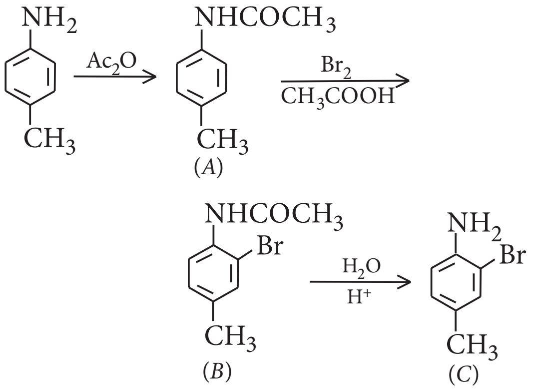
24. (d) : 2° aliphatic and aromatic amines react with nitrous acid to form *N*-nitrosoamine.



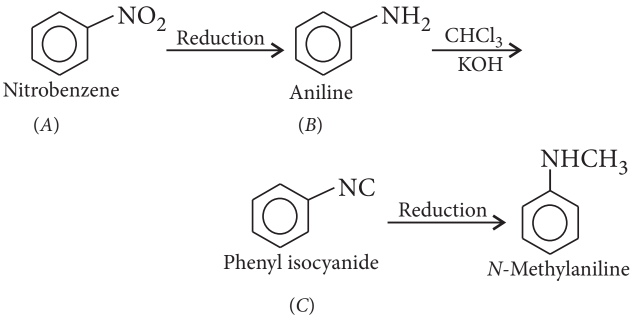
N-nitroso-*N*-methylaniline

25. (a) : Any group which when present on benzene ring has electron withdrawing nature ($-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-Cl$, $-C_6H_5$, etc.) decreases basicity of aniline *e.g.*, aniline is more basic than nitroaniline. Lone pair of electrons are more delocalised in diphenylamine and triphenylamine, thus these are less basic than aniline. In benzylamine the electron pair present on nitrogen is not delocalised with the benzene ring hence, it is more basic than aniline.

26. (c) :



27. (b) : '*C*' must be an isocyanide and it is obtained from a 1° amine by carbylamine reaction ($CHCl_3$ + KOH). Further 1° amine can be obtained by reduction of nitro compound so '*A*' is nitrobenzene.

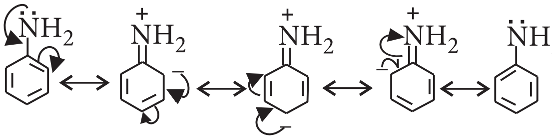


28. (b) : $C_6H_5-NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5-NC + 3KCl + 3H_2O$

The above reaction is called carbylamine reaction, which is a specific reaction of 1°-amine.

29. (c) : $\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$

30. (d) :



As, NO_2^+ electrophile can attack both *ortho* and *para* positions, therefore both (a) and (c) product will be obtained.

31. (c) : $\underset{\text{Primary amine}}{R-NH_2} + \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Alcohol}}{ROH} + N_2 + H_2O$

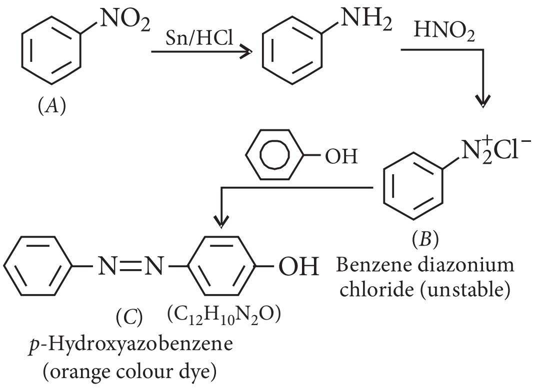
32. (b) : Basic strength decreases as,
cyclohexylamine > aniline > benzamide.
Lesser basicity in aniline and benzamide is due to participation of lone pair of electrons of $-NH_2$ group in resonance.

33. (a) : In carbylamine reaction, primary amines on heating with chloroform in presence of alcoholic KOH form isocyanides (or carbylamines). It is used to distinguish 1° amines from 2° and 3° amines.

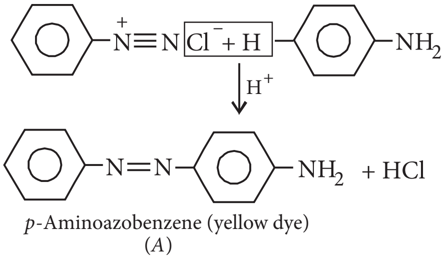
$$R-NH_2 + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \rightarrow RNC + 3KCl + 3H_2O$$

34. (b) : Aromatic diazonium salts are more stable due to dispersal of the positive charge in benzene ring.

35. (b) :

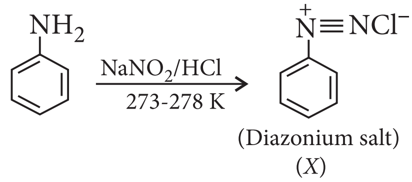


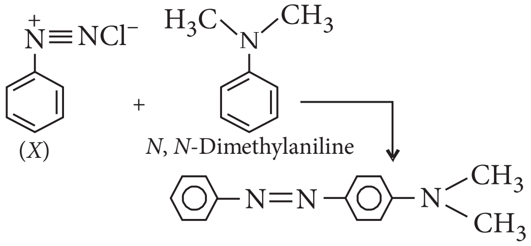
36. (d) :



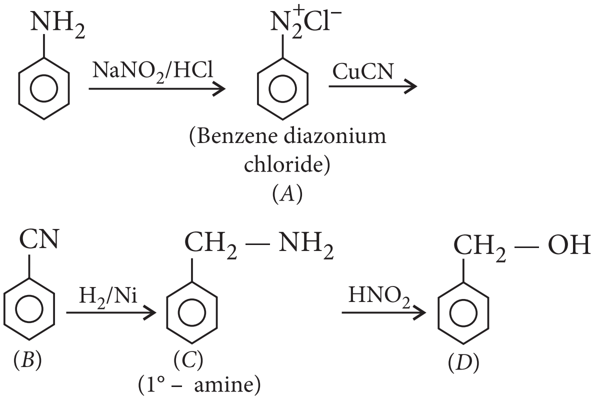
37. (a) : H_3PO_2 and H_2O reduces the $-\overset{+}{N_2}Cl^-$ to –H.

38. (a) :

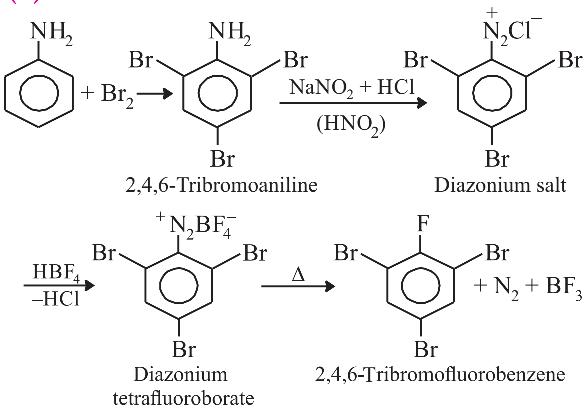




39. (d) :

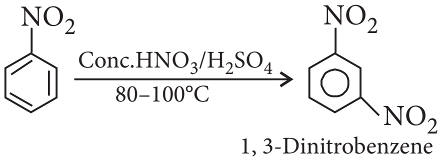


40. (d) :

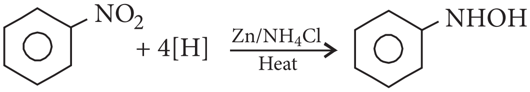


41. (c) : Tertiary nitroalkanes do not react with nitrous acid as they do not contain α-hydrogen atom.

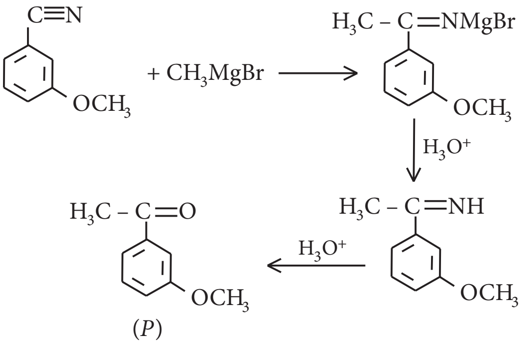
42. (d) :



43. (a) :



44. (b) :



45. (d) : $\underset{\text{Acetonitrile}}{CH_3 - C \equiv N} \xrightarrow[H_2O]{\text{conc. HCl}} \underset{\text{Acetamide}}{CH_3 - CONH_2}$

❖❖❖

CHAPTER 14

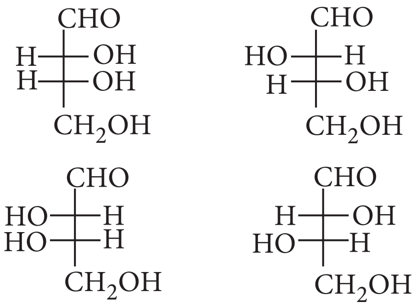
Biomolecules

14.1 Carbohydrates

1. Sucrose on hydrolysis gives
(a) β-*D*-glucose + α-*D*-fructose
(b) α-*D*-glucose + β-*D*-glucose
(c) α-*D*-glucose + β-*D*-fructose
(d) α-*D*-fructose + β-*D*-fructose. *(NEET 2020)*

2. The difference between amylose and amylopectin is
(a) amylopectin have 1 → 4 α-linkage and 1 → 6 α-linkage
(b) amylose have 1 → 4 α-linkage and 1 → 6 β-linkage
(c) amylopectin have 1 → 4 α-linkage and 1 → 6 β-linkage
(d) amylose is made up of glucose and galactose. *(NEET 2018)*

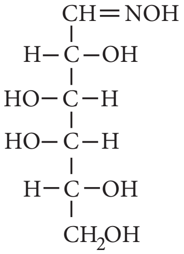
3. The correct corresponding order of names of four aldoses with configuration given below



respectively, is
(a) *L*-erythrose, *L*-threose, *L*-erythrose, *D*-threose
(b) *D*-threose, *D*-erythrose, *L*-threose, *L*-erythrose
(c) *L*-erythrose, *L*-threose, *D*-erythrose, *D*-threose
(d) *D*-erythrose, *D*-threose, *L*-erythrose, *L*-threose. *(NEET-II 2016)*

4. Which one given below is a non-reducing sugar?
(a) Glucose (b) Sucrose
(c) Maltose (d) Lactose *(NEET-I 2016)*

5. *D*(+)-glucose reacts with hydroxyl amine and yields an oxime. The structure of the oxime would be

(a)


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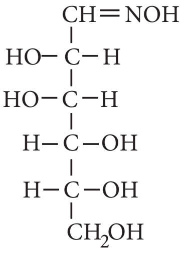
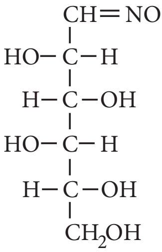
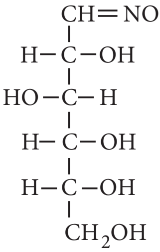


(c)


(d)


(2014)

6. Which one of the following sets of monosaccharides forms sucrose?
(a) α-*D*-galactopyranose and α-*D*-glucopyranose
(b) α-*D*-glucopyranose and β-*D*-fructofuranose
(c) β-*D*-glucopyranose and α-*D*-fructofuranose
(d) α-*D*-glucopyranose and β-*D*-fructopyranose *(2012)*

7. Which one of the following statements is not true regarding (+)–lactose?
(a) On hydrolysis (+)–lactose gives equal amount of *D*(+)–glucose and *D*(+)–galactose.
(b) (+)–Lactose is a β-glucoside formed by the union of a molecule of *D*(+)–glucose and a molecule of *D*(+)–galactose.
(c) (+)–Lactose is a reducing sugar and does not exhibit mutarotation.
(d) (+)–Lactose, $C_{12}H_{22}O_{11}$ contains 8 –OH groups. *(2011)*

8. Which one of the following does not exhibit the phenomenon of mutarotation?
(a) (+)–Sucrose (b) (+)–Lactose
(c) (+)–Maltose (d) (–)–Fructose *(2010)*

9. Fructose reduces Tollens' reagent due to
(a) asymmetric carbons
(b) primary alcoholic group
(c) secondary alcoholic group
(d) enolisation of fructose followed by conversion to aldehyde by base. *(Mains 2010)*

10. Number of chiral carbons in β-*D*-(+) glucose is
(a) five (b) six
(c) three (d) four. *(2004)*

11. Glycolysis is
(a) oxidation of glucose to glutamate
(b) conversion of pyruvate to citrate
(c) oxidation of glucose to pyruvate
(d) conversion of glucose to haem. *(2003)*

12. Cellulose is polymer of
(a) glucose (b) fructose
(c) ribose (d) sucrose. *(2002)*

13. Which of the following gives positive Fehling solution test?
(a) Sucrose (b) Glucose
(c) Fats (d) Protein *(2001)*

14. α-*D*-glucose and β-*D*-glucose are
(a) epimers (b) anomers
(c) enantiomers (d) diastereomers. *(2000)*

15. Which of the following is the sweetest sugar?
(a) Fructose (b) Glucose
(c) Sucrose (d) Maltose *(1999)*

16. Glucose molecule reacts with X number of molecules of phenyl hydrazine to yield osazone. The value of X is
(a) two (b) one
(c) four (d) three. *(1998)*

17. The oxidation of glucose is one of the most important reactions in a living cell. What is the number of ATP molecules generated in cells from one molecule of glucose?
(a) 28 (b) 38
(c) 12 (d) 18 *(1995)*

18. The α-*D*-glucose and β-*D*-glucose differ from each other due to difference in carbon atom with respect to its
(a) number of OH groups
(b) size of hemiacetal ring
(c) conformation
(d) configuration. *(1995)*

19. Chemically considering digestion is basically
(a) anabolism
(b) hydrogenation
(c) hydrolysis
(d) dehydrogenation. *(1994)*

20. On hydrolysis of starch, we finally get
(a) glucose (b) fructose
(c) both (a) and (b) (d) sucrose. *(1991)*

14.2 Proteins

21. Which of the following is a basic amino acid?
(a) Serine (b) Alanine
(c) Tyrosine (d) Lysine *(NEET 2020)*

22. The non-essential amino acid among the following is
(a) lysine (b) valine
(c) leucine (d) alanine.
(NEET 2019)

23. Which structure(s) of proteins remain(s) intact during denaturation process?
(a) Both secondary and tertiary structures
(b) Primary structure only
(c) Secondary structure only
(d) Tertiary structure only *(Odisha NEET 2019)*

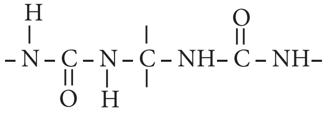
24. Which of the following compounds can form a zwitter ion?
(a) Aniline (b) Acetanilide
(c) Benzoic acid (d) Glycine
(NEET 2018)

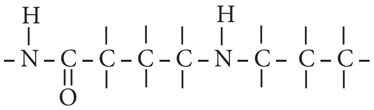
25. In a protein molecule various amino acids are linked together by
(a) peptide bond
(b) dative bond
(c) α-glycosidic bond
(d) β-glycosidic bond. *(NEET-I 2016)*

26. Which of the statements about "Denaturation" given below are correct?
(1) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
(2) Denaturation leads to the conversion of double strand of DNA into single strand.
(3) Denaturation affects primary structure which gets distorted.
(a) (2) and (3) (b) (1) and (3)
(c) (1) and (2) (d) (1), (2) and (3)
(Mains 2011)

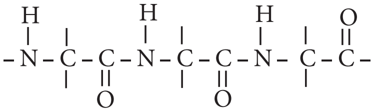
27. Which functional group participates in disulphide bond formation in proteins?
(a) Thioester (b) Thioether
(c) Thiol (d) Thiolactone *(2005)*

28. Which of the following structures represents the peptide chain?

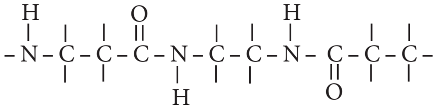
(a) 
$-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{||}{C}}-\underset{H}{\underset{|}{N}}-\overset{|}{\underset{|}{C}}-NH-\overset{O}{\overset{||}{C}}-NH-$

(b) 

$-\overset{\text{H}}{\overset{|}{\text{N}}}-\underset{\overset{\|}{\text{O}}}{\text{C}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-$

(c) 

$-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{|}{\underset{|}{\text{C}}}-\underset{\overset{\|}{\text{O}}}{\text{C}}-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{|}{\underset{|}{\text{C}}}-\underset{\overset{\|}{\text{O}}}{\text{C}}-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-$

(d) 

$-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\underset{\underset{\text{H}}{|}}{\text{N}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{\text{H}}{\overset{|}{\text{N}}}-\underset{\overset{\|}{\text{O}}}{\text{C}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-$

(2004)

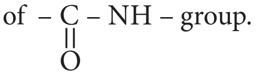
29. The correct statement in respect of protein haemoglobin is that it
(a) functions as a catalyst for biological reactions
(b) maintains blood sugar level
(c) acts as an oxygen carrier in the blood
(d) forms antibodies and offers resistance to diseases. *(2004)*

30. The helical structure of protein is stabilised by
(a) dipeptide bonds (b) hydrogen bonds
(c) ether bonds (d) peptide bonds. *(2004)*

31. Which is not true statement?
(a) α-Carbon of α-amino acid is asymmetric.
(b) All proteins are found in *L*-form.
(c) Human body can synthesise all proteins they need.
(d) At pH = 7 both amino and carboxylic groups exist in ionised form. *(2002)*

32. 

$-\overset{\text{O}}{\overset{\|}{\text{C}}}-\ddot{\text{N}}\text{H}-$ (peptide bond).

Which statement is incorrect about peptide bond?
(a) C – N bond length in proteins is longer than usual bond length of N – C bond.
(b) Spectroscopic analysis shows planar structure of  $-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{NH}-$ group.
(c) C – N bond length in proteins is smaller than usual bond length of C – N bond.
(d) None of the above. *(2001)*

33. Which is the correct statement?
(a) Starch is a polymer of α-glucose.
(b) Amylose is a component of cellulose.
(c) Proteins are composed of only one type of amino acid.
(d) In cyclic structure of fructose, there are four carbons and one oxygen atom. *(2001)*

34. Haemoglobin is
(a) a vitamin (b) a carbohydrate
(c) an enzyme (d) a globular protein. *(1997)*

35. The secondary structure of a protein refers to
(a) regular folding patterns of continuous portions of the polypeptide chain
(b) three-dimensional structure, specially the bond between amino acid residues that are distant from each other in the polypeptide chain
(c) mainly denatured proteins and structures of prosthetic groups
(d) linear sequence of amino acid residues in the polypeptide chain. *(1995)*

14.3 Enzymes

36. During the process of digestion, the proteins present in food materials are hydrolysed to amino acids. The two enzymes involved in the process

$$\text{proteins} \xrightarrow{\text{enzyme } (A)} \text{polypeptides} \xrightarrow{\text{enzyme } (B)} \text{amino acids,}$$

are respectively
(a) invertase and zymase
(b) amylase and maltase
(c) diastase and lipase
(d) pepsin and trypsin. *(2006)*

37. Enzymes are made up of
(a) edible proteins
(b) proteins with specific structure
(c) nitrogen containing carbohydrates
(d) carbohydrates. *(2002)*

38. Which of the following is correct?
(a) Cycloheptane is an aromatic compound.
(b) Diastase is an enzyme.
(c) Acetophenone is an ether.
(d) All of these. *(2001)*

39. The function of enzymes in the living system is to
(a) catalyse biochemical reactions
(b) provide energy
(c) transport oxygen
(d) provide immunity. *(1997)*

40. Which of the following statements about enzymes is true?
(a) Enzymes catalyse chemical reactions by increasing the activation energy.
(b) Enzymes are highly specific both in binding chiral substrates and in catalysing their reactions.
(c) Enzymes lack in nucleophilic groups.
(d) Pepsin is proteolytic enzyme. *(1995)*

41. Enzymes take part in a reaction and
(a) decrease the rate of a chemical reaction
(b) increase the rate of a chemical reaction
(c) both (a) and (b)
(d) none of these. *(1993)*

14.4 Vitamins

42. Deficiency of vitamin B_1 causes the disease
(a) convulsions (b) beri-beri
(c) cheilosis (d) sterility. *(2012)*

43. Which of the following is not a fat soluble vitamin?
(a) Vitamin B complex
(b) Vitamin D
(c) Vitamin E
(d) Vitamin A *(Mains 2011)*

44. Which of the following vitamins is water soluble?
(a) Vitamin E (b) Vitamin K
(c) Vitamin A (d) Vitamin B *(2007)*

45. The human body does not produce
(a) enzymes (b) DNA
(c) vitamins (d) hormones. *(2006)*

46. Vitamin B_{12} contains
(a) Fe (II) (b) Co (III)
(c) Zn (II) (d) Ca (II) *(2003)*

14.5 Nucleic Acids

47. The central dogma of molecular genetics states that the genetic information flows from
(a) Amino acids $\rightarrow$ Proteins $\rightarrow$ DNA
(b) DNA $\rightarrow$ Carbohydrates $\rightarrow$ Proteins
(c) DNA $\rightarrow$ RNA $\rightarrow$ Proteins
(d) DNA $\rightarrow$ RNA $\rightarrow$ Carbohydrates
(NEET-II 2016)

48. The correct statement regarding RNA and DNA, respectively is
(a) the sugar component in RNA is a arabinose and the sugar component in DNA is ribose
(b) the sugar component in RNA is 2′-deoxyribose and the sugar component in DNA is arabinose
(c) the sugar component in RNA is arabinose and the sugar component in DNA is 2′-deoxyribose
(d) the sugar component in RNA is ribose and the sugar component in DNA is 2′-deoxyribose. *(NEET-I 2016)*

49. In DNA, the linkages between different nitrogenous bases are
(a) phosphate linkage
(b) H-bonding
(c) glycosidic linkage
(d) peptide linkage. *(Karnataka NEET 2013)*

50. The segment of DNA which acts as the instrumental manual for the synthesis of the protein is
(a) ribose (b) gene
(c) nucleoside (d) nucleotide. *(2009)*

51. In DNA, the complimentary bases are
(a) adenine and guanine; thymine and cytosine
(b) uracil and adenine; cytosine and guanine
(c) adenine and thymine; guanine and cytosine
(d) adenine and thymine; guanine and uracil.
(2008, 1998)

52. RNA and DNA are chiral molecules, their chirality is due to
(a) chiral bases
(b) chiral phosphate ester units
(c) *D*-sugar component
(d) *L*-sugar component. *(2007)*

53. A sequence of how many nucleotides in messenger RNA makes a codon for an amino acid?
(a) Three (b) Four
(c) One (d) Two *(2004)*

54. Chargaff's rule states that in an organism
(a) amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C)
(b) amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C)
(c) amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G)
(d) amounts of all bases are equal. *(2003)*

55. Which of the following is correct about H-bonding in nucleotide?
(a) A – T, G – C (b) A – G , T – C
(c) G – T, A – C (d) A – A, T – T
(2001)

56. An example of biopolymer is
(a) teflon (b) neoprene
(c) nylon-6, 6 (d) DNA. *(1994)*

57. The couplings between base units of DNA is through
(a) hydrogen bonding
(b) electrostatic bonding
(c) covalent bonding
(d) van der Waals' forces. *(1992)*

14.6 Hormones

58. Which of the following statements is not correct?
(a) Ovalbumin is a simple food reserve in egg-white.
(b) Blood proteins thrombin and fibrinogen are involved in blood clotting.
(c) Denaturation makes the proteins more active.
(d) Insulin maintains sugar level in the blood of a human body. *(NEET 2017)*

59. Which of the following hormones is produced under the conditions of stress which stimulate glycogenolysis in the liver of human beings?
(a) Thyroxin (b) Insulin
(c) Adrenaline (d) Estradiol *(2014)*

60. Which of the following hormones contains iodine?
(a) Testosterone (b) Adrenaline
(c) Thyroxine (d) Insulin *(2009)*

61. Which of the following is an amine hormone?
(a) Insulin (b) Progesterone
(c) Thyroxine (d) Oxypurin *(2008)*

62. Which one of the following is a peptide hormone?
(a) Adrenaline (b) Glucagon
(c) Testosterone (d) Thyroxine *(2006)*

63. The hormone that helps in the conversion of glucose to glycogen is
(a) cortisone (b) bile acids
(c) adrenaline (d) insulin. *(2004)*

64. Which one is responsible for production of energy in biochemical reaction?
(a) Thyroxine (b) Adrenaline
(c) Oestrogen (d) Progesterone *(2000)*

14.A Lipids

65. The cell membranes are mainly composed of
(a) fats (b) proteins
(c) phospholipids
(d) carbohydrates. *(2005)*

66. Phospholipids are esters of glycerol with
(a) three carboxylic acid residues
(b) two carboxylic acid residues and one phosphate group
(c) one carboxylic acid residue and two phosphate groups
(d) three phosphate groups. *(2003)*

67. The number of molecules of ATP produced in the lipid metabolism of a molecule of palmitic acid is
(a) 56 (b) 36
(c) 130 (d) 86 *(1998)*

ANSWER KEY

1.	(c)	**2.**	(a)	**3.**	(d)	**4.**	(b)	**5.**	(d)	**6.**	(b)	**7.**	(c)	**8.**	(a)	**9.**	(d)	**10.**	(d)
11.	(c)	**12.**	(a)	**13.**	(b)	**14.**	(b)	**15.**	(a)	**16.**	(d)	**17.**	(b)	**18.**	(d)	**19.**	(c)	**20.**	(a)
21.	(d)	**22.**	(d)	**23.**	(b)	**24.**	(d)	**25.**	(a)	**26.**	(c)	**27.**	(c)	**28.**	(c)	**29.**	(c)	**30.**	(b)
31.	(b)	**32.**	(a)	**33.**	(a)	**34.**	(d)	**35.**	(a)	**36.**	(d)	**37.**	(b)	**38.**	(b)	**39.**	(a)	**40.**	(b)
41.	(b)	**42.**	(b)	**43.**	(a)	**44.**	(d)	**45.**	(c)	**46.**	(b)	**47.**	(c)	**48.**	(d)	**49.**	(b)	**50.**	(b)
51.	(c)	**52.**	(c)	**53.**	(a)	**54.**	(a)	**55.**	(a)	**56.**	(d)	**57.**	(a)	**58.**	(c)	**59.**	(c)	**60.**	(c)
61.	(c)	**62.**	(b)	**63.**	(d)	**64.**	(a)	**65.**	(c)	**66.**	(b)	**67.**	(c)						

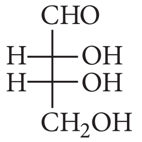
Hints & Explanations

1. (c) : In sucrose, two monosaccharides are held together by a glycosidic linkage between C-1 of α-*D*-glucose and C-2 of β-*D*-fructose.

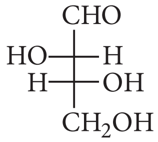
$$\text{Sucrose} \xrightarrow{\text{Hydrolysis}} \alpha\text{-}D\text{-glucose} + \beta\text{-}D\text{-fructose}$$

2. (a) : Amylose is a linear polymer of α-*D*-glucose held by C_1-C_4 glycosidic linkage whereas amylopectin is branched chain polymer of α-*D*-glucose units in which chain is held by C_1-C_4 glycosidic linkage while branching occurs by C_1-C_6 glycosidic linkage.

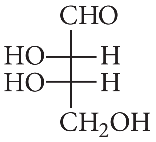
3. (d) :



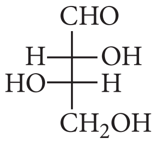
D-erythrose



D-threose



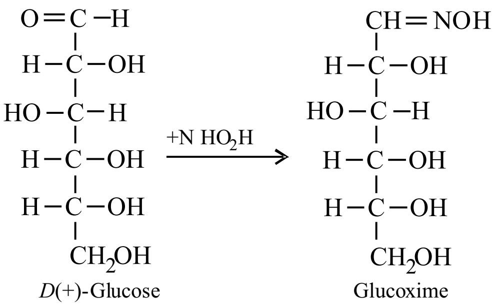
L-erythrose



L-threose

4. (b) : All monosaccharides whether aldoses or ketoses are reducing sugars. Disaccharides such as sucrose in which the two monosaccharide units are linked through their reducing centres *i.e.,* aldehydic or ketonic groups are non-reducing.

5. (d) :



6. (b) : Sucrose is formed by the condensation of α-*D*-glucopyranose and β-*D*-fructofuranose.

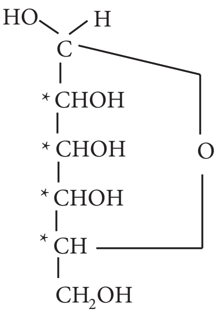
7. (c) : (+)-Lactose is a reducing sugar and all reducing sugars show mutarotation.

8. (a) : Sucrose does not show mutarotation.

Mutarotation is the phenomenon of change in optical rotation shown by freshly prepared solutions of sugars. However, this property is not exhibited by all sugars. Only those sugars which have a free aldehyde (—CHO) or ketone (>C ═ O) group are capable of showing mutarotation. Sucrose lacks free aldehyde or ketone group and is therefore, incapable of showing mutarotation.

9. (d) : Under alkaline conditions of the reagent, fructose gets converted into a mixture of glucose and mannose (Lobry de Bruyn van Ekenstein rearrangement) both of which contain the –CHO group and hence, reduce Tollens' reagent to give silver mirror test.

10. (d) :



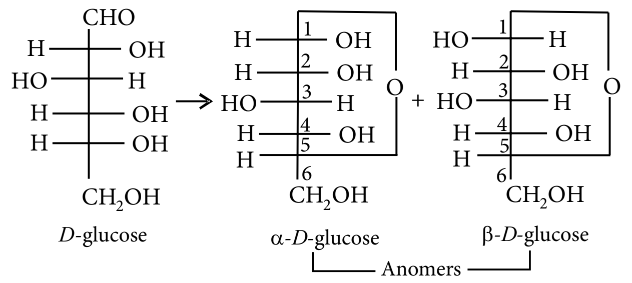
This structure of β-*D*-glucose has four asymmetric carbon atoms.

11. (c) : Glycolysis is the first stage in the oxidation of glucose. It is an anaerobic process and involves the degradation of glucose into two molecules of pyruvate with the generation of two molecules of ATP.

12. (a) : Cellulose is a straight chain polysaccharide composed of β-*D*-glucose units joined by β-glycosidic linkage between C_1 of one glucose unit and C_4 of the next glucose unit.

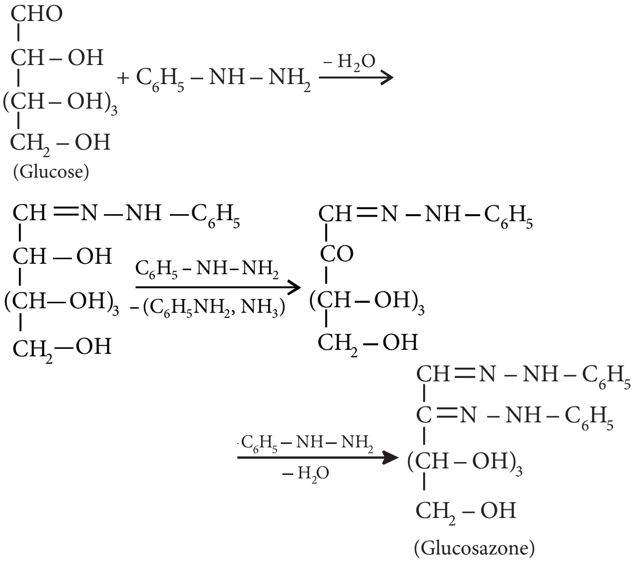
13. (b) : Glucose reduces Fehling solution because glucose has free –CHO group which is readily oxidised.

14. (b) : Glucose forms a stable hemiacetal between the —CHO group and the —OH group on the 5th carbon. In this process, the 1st 'C' atom becomes asymmetric giving two isomers which differ in the configuration of the asymmetric carbon. These two isomers are called as anomers.



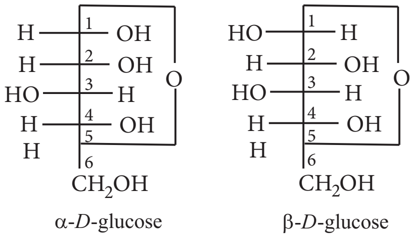
15. (a) : Fructose is the sweetest among all the sugars and is highly soluble in water.

16. (d) : Glucose first reacts with phenyl hydrazine giving phenylhydrazone. Then the adjacent —CHOH group is oxidized by a 2nd phenyl hydrazine molecule and itself is reduced to aniline. The resulting carbonyl group reacts with 3rd phenyl hydrazine molecule giving osazone.



17. (b) : $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 38ATP$

18. (d) :



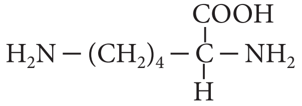
These isomers differ only in the orientation (or configuration) at C1 atom.

19. (c)

20. (a) : Glucose is produced commercially by the hydrolysis of starch by boiling it with dil. H_2SO_4 at 393 K under pressure of 2-3 bar.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{393 K, 2-3 bar}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

21. (d) : Lysine is a basic amino acid.



$$H_2N-(CH_2)_4-\underset{\displaystyle H}{\overset{\displaystyle COOH}{C}}-NH_2$$

22. (d)

23. (b) : During denaturation of proteins, 2° and 3° structures are destroyed but 1° structure remains intact.

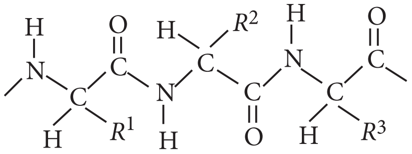
24. (d) : $\underset{\text{Glycine}}{HOOC-CH_2-NH_2} \rightleftharpoons \underset{\text{Zwitter ion}}{{}^-OOC-CH_2-\overset{+}{N}H_3}$

25. (a)

26. (c) : Denaturation does not change the primary structure of protein.

27. (c) : Disulphide bond may be reduced to thiol by means of reagents *i.e.*, $NaBH_4$, which shows the presence of thiol group in disulphide bond formation.

28. (c) : In peptide linkage *i.e.*, – CONH – group, the carboxyl group of one amino acid molecule forms an amide by combination with the amino group of the next amino acid molecule with the liberation of water molecule.

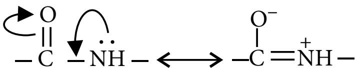


29. (c) : Four Fe^{2+} ions of each haemoglobin can bind with four molecules of O_2 and it is carried as oxyhaemoglobin.

30. (b) : α-Helix structure is formed when the chain of α-amino acids coil as a right handed screw because of the formation of hydrogen bonds between amide groups of the same peptide chain, *i.e.*, NH group in one unit is linked to carbonyl oxygen of the fourth unit by hydrogen bonding. This H-bonding is responsible for holding helix in a stable position.

31. (b) : Some proteins are also found in *D*-form.

32. (a) : Peptide bond is formed by the reaction of —COOH group of one amino acid with the —NH_2 group of another amino acid and represented as



As some double bond character is found between C – N bond, the bond length of C–N in protein should be smaller than the usual C–N bond.

33. (a) : Starch is also known as amylum which occurs in all green plants. A molecule of starch $(C_6H_{10}O_5)_n$ is built of a large number of α-glucose rings joined through oxygen atoms.

34. (d) : Haemoglobin is a globular protein of four subunits, each subunit having a heme moiety and a polypeptide chain (Two α and two β chains).

35. (a)

36. (d) : Proteins $\xrightarrow[\text{proteases}]{\text{pepsin}}$ Polypeptides $\xrightarrow[\text{chemotrypsin}]{\text{trypsin}}$ Amino acids

37. (b)

38. (b) : Diastase is an enzyme that hydrolyses starch into maltose.

39. (a) **40. (b)**

41. (b) : Enzymes being biocatalyst increases the rate of a chemical reaction by providing alternative lower activation energy pathways.

42. (b) :

Deficiency disease	**Vitamin**
Convulsions	B_6
Beri-beri	B_1
Cheilosis	B_2
Sterility	E

43. (a) : Vitamin B complex is not a fat soluble vitamin. It is a water soluble vitamin.

44. (d) : Vitamin B and C are water soluble whereas vitamin A, D, E and K are fat soluble.

45. (c) : Certain organic substances required for regulating some of the body processes and preventing certain diseases are called vitamins, which cannot be synthesised by human body.

46. (b) : Vitamin B_{12} is chemically named as cyanocobalamine having molecular formula $C_{63}H_{88}O_{14}N_{14}PCo$.

47. (c) : Genetic information flows from

DNA $\xrightarrow{\text{Transcription}}$ RNA $\xrightarrow{\text{Translation}}$ Proteins

48. (d)

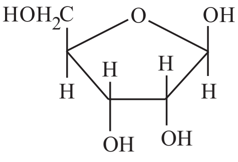
49. (b) : Nitrogeneous bases are linked together by hydrogen bonds.

50. (b) : Genes are responsible for protein synthesis.

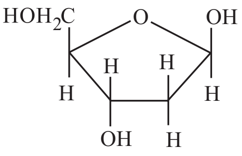
51. (c) : DNA contains two types of nitrogeneous bases Purine → Adenine (A) and guanine (G)

Pyrimidine → Cytosine (C) and thymine (T)
The purine and pyrimidine bases pair only in certain combination. Adenine pairs with thymine (A : T) by two hydrogen bonds and guanine with cytosine (G : C) by three hydrogen bonds.

52. (c) : The constituents of nucleic acids are nitrogenous bases, sugar and phosphoric acid. The sugar present in DNA is *D*(–)-2-deoxyribose and the sugar present in RNA is *D*(–)-ribose. Due to these *D*(–)-sugar components, DNA and RNA molecules are chiral molecules.



β-*D*(–)-ribose



β-*D*(–)-2-deoxyribose

53. (a) : The four bases in *m*RNA : adenine, cytosine, guanine and uracil have been shown to act in the form of triplets; each triplet behaving as a code for the synthesis of a particular amino acid.

54. (a) : Amount of A = T and that of G = C.

55. (a)

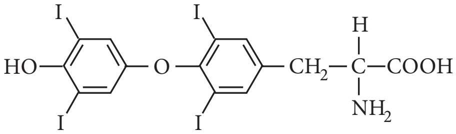
56. (d) : DNA is an example of biopolymer.

57. (a)

58. (c) : Denaturation changes the structure of a protein and protein loses its activity.

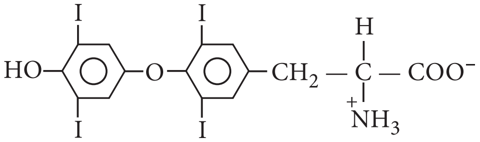
59. (c) : Adrenaline hormone helps to release fatty acids from fat and glucose from liver glycogen under the condition of stress. Hence, it is also called 'flight or fight hormone'.

60. (c) :



Thyroxine

61. (c) : Thyroxine is an amine hormone and water soluble hormone containing amino group.



Thyroxine

62. (b) : Glucagon is a peptide hormone, synthesised by the α-cells of the pancreas.

63. (d) : Insulin is a hormone secreted by the pancreas that lowers blood glucose level by promoting the uptake of glucose by cells and the conversion of glucose to glycogen by the liver and skeletal muscle.

64. (a) : It is a hormone secreted from thyroid gland. It controls various biochemical reactions involving burning of proteins, carbohydrates, fats to release energy.

65. (c) : Cell membranes are mainly composed of phospholipids.

66. (b) : Phospholipids may be regarded as derivatives of glycerol in which two of the hydroxyl groups are esterified with fatty acids while the third is esterified with some derivatives of phosphoric acid.

67. (c) : In the lipid metabolism, a molecule of palmitic acid ($C_{15}H_{31}$ – COOH) produces 130 adenosine triphosphate molecules (ATP).

❖❖❖

CHAPTER
15

Polymers

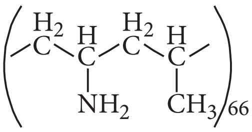
15.2 Types of Polymerisation Reactions

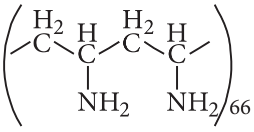
1. Which of the following is a natural polymer?
(a) *cis*-1, 4-polyisoprene
(b) poly (Butadiene-styrene)
(c) polybutadiene
(d) poly (Butadiene-acrylonitrile) *(NEET 2020)*

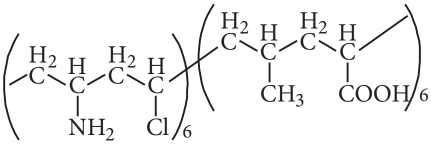
2. The polymer that is used as a substitute for wool in making commercial fibres is
(a) melamine (b) nylon-6, 6
(c) polyacrylonitrile (d) buna-N.
(Odisha NEET 2019)

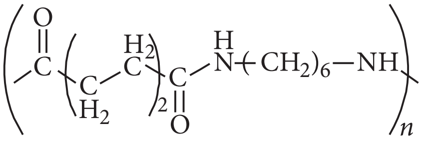
3. Regarding cross-linked or network polymers, which of the following statements is incorrect?
(a) They contain covalent bonds between various linear polymer chains.
(b) They are formed from bi- and tri-functional monomers.
(c) Examples are bakelite and melamine.
(d) They contain strong covalent bonds in their polymer chains. *(NEET 2018)*

4. Which one of the following structures represents nylon 6, 6 polymer?

(a)


(b)


(c)


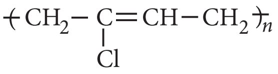
(d)


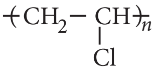
(NEET-II 2016)

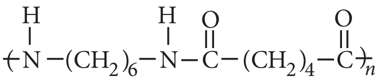
5. Natural rubber has
(a) alternate *cis*- and *trans*-configuration
(b) random *cis*- and *trans*-configuration
(c) all *cis*-configuration
(d) all *trans*-configuration. *(NEET-I 2016)*

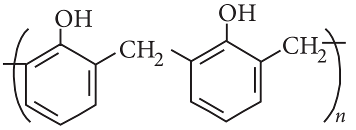
6. Caprolactam is used for the manufacture of
(a) teflon (b) terylene
(c) nylon 6, 6 (d) nylon 6. *(2015)*

7. Which one of the following is an example of thermosetting polymer?

(a)

$\left(CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2\right)_n$

(b)

$\left(CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}\right)_n$

(c)

$\left(\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_6-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{||}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{||}{C}}\right)_n$

(d)


(2014)

8. Which of the following organic compounds polymerizes to form the polyester dacron?
(a) Propylene and *para* HO—(C_6H_4)—OH
(b) Benzoic acid and ethanol
(c) Terephthalic acid and ethylene glycol
(d) Benzoic acid and *para* HO—(C_6H_4)—OH
(2014)

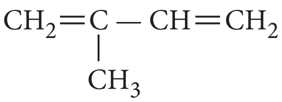
9. Nylon is an example of
(a) polyamide (b) polythene
(c) polyester (d) polysaccharide.
(NEET 2013)

10. Which is the monomer of neoprene in the following?

(a) 
$CH_2=\underset{Cl}{\underset{|}{C}}-CH=CH_2$

(b) $CH_2=CH-C\equiv CH$

(c) $CH_2=CH-CH=CH_2$

(d) 
$CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH_2$ *(NEET 2013, 2003)*

11. Which one of the following is not a condensation polymer?

(a) Melamine (b) Glyptal

(c) Dacron (d) Neoprene *(2012)*

12. Which of the following statements is false?

(a) Artificial silk is derived from cellulose.

(b) Nylon-6,6 is an example of elastomer.

(c) The repeat unit in natural rubber is isoprene.

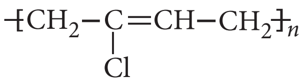
(d) Both starch and cellulose are polymers of glucose. *(2012)*

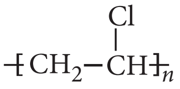
13. Of the following which one is classified as polyester polymer?

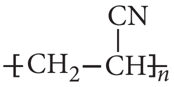
(a) Terylene (b) Bakelite

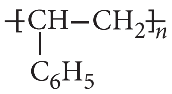
(c) Melamine (d) Nylon-6,6 *(2011)*

14. Which of the following structures represents neoprene polymer?

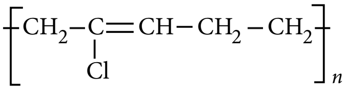
(a) 
$\left[CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2\right]_n$

(b) 
$\left[CH_2-\overset{Cl}{\overset{|}{CH}}\right]_n$

(c) 
$\left[CH_2-\overset{CN}{\overset{|}{CH}}\right]_n$

(d) 
$\left[\underset{C_6H_5}{\underset{|}{CH}}-CH_2\right]_n$ *(2010)*

15. Structures of some common polymers are given. Which one is not correctly presented?

(a) Neoprene- 
$\left[CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2-CH_2\right]_n$

(b) Terylene - 

(c) Nylon 6,6 - $\left[NH(CH_2)_6NHCO(CH_2)_4-CO\right]_n$

(d) Teflon - $\left[CF_2-CF_2\right]_n$ *(2009)*

16. Which one of the following statements is not true?

(a) Buna-S is a copolymer of butadiene and styrene.

(b) Natural rubber is a 1,4-polymer of isoprene.

(c) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.

(d) Natural rubber has the *trans*-configuration at every double bond. *(2008)*

17. Which one of the following polymers is prepared by condensation polymerisation?

(a) Teflon (b) Natural rubber

(c) Styrene (d) Nylon-6,6 *(2007)*

18. $\sim\!\!\sim\left[NH(CH_2)_6NHCO(CH_2)_4CO\right]_n\sim\!\!\sim$ is a

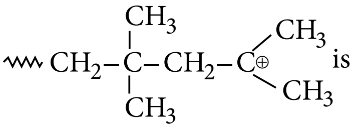
(a) homopolymer

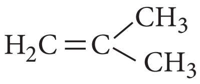
(b) copolymer

(c) addition polymer

(d) thermosetting polymer. *(2006)*

19. The monomer of the polymer


$\sim\!\!\sim CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-\overset{\oplus}{C}\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$ is

(a) 
$H_2C=C\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$

(b) $CH_3CH=CHCH_3$

(c) $CH_3CH=CH_2$

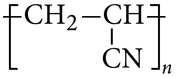
(d) $(CH_3)_2C=C(CH_3)_2$ *(2005)*

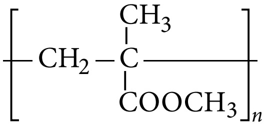
20. Which one of the following is a chain growth polymer?

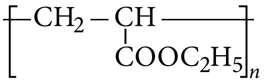
(a) Starch (b) Nucleic acid

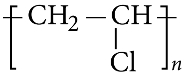
(c) Polystyrene (d) Protein *(2004)*

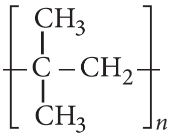
21. Acrilan is a hard, horny and a high melting material. Which one of the following represents its structure?

(a) 
$\left[CH_2-\underset{CN}{\underset{|}{CH}}\right]_n$

(b) 
$\left[CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}\right]_n$

(c) 
$\left[CH_2-\underset{COOC_2H_5}{\underset{|}{CH}}\right]_n$

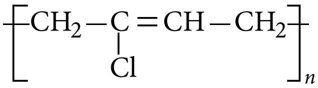
(d) 
$\left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_n$ *(2003)*

22. Monomer of  $\left[-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\right]_n$ is

(a) 2-methylpropene (b) styrene
(c) propylene (d) ethene. *(2002)*

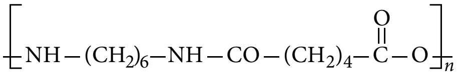
23. Which of the following is not correctly matched?

(a) Neoprene :



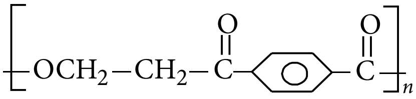
$\left[-CH_2-\underset{Cl}{C}=CH-CH_2-\right]_n$

(b) Nylon-6,6 :

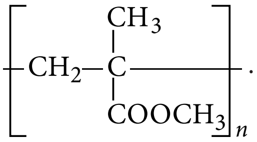


$\left[-NH-(CH_2)_6-NH-CO-(CH_2)_4-\overset{O}{\overset{||}{C}}-O-\right]_n$

(c) Terylene :



(d) PMMA :



$\left[-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-\right]_n$. *(2001)*

24. $CF_2=CF_2$ is monomer of

(a) teflon (b) orlon
(c) polythene (d) nylon-6. *(2000)*

25. Which compound forms linear polymer due to H-bond?

(a) H_2O (b) NH_3
(c) HF (d) HCl *(2000)*

26. Natural rubber is a polymer of

(a) styrene (b) ethyne
(c) butadiene (d) isoprene. *(1999)*

27. Terylene is a condensation polymer of ethylene glycol and

(a) salicylic acid
(b) phthalic acid
(c) benzoic acid
(d) terephthalic acid. *(1999)*

28. Which one of the following is used to make 'non-stick' cookware?

(a) Polyethylene terephthalate
(b) Polytetrafluoroethylene
(c) PVC
(d) Polystyrene *(1997)*

29. The bakelite is prepared by the reaction between

(a) phenol and formaldehyde
(b) tetramethylene glycol
(c) urea and formaldehyde
(d) ethylene glycol. *(1995)*

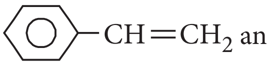
15.4 Biodegradable Polymers

30. The biodegradable polymer is

(a) buna-S (b) nylon-6,6
(c) nylon-2-nylon 6 (d) nylon-6. *(NEET 2019)*

31. Which one of the following sets forms the biodegradable polymer?

(a) $CH_2=CH-CN$ and
$CH_2=CH-CH=CH_2$
(b) H_2N-CH_2-COOH
and $H_2N-(CH_2)_5-COOH$
(c) $HO-CH_2-CH_2-OH$ and

(d)  and
$CH_2=CH-CH=CH_2$ *(Mains 2012)*

ANSWER KEY

1.	(a)	**2.**	(c)	**3.**	(d)	**4.**	(d)	**5.**	(c)	**6.**	(d)	**7.**	(d)	**8.**	(c)	**9.**	(a)	**10.**	(a)
11.	(d)	**12.**	(b)	**13.**	(a)	**14.**	(a)	**15.**	(a)	**16.**	(d)	**17.**	(d)	**18.**	(b)	**19.**	(a)	**20.**	(c)
21.	(a)	**22.**	(a)	**23.**	(c)	**24.**	(a)	**25.**	(c)	**26.**	(d)	**27.**	(d)	**28.**	(b)	**29.**	(a)	**30.**	(c)
31.	(b)																		

Hints & Explanations

1. **(a) :** *cis*-1, 4-polyisoprene is a natural rubber.

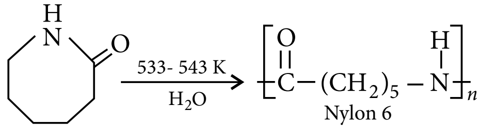
2. **(c)**

3. **(d) :** Cross-linked or network polymers are usually formed from bi-functional and tri-functional monomers and contains strong covalent bonds between various linear polymer chains like melamine, bakelite, etc.

4. **(d) :** Nylon 6,6 is obtained by condensing adipic acid ($HOOC(CH_2)_4COOH$) with hexamethylenediamine ($H_2N(CH_2)_6NH_2$).

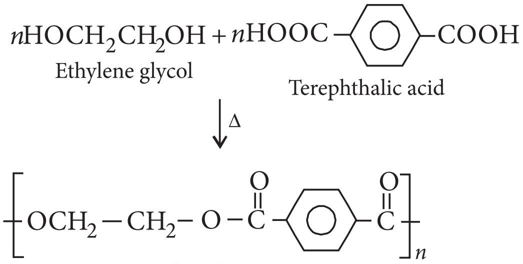
5. **(c) :** Natural rubber is *cis*-polyisoprene.

6. **(d) :**



7. **(d) :** (a) Neoprene rubber (elastomer)
(b) PVC (thermoplastic polymer)
(c) Nylon-6,6 (fibre)
(d) Novolac which further undergoes cross linking to produce bakelite (thermosetting polymer).

8. **(c) :**

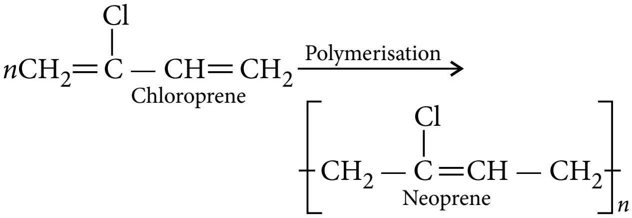


Terylene (Dacron)

9. **(a)**

10. **(a) :**

$CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}-CH{=}CH_2$ is the monomer of neoprene.



$$nCH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}-CH{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-\overset{\displaystyle Cl}{\overset{|}{C}}{=}CH-CH_2\right]_n$$

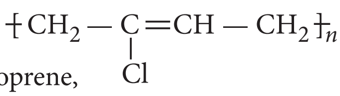
Chloroprene — Neoprene

11. **(d) :** Neoprene is an addition polymer.

12. **(b) :** Nylon 6,6 is an example of fibre.

13. **(a) :** Terylene (Dacron) is a polyester polymer because it is made by monomer units ethylene glycol and terephthalic acid.

14. **(a) :** Neoprene is :

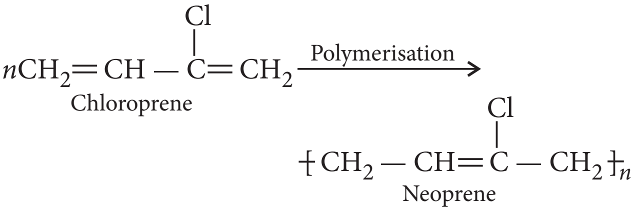


$\left[CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}{=}CH-CH_2\right]_n$

It is a polymer of chloroprene,

$CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}-CH{=}CH_2$

15. **(a) :** Neoprene is a polymer of chloroprene.

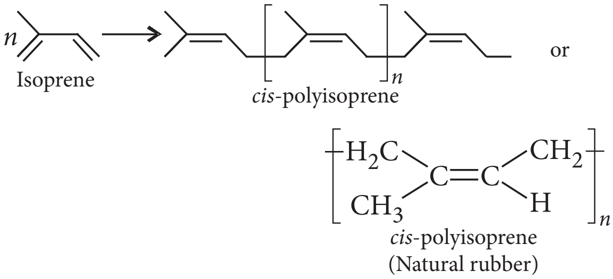


$$nCH_2{=}CH-\overset{\displaystyle Cl}{\overset{|}{C}}{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-CH{=}\overset{\displaystyle Cl}{\overset{|}{C}}-CH_2\right]_n$$

Chloroprene — Neoprene

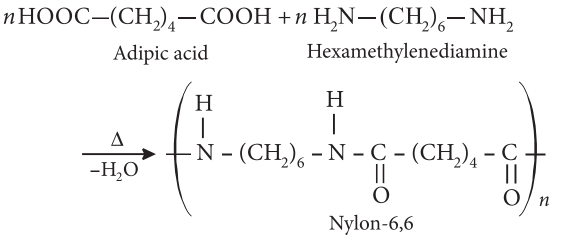
Rest of the polymers are correctly represented.

16. **(d) :** Natural rubber is *cis*-1,4-polyisoprene and has only *cis*-configuration about the double bond as shown below :



whereas in Gutta-percha, only *trans*-configuration exists about the double bond.

17. **(d) :** Nylon-6,6 is a condensation polymer of adipic acid and hexamethylenediamine.



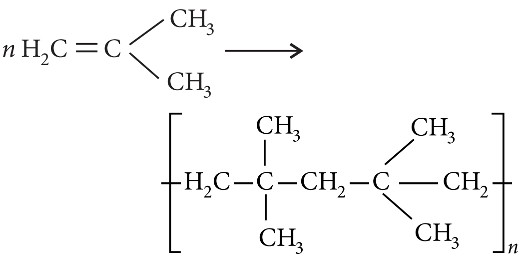
$$nHOOC{-}(CH_2)_4{-}COOH + n\,H_2N{-}(CH_2)_6{-}NH_2 \xrightarrow[-H_2O]{\Delta} \left(\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_6-\overset{\displaystyle H}{\overset{|}{N}}-\underset{\underset{\displaystyle O}{||}}{C}-(CH_2)_4-\underset{\underset{\displaystyle O}{||}}{C}\right)_n$$

Adipic acid — Hexamethylenediamine — Nylon-6,6

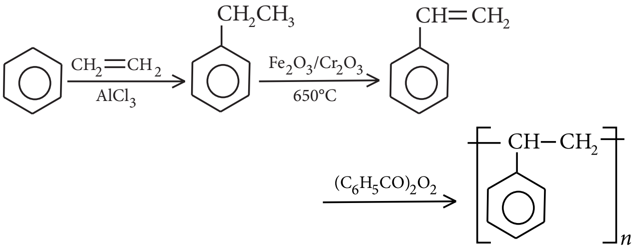
18. **(b) :** $\sim\!\!\sim[NH(CH_2)_6NHCO(CH_2)_4CO]_n\sim\!\!\sim$

is formed by the condensation of adipic acid and hexamethylenediamine. It is a copolymer (a polymer made from more than one type of monomer molecules is referred to as copolymer).

19. **(a) :**

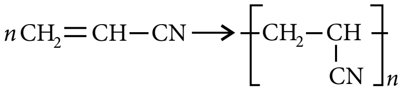


20. (c) : Chain-growth polymers involve a series of reactions each of which consume a reactive particle and produces another similar one. The reactive particles may be free radicals or ions (cation or anion) to which monomers get added by a chain reaction. It is an important reaction of alkenes and conjugated dienes or indeed of all kinds of compounds that contains C – C double bonds.



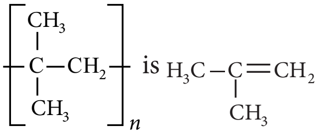
Polystyrene

21. (a) : Acrilan is an addition polymer of acrylonitrile.



$$n\,CH_2{=}CH{-}CN \longrightarrow \left[CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}} \right]_n$$

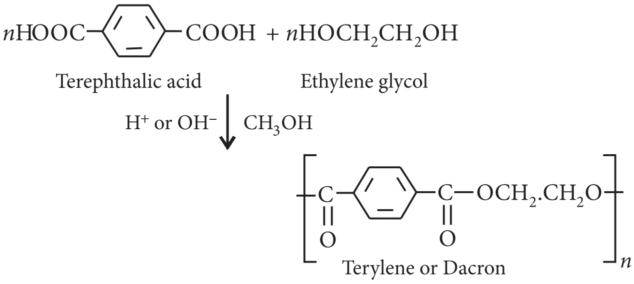
22. (a) : The monomer of



$$\left[\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2 \right]_n \text{ is } H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

(2-methylpropene)

23. (c) : Terylene is an example of condensation polymer and formed by the condensation of terephthalic and ethylene glycol.



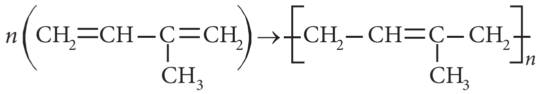
24. (a) : $n(CF_2{=}CF_2) \rightarrow \left[CF_2 - CF_2 \right]_n$

Polytetrafluoroethylene
(Teflon)

25. (c) : H-F – – – H-F– – – H-F– – – H-F

Dotted lines represent hydrogen bond between HF molecules and hence, it is a linear polymer. Due to high electronegativity value of 'F' atom, it forms effective hydrogen bonding.

26. (d) :

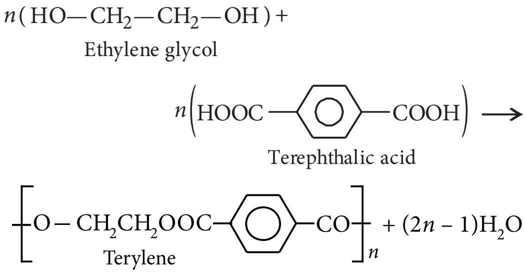


$$n\left(CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \right) \rightarrow \left[CH_2{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2 \right]_n$$

Isoprene Polyisoprene

Polyisoprene is the natural rubber, which is the polymer of isoprene.

27. (d) :



Terylene is the condensation polymer of ethylene glycol and terephthalic acid.

28. (b) : Polytetrafluoroethylene or teflon is a tough material, resistance to heat and bad conductor of electricity. It is used for coating the cookware to make them non-sticky.

29. (a) : Phenol and formaldehyde undergo condensation polymerisation under two different conditions to give a cross linked polymer called bakelite.

30. (c) : Nylon-2-nylon-6 is a biodegradable polymer.

31. (b) : Nylon-2-nylon-6 is an alternating polyamide copolymer of glycine (H_2NCH_2COOH) and aminocaproic acid ($H_2N(CH_2)_5COOH$) and is biodegradable.

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CHAPTER
16

Chemistry in Everyday Life

16.3 Therapeutic Action of Different Classes of Drugs

1. Among the following, the narrow spectrum antibiotic is
(a) chloramphenicol (b) penicillin G
(c) ampicillin (d) amoxycillin.
(NEET 2019)

2. Mixture of chloroxylenol and terpineol acts as
(a) antiseptic (b) antipyretic
(c) antibiotic (d) analgesic.
(NEET 2017)

3. Which of the following is an analgesic?
(a) Streptomycin (b) Chloromycetin
(c) Novalgin (d) Penicillin
(NEET-I 2016)

4. Bithional is generally added to the soaps as an additive to function as a/an
(a) buffering agent (b) antiseptic
(c) softener (d) dryer.
(2015, Cancelled)

5. Antiseptics and disinfectants either kill or prevent growth of microrganisms. Identify which of the following statements is not true.
(a) Dilute solutions of boric acid and hydrogen peroxide are strong antiseptics.
(b) Disinfectants harm the living tissues.
(c) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.
(d) Chlorine and iodine are used as strong disinfectants. *(NEET 2013)*

6. Dettol is the mixture of
(a) chloroxylenol and bithionol
(b) chloroxylenol and terpineol
(c) phenol and iodine
(d) terpineol and bithionol.
(Karnataka NEET 2013)

7. Chloroamphenicol is an
(a) antifertility drug
(b) antihistamine
(c) antiseptic and disinfectant
(d) antibiotic-broad spectrum. *(Mains 2012)*

8. Which one of the following is employed as Antihistamine?
(a) Chloramphenicol
(b) Diphenylhydramine
(c) Norethindrone
(d) Omeprazole *(2011)*

9. Which one of the following is employed as a tranquilizer drug?
(a) Promethazine (b) Valium
(c) Naproxen (d) Mifepriston *(2010)*

10. Which one of the following is employed as a tranquilizer?
(a) Naproxen (b) Tetracycline
(c) Chlorpheniramine (d) Equanil *(2009)*

11. Chloropicrin is obtained by the reaction of
(a) steam on carbon tetrachloride
(b) nitric acid on chlorobenzene
(c) chlorine on picric acid
(d) nitric acid on chloroform. *(2004)*

12. Aspirin is an acetylation product of
(a) *m*-hydroxybenzoic acid
(b) *o*-dihydroxybenzene
(c) *o*-hydroxybenzoic acid
(d) *p*-dihydroxybenzene. *(1998)*

13. Which of the following can possibly be used as analgesic without causing addiction and mood modification?

(a) Diazepam
(b) Tetrahydrocatinol
(c) Morphine
(d) *N*-Acetyl-para-aminophenol. *(1997)*

14. Which one of the following statements is not true?
(a) Ampicillin is a natural antibiotic.
(b) Aspirin is both analgesic and antipyretic.
(c) Sulphadiazine is a synthetic antibacterial drug.
(d) Some disinfectants can be used as antiseptics. *(1994)*

15. Diazo coupling is useful to prepare some
(a) pesticides (b) dyes
(c) proteins (d) vitamins. *(1994)*

16.4 Chemicals in Foods

16. The artificial sweetner stable at cooking temperature and does not provide calories is
(a) saccharin (b) aspartame
(c) sucralose (d) alitame. *(Odisha NEET 2019)*

17. Artificial sweetner which is stable under cold conditions only is
(a) saccharine
(b) sucralose
(c) aspartame
(d) alitame. *(2014)*

16.5 Cleansing Agents

18. Which of the following is a cationic detergent?
(a) Sodium lauryl sulphate
(b) Sodium stearate
(c) Cetyltrimethyl ammonium bromide
(d) Sodium dodecylbenzene sulphonate *(NEET 2020)*

19. Which of the following forms cationic micelles above certain concentration?
(a) Sodium dodecyl sulphate
(b) Sodium acetate
(c) Urea
(d) Cetyltrimethylammonium bromide *(2004)*

ANSWER KEY

1.	(b)	**2.**	(a)	**3.**	(c)	**4.**	(b)	**5.**	(a)	**6.**	(b)	**7.**	(d)	**8.**	(b)	**9.**	(b)	**10.**	(d)
11.	(d)	**12.**	(c)	**13.**	(d)	**14.**	(a)	**15.**	(b)	**16.**	(c)	**17.**	(c)	**18.**	(c)	**19.**	(d)		

Hints & Explanations

1. (b) : Penicillin *G* has a narrow spectrum. Chloramphenicol is a broad spectrum antibiotic. Ampicillin and amoxycillin are synthetic modifications of penicillins. These have broad spectrum.

2. (a) : Dettol which is a well known antiseptic is a mixture of chloroxylenol and α-terpineol in a suitable solvent.

3. (c) : Streptomycin, chloromycetin and penicillin are antibiotics while novalgin is an analgesic.

4. (b)

5. (a) : Dilute solutions of boric acid and hydrogen peroxide are weak antiseptics.

6. (b) : Dettol is the mixture of chloroxylenol and α-terpineol.

7. (d)

8. (b) : Diphenylhydramine is employed as antihistamine drug.

9. (b) : Valium is a tranquilizer.

10. (d) : Equanil is used for the treatment of stress, mild and severe mental diseases *i.e.*, as a tranquilizer.

11. (d) : When chloroform is treated with concentrated nitric acid, its hydrogen is replaced by nitro group.

$$CHCl_3 + HONO_2 \rightarrow \underset{\text{Chloropicrin}}{CNO_2Cl_3} + H_2O$$

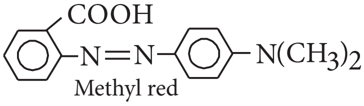
12. (c) : Aspirin is acetyl salicylic acid, which is formed by acetylation of *o*-hydroxybenzoic acid.

o-Hydroxybenzoic acid Aspirin

13. (d) : *N*-Acetyl-para-aminophenol (or paracetamol) is an antipyretic which can also be used as an analgesic to relieve pain without addition and mood modification.

14. (a) : Ampicillin is a modification of penicillin and thus is a synthetic antibiotic.

15. (b) : Azo dyes are derived by coupling of a phenol adsorbed on the surface of a fabric with a diazonium salt. Dyes can be prepared by diazo coupling. For example,

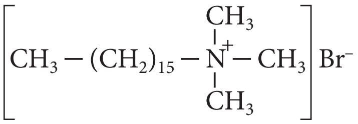


Methyl red

16. (c) : Sucralose is trichloro derivative of sucrose. Its appearance and taste is like sugar. It is stable at cooking temperature and it does not provide calories.

17. (c) : Aspartame is stable under cold conditions and unstable at cooking temperature.

18. (c) : Cetyltrimethyl ammonium bromide is a cationic detergent.



$$\left[CH_3-(CH_2)_{15}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{N}}}-CH_3\right]Br^-$$

19. (d) : Cetyltrimethylammonium bromide is a popular cationic detergent.

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